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Preparation of polyaniline particles in an inverse microemulsion

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Summary

Aniline has been successfully polymerised in a stable inverse microemulsion. The microemulsion polymerization of aniline produced ultrafine particles of conducting polyaniline. The particles were rather spherical and they ranged from 10 to 35 nm in diameter. The electrical conductivity of the polyaniline was about 8 S cm^{-1}, which has been improved to several hundred S cm^{-1} recently based on the similar process filed for an US patent.

Introduction

Conducting polyaniline is typically prepared by oxidation of aniline in aqueous acidic media using ammonium persulfate or potassium dichromate. Polyaniline is only slightly soluble in a limited range of polar solvents, e.g., dimethyl formamide (DMF) or dimethyl sulfoxide (DMSO). When the normally intractable electroactive polymers are prepared in the form of colloidal dispersions, their processibilities are enhanced significantly [1].

Polyaniline has been prepared with three morphologies, i.e., rice-grains, needles and spheres, depending on the choice of stabilizer. Using a graft copolymer backbone and poly(ethylene oxide) side chains, the 'rice-grain' polyaniline particles [2] were obtained. The same morphology of polyaniline could be prepared using the random copolymer poly(2-vinylpyridine-co-*p*-aminostyrene) as a steric stabilizer [1, 3]. This stabilizer, containing pendant aniline units, participated in the aniline polymerization. On the other hand, the long needle-shaped polyaniline was formed from the system which was stabilized by poly(ethylene oxide) having $M_w > 10^5$. It is only very recently that Vincent and Waterson [4] have first prepared spherical polyaniline particles using a more efficient steric stabilizer. This stabilizer (ICI product) is a grafted copolymer of polyacrylate backbone containing pendant polymerizable groups as well as the pendant PEO chains. However, the copolymerizable stabilizer could not be removed subsequently to produce the 'bare' electroactive polymers.

Microemulsions are transparent or translucent dispersions of water, oil and surfactant, and often with a cosurfactant as well. They form spontaneously upon mixing the appropriate type and amount of the components. Most of the microemulsions are thermodynamically stable. The microdomains of microemulsions are believed to be roughly spherical droplets (5-10 nm) of oil or water dispersed in the continuous medium of water or oil respectively. The former is known as oil-in-water (o/w) microemulsion while the latter water-in-oil (w/o) microemulsion. Due to the dynamic nature of the microemulsion, the reacting species solubilized in the droplets can mix rapidly among

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droplets. This seems to be an ideal method for preparing fine particles of different materials, if the microemulsion system remains stable throughout the reaction.

The inverse (w/o) microemulsion technique has been successfully used recently for producing stable microparticles of water-soluble polymers such as polyacrylamide [5], poly(ethylene oxide) [6], urea-formaldehyde resins [7], and water-insoluble inorganic compounds such as silver bromide [8]. Except for the system of reference 6, the other microemulsion systems were stabilized by a commercially available surfactant Aerosol-OT. A similar microemulsion system has also been recently studied by Matkham, Obey and Vincent [9] to produce water-insoluble polypyrrole. But their microemulsion system eventually led to a sedimented coagulum. If the reaction was suppressed at various intervals by diluting the microemulsion into a large excess of aqueous poly(vinyl pyrrolidone) solution, stable dispersions of small polypyrrole particles could then be prepared. This short communication describes the preparation of polyaniline nanoparticles from an inverse microemulsion.

Experimental

Materials

Aniline (Aldrich) was distilled and stored in the dark under nitrogen. Potassium persulfate (Fluka), nonionic surfactant Empilan NP5 (Albright & Wilson Asia) and petroleum ether (b.p. 60-80°C) were used as received.

Polymerization of Aniline in a Microemulsion

Aniline was first dissolved in an aqueous solution of 2M or 3M HCl. The acidified aniline was then mixed together with Empilan NP5 and petroleum ether to produce a stable inverse microemulsion in a conical flask. After introducing potassium persulfate to the flask, polymerization of aniline proceeded readily at room temperature and it could be completed within a few hours. Polyaniline particles were recovered from the microemulsion system by induced precipitation using an excess amount of ethanol or methanol.

Results and Discussion

Polymerization

The choice of a surfactant was very crucial to the stability of microemulsion polymerization of aniline which produced stable polyaniline microparticles. Nonionic surfactants, such as poly(oxyethylene)$_{5-9}$ nonyl phenol ether were found to be rather effective in stabilising the system. The microemulsions used in this study consisted of an appropriate amount of the surfactant, aniline, 2-3M HCl aqueous solution, and petroleum ether (60-80°C). In fact, two transparent microemulsions were first prepared separately. One consisted of 20 wt% aniline solution (5% aniline in 2M HCl aqueous solution), 45% petroleum ether and 35% Empilan NP-5 surfactant. The other contained similar compositions, except 5% $K_2S_2O_8$ in water was used in place of aniline. Upon mixing the two microemulsions with stirring, polymerization of aniline occurred readily within 10 minutes at room temperature. The color changed from clear to yellowish green and finally dark green. The polymerized microemulsion system was continuously stirred for 6-8 hours. The system was then left standing without stirring for observation about its colloidal stability. The colloidal particles of the formed polyaniline remained stable in the microemulsion for at least another 30 hours before a thin layer of fine precipitates could be observed from the bottom of the reaction flask. Other compositions of the similar microemulsion had also been studied. However, the formation of polyaniline in those systems was less stable. For emulsion (tubid) compositions, the formed polyaniline

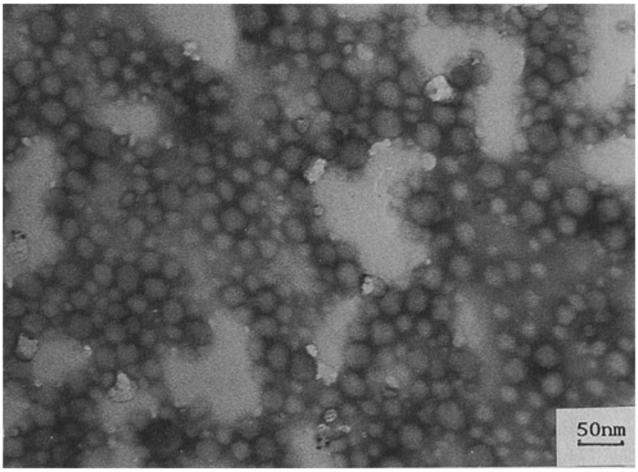


Fig. 1 TEM of polyaniline particles dispersed in 2M HCl aqueous solution

particles were coarse and they precipitated down to the bottom of the reaction flask within half an hour after stirring was stopped.

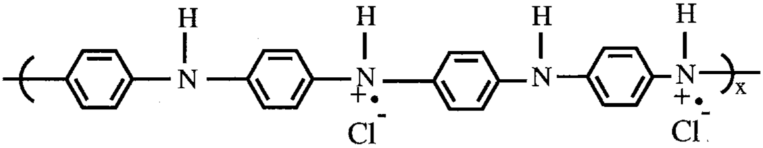
Polyaniline particles could be precipitated from the microemulsion system by adding an excess amount of ethanol or methanol. The very fine precipitated particles were repeatedly washed with ethanol or methanol and finally with water in order to remove the surfactant and $K_2S_2O_8$. As the sedimentation of the fine polyaniline particles was very slow, it was facilitated by centrifugation during each washing. Complete removal of the surfactant and $K_2S_2O_8$ from the polyaniline particles was confirmed by X-ray photoelectron spectroscopec (XPS) analysis.

The Particle Size

The clean polyaniline microparticles were then redispersed by sonication in 2M HCl aqueous solution to effect doping. The redispersed polyaniline particles were relatively unstable in the acidic medium, i.e., precipitation occurred within 10-20 minutes without stirring. A drop of the dispersion was immediately examined with a transmission electron microscope (TEM). Figure 1 shows the micrograph of the polyaniline particles. The particles appeared to be rather spherical and their sizes varied from 10 to 50 nm in diameter. The majority of the particles was in the size range of 10-35 nm. The number average diameter (d_n) of the particles and their size distribution (d_w/d_n) were calculated to be 22 nm and 1.5 respectively. However, when ammonium persulfate was used as an oxidant instead of potassium persulfate, the particle size distribution became much broader.

Electrical Conductivity

The dried polyaniline fine powder was compacted into a disc pellet and its conductivity was measured by a four-point probe connected to a Keithley voltmeter constant-current source system. The conductivity of polyaniline sample prepared in this form was about 8 S cm^{-1}. It is noted that the conductivity of the polyaniline sample was dependent on the concentration of HCl used during the polymerization. This is expected because only one form of polyaniline, known as an emeraldine salt, is electrically conducting. The fully protonated emeraldine salt of HCl may be represented by two separated polarons [10], i.e.,



Higher conductivity of polyaniline could be obtained for the samples prepared at higher HCl concentrations. But the microemulsion system became very unstable at higher acidity. In the present study, 2M HCl was found to give the optimum acidity to maintain the stability of the microemulsion during polymerization. After the polyaniline particles were washed repeatedly to get rid of the surfactant and the oxidant, the clean polyaniline particles were re-doped with 2M HCl to reform the emeraldine salt which was neutralised during the repeated washing.

Recently we have successfully filed an US patent based on the similar process which increases the conductivity of polyaniline to a few hundred S cm^{-1}.

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