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Quasi-Elastic Light Scattering Study of the Synthesis of Tailor-Made Suspensions of Uniform Polyaniline-Based Nanoparticles

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The understanding of the mechanism of aniline oxidative polymerization allows one to regulate the synthesis of the colloidal particle suspensions in such a way that a product of controlled average particle size and particle size distribution is obtained. Quasi-elastic light scattering was used to determine these parameters for the particles taken from a reaction mixture at various stages of the polymerization. It has been found that the particle size and the particle size distribution of the product depend on the reactivity of the monomer (*m*-, *o*-toluidine, or aniline), on the concentrations of the monomer, oxidant and stabilizer-poly(vinyl alcohol-*co*-acetate), and on the temperature. The particles of uniform size are formed within a limited period of time during the polymerization; in some cases until termination. Their sizes lie within the range of 200–600 nm for the polyaniline and within 400–3000 nm for poly(*m*-toluidine). Comparison of the prepared samples with commercially available uniform polystyrene latex standards shows that the polyaniline- and poly(toluidine)-based particle suspensions exhibit at least the same but in most cases narrower particle size distributions. The obtained color particles can be used in many practical applications, for example, as markers for studies of the transport phenomena in colloidal suspensions.

Keywords: Uniform size particle suspensions, controlled average particle size, poly(aniline, *o*-, and *m*-toluidine)—poly(vinyl alcohol-*co*-acetate) composite particles, dynamic light scattering

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INTRODUCTION

Preparation of colloidal polyaniline (PANI) suspensions stabilized by water-soluble polymers is one of the routes to improve polymer processability.^[1–5] Poly(vinyl alcohol-*co*-acetate) (PVA) has been used in the past as one of the possible steric stabilizers.^[6] However, it was not clear how to regulate the average size and particle size distribution (PSD) of colloidal PANI particles. This problem is, to a certain extent, related with the understanding of the mechanism of aniline oxidative polymerization.

Our previous study of the evolution of the electric potential established between the redox Pt-electrode and the SCE immersed in the polymerization mixture during the chemical oxidation of the aniline,^[7] the analysis of the intermediate reaction products by electron absorption spectroscopy,^[8,9] as well as the theoretical calculations performed by using Hueckel method,^[7,10] resulted in a proposal of the coherent reaction mechanism on which the following idea is based.

The oxidation of the aniline into nitrenium cation is accompanied by instantaneous addition of another molecule of aniline. Considerably lower electrochemical potential corresponding to the oxidation of the dimer, *p*-aminodiphenylamine (PADPA), and of higher aniline oligomers and polymer chains, as compared to the electrochemical potential of the aniline oxidation, suggests that the formation of PADPA is possible only at the initial stage of the polymerization. As a result, the growth of already existing active species (oxidized and protonated oligomers and polymer chains) is much more probable at the following propagation stage compared with the formation of new monomer nitrenium cations. The propagation of the polymer chains proceeds by a redox reaction between the growing active species (oxidant) and aniline (reducer) with the addition of the monomer to the chain end under the following conditions: the degree of oxidation of the chains should be higher than that of the emeraldine form of PANI and the pH of the reaction medium should be lower than 6.

The crucial moment in the chain growth of the PANI is the addition of the monomer to the oxidized dimer. It is preceded by an induction period during which only the PADPA is formed and the Pt-electrode potential remains constant.^[7] Thereafter, its rapid increase up to a value corresponding to the formation of the pernigraniline (fully oxidized form of PANI) is observed, followed by a rapid decrease corresponding to the reduction of the pernigraniline into emeraldine.

Compared with the aniline, the induction period was not observed during the polymerization of *o*-, and *m*-toluidines,^[11] but the electric potential of the Pt-electrode increased up to a plateau corresponding to the formation of the pernigraniline. The time of polymerization, until the thermodynamic equilibrium (corresponding to the formation of the emeraldine) has been reached, was about the same for *o*-toluidine and aniline but longer for *m*-toluidine.^[11,12] The electric potentials on the Pt-electrode corresponding to the oxidation of toluidines and those corresponding to the oxidation of poly(toluidine)s up to the formation of the pernigraniline were found lower as compared with the aniline and polyaniline.^[11,13] Higher reactivity of the poly(toluidine)s, regarding the addition of the monomer to the growing chain, was demonstrated by the prevailing formation of the poly(toluidine)s^[11,12] in the reaction mixtures of each of the toluidines with the aniline. The consequence of this higher reactivity is that the growth of the polymer chains proceeds at lower concentration of the active sites in comparison with the aniline.

It seemed reasonable that the choice of a monomer of a given reactivity and its concentration, as well as the concentration of the oxidant, would allow for the control of the concentration of the active species and, consequently, the rate of growth of the colloidal particles. In combination with a convenient steric stabilizer, it might result in the synthesis of stabilized suspensions of particles of tailor-made size. The increase of the temperature facilitates the monomer addition to the oxidized dimer that should lead to the lowering of the concentration of the growing chains.

Quasi-elastic light scattering (QELS) measurements of samples taken from the reaction mixture at various stages of the polymerization was used to study the influence of the above mentioned polymerization conditions on the average size and PSD of the formed colloidal particles.

EXPERIMENTAL

Reagent-grade aniline, *m*-, and *o*-toluidine, as well as all other reagents, were purchased from Fluka Chemica-BioChemika (Buchs, Switzerland). The suspensions of PANI and poly(toluidine)s were prepared by oxidative polymerization of monomers by using PVA (degree of polymerization 1600, degree of hydrolysis 86 mol %) as a steric stabilizer and ammonium peroxydisulphate as an oxidant in the presence of formic acid.

Small quantities of samples were taken at different times from the polymerization mixture for the measurement of the average particle size and PSD by QELS. The polymerization in these samples was immediately stopped by the addition of NaOH solution to obtain a pH value of 9 to 10. Preliminary measurement of the average particle size and PSD of a PANI sample suspended in aqueous acid or base solutions at different pH values has shown a negligible influence of pH of the medium on the particle size and PSD of the suspensions.

A model Zetamaster (Malvern Instruments, Ltd., Malvern, Worcestershire, U.K.) was used to measure the average particle size and PSD of the polymerized samples, and of the commercial uniform polystyrene (PS) latex standards.

RESULTS AND DISCUSSION

The evolution of the particle size and PSD during the polymerization was studied as a function of the polymerization conditions and the results are presented in Figures 1 to 5. Colloidal suspensions with narrow PSD (with the exception of the *o*-toluidine) are formed during a limited period of time, in some cases until the thermodynamic equilibrium at which the polymerization was finished.

It is a well-known fact that PVA forms the supramolecular structures in pure water solutions.^[14] The comparison of the average particle size and PSD of these structures in the initial PVA solution (see Fig. 1) and of the suspensions obtained by the polymerization of aniline or toluidines in PVA solutions suggests that the PVA supramolecular structures are destroyed during the polymerization and the PVA chains are integrated into the colloidal particles containing the PANI or poly(toluidines). Different reactivities of the monomers used are the main factors determining the existence and the duration of different stages in the polymerization process and, in our opinion, also the particle size and PSD of the products.

The polymerizations of aniline and toluidines were carried out first under identical conditions. The aniline exhibited the longest induction period, thereafter small diameter particles (about 400 nm) appeared (Fig. 1a). Their average size and PSD did not change substantially by keeping the polymerization mixture during several days. The repeated QELS measurements did not indicate any changes even after several months.

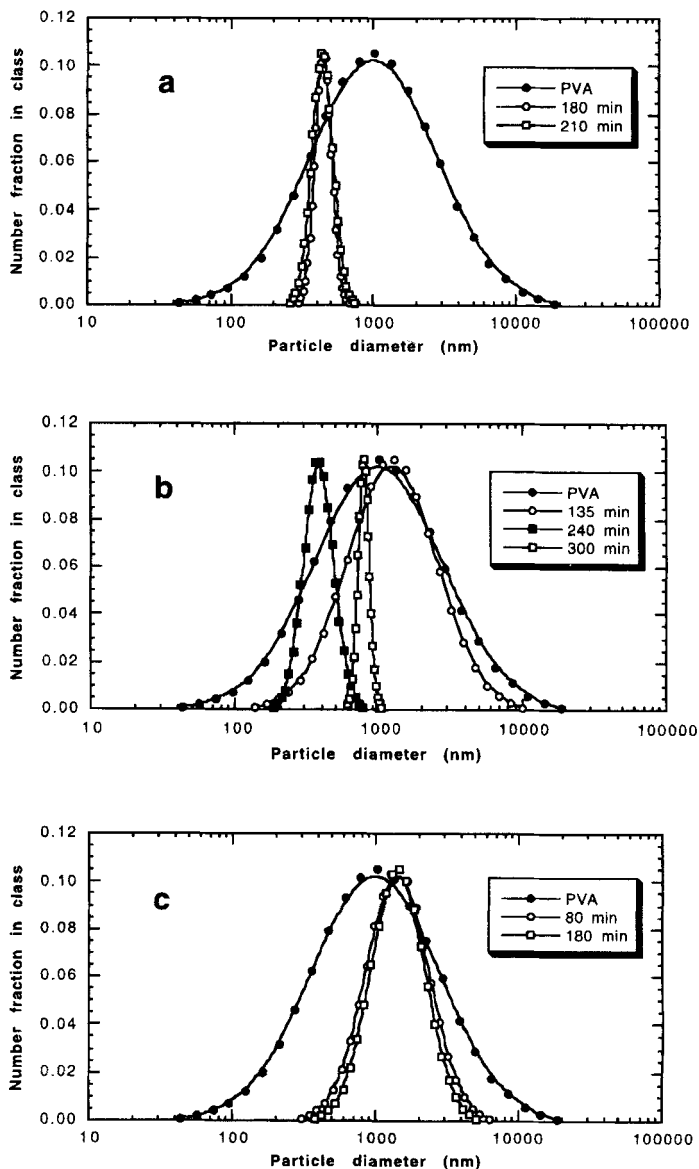


FIGURE 1 Evolution of the particle size distributions of samples taken from the reaction mixture at different stages of the polymerization of aniline (a), *m*-toluidine (b), and *o*-toluidine (c), starting from the initial PVA solution until the end of polymerization. Reaction conditions: concentration of monomers, 0.3 wt %; molar ratio of monomer/oxidant = 1; concentration of PVA, 7.7 wt %; concentration of formic acid, 14.4 wt %; temperature, 20°C.

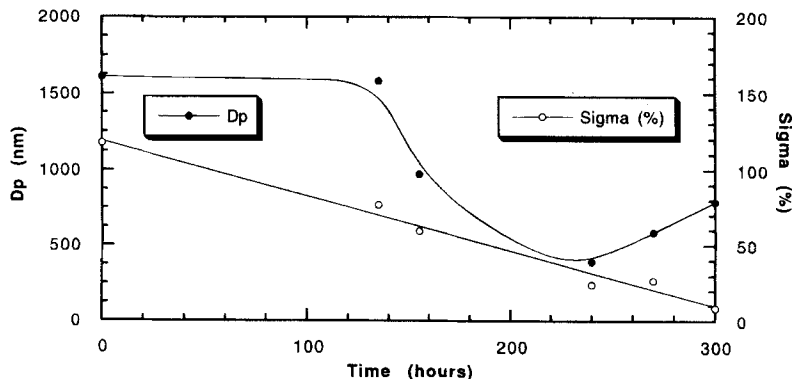


FIGURE 2 Variation of the average particle size and percentage standard deviation of the PSD during the polymerization of *m*-toluidine.

The course of the polymerization of *m*-toluidine was different. The induction period was shorter and the average particle size and PSD varied more significantly. The particle size decreased during the initial stage of polymerization and then increased until the formation of the final suspension of a constant particle size of about 800 nm (see Fig. 1b). The PSD of the product decreased constantly from that corresponding to the initial PVA structures until extremely narrow PSD colloidal particles were

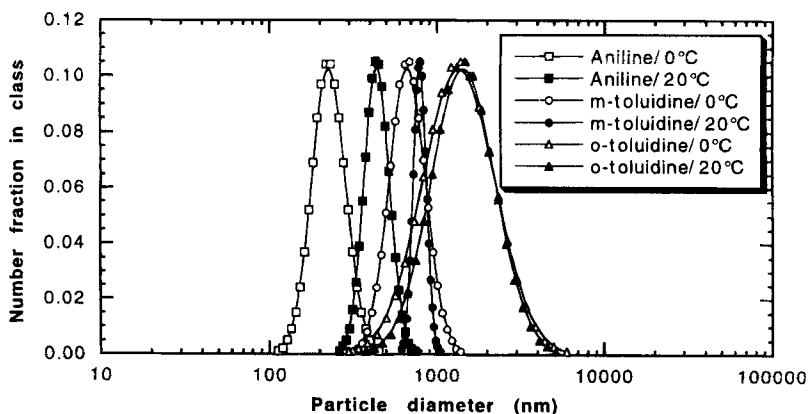


FIGURE 3 Effect of the temperature on the particle size distribution of the polyaniline-based colloidal suspensions polymerized at 0°C and 20°C. Reaction conditions: Concentration of monomers, oxidant, PVA, and formic acid as in Figure 1.

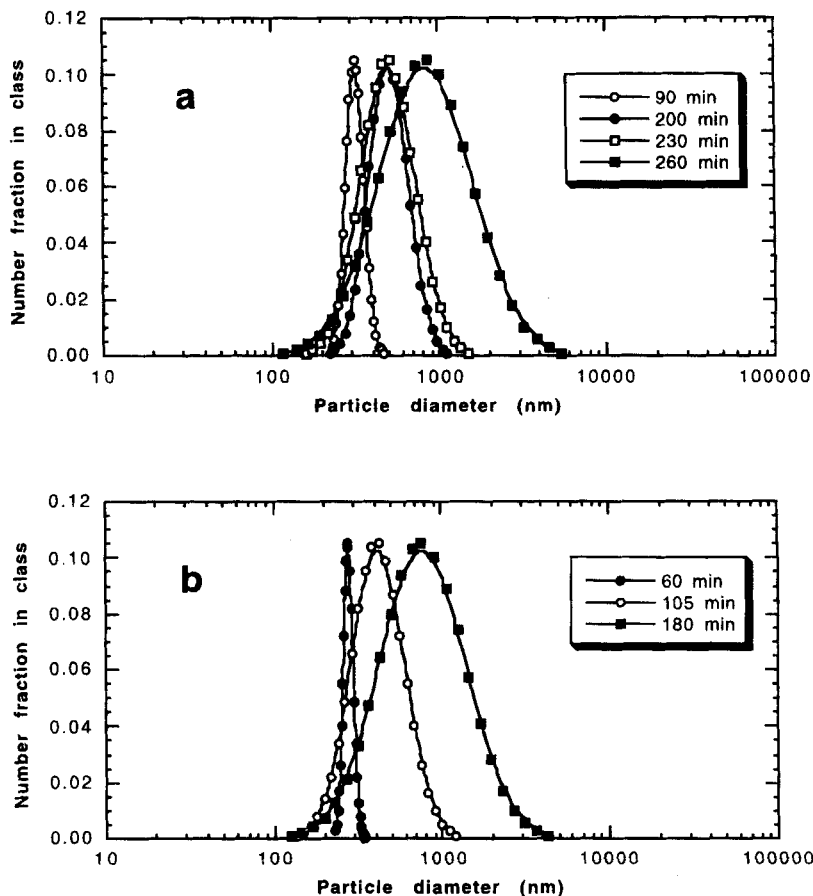


FIGURE 4 Effect of the molar ratio of monomer/oxidant on the evolution of the particle size distribution of the samples formed at different stages of the polymerization of *m*-toluidine starting from the stage of uniform particles formation until the end of polymerization. Reaction conditions: (a) concentration of monomer, 1.2 wt.%; molar ratio of monomer/oxidant = 1. (b) concentration of monomer, 2.4 wt.%; molar ratio of monomer/oxidant = 0.5; Concentration of PVA, formic acid, and temperature as in Figure 1.

obtained. Both variations of the average particle size and of the percentage standard deviation of the PSD are shown in Figure 2.

The induction period of the polymerization of *o*-toluidine was the shortest one (see Fig. 1c), the average particle size was the largest of all three monomers and remained practically constant during several days. The PSD

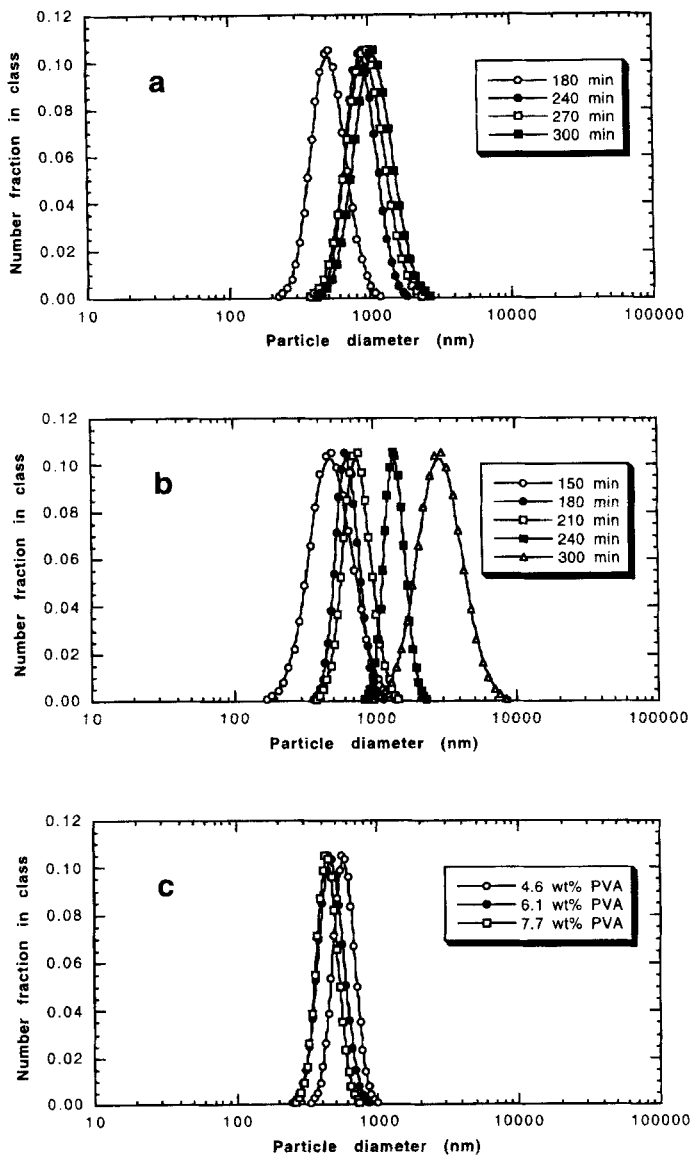


FIGURE 5 Evolution of the particle size distribution of poly(*m*-toluidine) as a function of different concentrations of the solutions of PVA. (a) 6.1 wt % PVA (b) 4.6 wt % PVA (c) and of the final suspension of PANI prepared at different concentrations of PVA. Reaction conditions: concentration of monomers, 0.3wt%; molar ratio of monomer/oxidant = 1; concentration of formic acid, 14.4 wt %; temperature, 20°C.

was also constant but broader regarding the final products of all above described polymerizations.

A decrease of the temperature should lead to an extension of the induction period of the polymerization of aniline and, whereby, it should increase the initial concentration of the nitrenium cations. As a result, the particles of smaller size should be obtained, nevertheless, more reactive monomers should occur, but to a lesser extent. The experimental results shown in Figure 3 agree with these assumptions.

A substantial decrease of the particle size can be achieved by increasing the concentrations of monomer and oxidant but uniform particles can occur only within a limited period of time. Obviously, flocculation of the particles resulting from the high polymerization rate leads to an increase of the average particle size and broadening of the PSD at the final stage of polymerization. This approach to decrease the particle size of poly(*m*-toluidine) and PANI is applicable only by stopping the polymerization at the stage of formation of the particles of required size, as can be seen from Figure 4.

The PANI and poly(*m*-toluidine) particles of larger size were obtained by decreasing the concentration of PVA stabilizer as shown in Figure 5. Lower viscosity of the reaction medium makes the transport of the monomer to the growing chains probably easier and, consequently, the polymerization rate can be modulated more cautiously. Larger size particles are formed without substantial broadening of the PSD.

CONCLUSION

It has been found that particles of uniform size are formed within a limited period of time during polymerization, in some cases until termination. Their sizes lie within the range of 200 to 600 nm for PANI and within 400–3000 nm for poly(*m*-toluidine). The PANI-based colloidal particles synthesized in this work exhibit at least the same but in most cases narrower PSD compared with the commercially available uniform PS latex standards, as can be seen in Figure 6.

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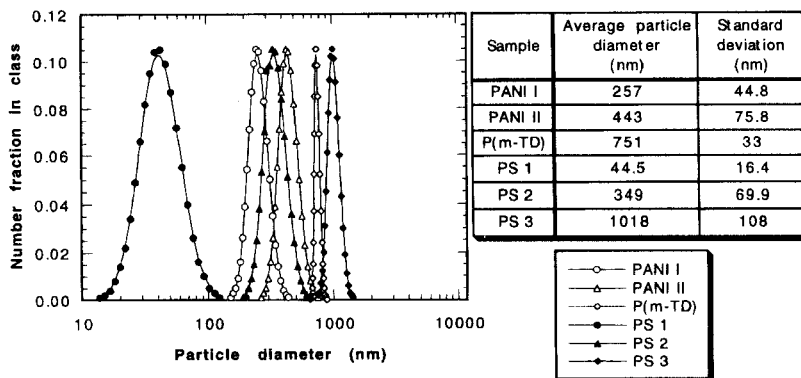


FIGURE 6 Comparison of the particle size distributions of some of the PANI-based uniform colloidal suspensions with polystyrene latex standard particles.

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