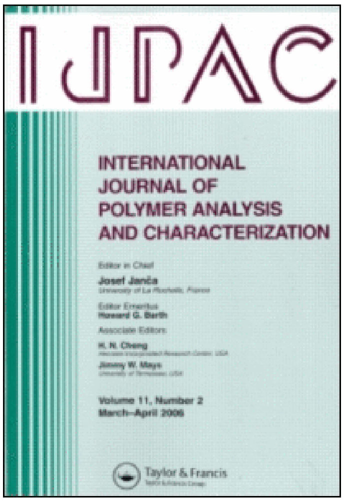

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# Characterization of Polyaniline and Poly(*m*-toluidine)-based Nanoparticles of Ultranarrow Particle Size Distribution

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The oxidative polymerization of aniline or *m*-toluidine, carried out in concentrated solutions of poly(vinyl alcohol-*co*-acetate) (PVA), was used to prepare colloidal composite particles of polyaniline-PVA or poly(*m*-toluidine)-PVA of ultranarrow particle size distribution and of controlled average particle size. The particle size distributions were measured by quasi-elastic light scattering in diluted polymerization products. Such a measurement can be influenced by undestroyed PVA aggregates formed in the initial solution. The aim of this work was to determine conditions under which the true particle size distribution of the composite particles can be measured or, at least, estimate the degree such a determination is influenced by PVA aggregates not incorporated into the composite particles. Quasi-elastic light scattering measurements of the diluted polymerization products were carried out under various experimental conditions. The composite particles were separated from the PVA solution by centrifugation and redispersed in water. The size of the redispersed composite particles and of the PVA aggregates in the supernatant solution was measured again by quasi-elastic light scattering. Scanning electron microscopy showed the spherical shape of the synthesized composite particles and confirmed their ultranarrow size distribution.

*Keywords*: Colloidal particles; Poly(aniline or *m*-toluidine)-poly(vinyl alcohol-*co*-acetate) composite particles; Quasi-elastic light scattering; Viscometry; Centrifugation; Scanning electron microscopy

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## INTRODUCTION

Studies of the oxidative polymerization of the aniline and *m*-toluidine have shown higher reactivity of *m*-toluidine,[1,2] concerning the addition of the monomer to the growing chains. Consequently, the polymerization of *m*-toluidine proceeds at a lower concentration of active sites in comparison with aniline. The increase of temperature also facilitates monomer addition to the oxidized dimer with the same consequence, *i.e.*, lowering the concentration of the growing chains. As a result, it has been proposed[3] that a monomer of adequate reactivity (aniline or *m*-toluidine) with an appropriate steric stabilizer, such as the poly(vinyl alcohol-*co*-acetate) (PVA), and a suitable choice of monomer and oxidant concentrations could be used to manipulate the growth rate of the colloidal particles. This idea was verified[3] by preparing tailor-made suspensions of the colloidal composite particles of polyaniline-PVA and poly(*m*-toluidine)-PVA (PMTD-PVA) of ultranarrow particle size distribution (PSD) and a controlled average particle size within the range of 200–3000 nm. The polymerizations were carried out in concentrated PVA solutions.

The average particle size and the PSD of the poly(aniline or *m*-toluidine)-PVA composite particles were obtained from quasi-elastic light scattering (QELS) measurements[3] of diluted polymerization products. Unfortunately, the results of the QELS measurements can be influenced by the PVA aggregates. As a matter of fact, the initial PVA solutions before the polymerization contain large PVA aggregates whose average size is of the order of 1 μm and it was not known whether or not these aggregates are destroyed during the polymerization of the aniline or *m*-toluidine. Consequently, our previous study[3] is extended here in order to confirm our conclusions concerning the average size and the size uniformity of the tailor-made composite particles.

The principal objectives of this study were to determine: the amount of the PVA remaining free in solution after polymerization of aniline or *m*-toluidine relative to the PVA that is incorporated in the synthesized composite particles; the size of the PVA aggregates in the supernatant solution of the centrifuged suspension after polymerization, as well as in the centrifuged initial PVA solutions before polymerization; and the true size and shape of the composite particles.

## EXPERIMENTAL

### Polymerization

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

The course of the polymerization of *m*-toluidine was studied by taking small quantities of samples from the reaction mixture at different times and by measuring the average particle size and PSD by QELS and the relative viscosity of the diluted reaction mixture. Polymerization in these samples was stopped immediately after sampling by the addition of NaOH solution to obtain pH value of 9 – 10. Preliminary measurements of the average particle size and PSD of a PANI-PVA sample suspended in aqueous acid or alkaline solutions at different pH values showed negligible influence of the pH value of the medium on the particle size and PSD of the suspensions.

### Quasi-elastic Light Scattering

Model Zetamaster, Malvern Instruments, Ltd., Malvern, Worcestershire (U. K.) was used to measure the average particle size and PSD of the PVA aggregates in solution and of the polymerized samples.

The QELS measurements were made on i. the initial PVA solutions of different concentrations without and with the addition of the polymerization reaction components, of the resulting suspensions after the polymerization of the aniline or *m*-toluidine, ii. the supernatant PVA solution after the elimination of the composite particles by centrifugation, and iii. the redispersed composite particles in water. These measurements were made to estimate the degree in which determination of the PSD of the composite particles is influenced by free PVA remaining in solution and form aggregates, and whether or not PVA aggregates are destroyed or their size modified during polymerization.

### Viscometry

A standard Ubbelohde capillary viscometer with AVS 410 model, Schott, (Germany) automatic viscometer was used to measure the relative viscosities (relative to water) of all PVA solutions and of the polymerization products. The measurements were performed at 25°C.

The viscometry was used to determine the concentration of the PVA in the supernatant solution after polymerization of aniline or *m*-toluidine and after the separation of the composite particles by centrifugation. The amount of PVA incorporated into the composite particles can be calculated from the viscometry data. Since the viscosity of the PVA supernatant solutions can be influenced by the components of the polymerization reaction, the relative viscosities of the PVA solutions of different concentrations were measured without and with the addition of the reaction components (aniline or *m*-toluidine and formic acid, but not the oxidant which starts the polymerization).

### Centrifugation

Model 4239 R, ALC, Milan (Italy) high-speed refrigerated centrifuge equipped with a swinging-bucket rotor was used to separate the composite particles from the supernatant PVA solution. A rotation speed of 6000 rpm, corresponding to the acceleration of 6500 G, was chosen with respect to the time of centrifugation. All centrifugations were carried out at 25°C.

### Scanning Electron Microscopy

Model Jeol 7410 LV, (Japan) scanning electron microscope was used to visualize the form of the synthesized composite particles and to check their size and size distribution under dry conditions where the thickness of the adsorbed PVA chains forming the shell of the particles was minimized.

## RESULTS AND DISCUSSION

### Effect of the Components of Polymerization Reaction of Aniline on the Relative Viscosity of PVA Solutions and on the Size of PVA Aggregates

The relative viscosities of the PVA solutions as a function of the concentration without and with the addition of the same amount of aniline and formic acid as for the polymerization is shown in Figure 1. It can be seen that the addition of the polymerization reaction components results in a small increase of the relative viscosity of PVA solutions. This can be due to the modified swelling of the polymer chains or due to the displacement of the equilibrium between the free polymer chains and PVA aggregates in solution.

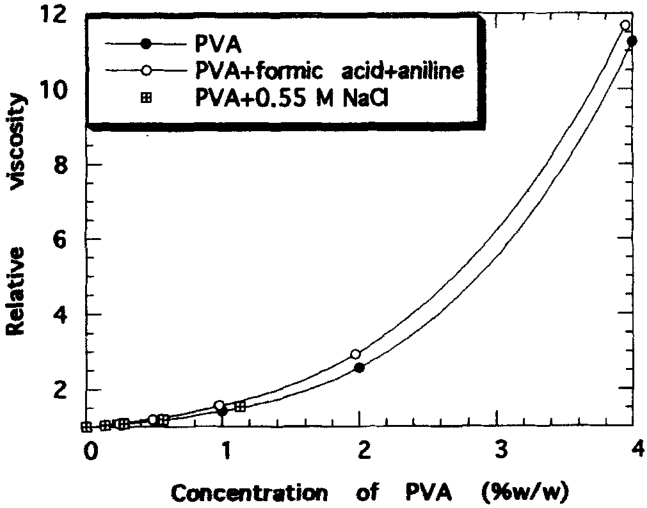

FIGURE 1 Relative viscosities of PVA solutions at different concentrations without and with the addition of the components of the aniline polymerization and with the addition of NaCl. The experimental data concerning the PVA solutions with NaCl are taken from Ref. [4].

The results of the QELS measurements of the particle size of the PVA aggregates shown in Figure 2 are strongly concentration dependent. The increase of the size of the PVA aggregates is most pronounced above a concentration of 2% (w/w) of the PVA. However, it must be taken into account that the autocorrelation function used to treat the QELS measurements provides the diffusion coefficient values and the corresponding particle sizes are, in fact, calculated from

$$d = \frac{kT}{3\pi\eta D} \tag{1}$$

where $d$ is the particle diameter, $k$ is the Boltzmann constant, $T$ is the temperature, $\eta$ is the viscosity of the suspending liquid, and $D$ is the diffusion coefficient. The value of the viscosity of the suspending liquid (water in this case) must be introduced as one of the QELS software input data for the calculation of the PSD. The problem is that some of the measurements were performed in relatively concentrated PVA solutions whose bulk viscosities were much higher than the viscosity of pure water. Consequently, the effective diffusion coefficients of the

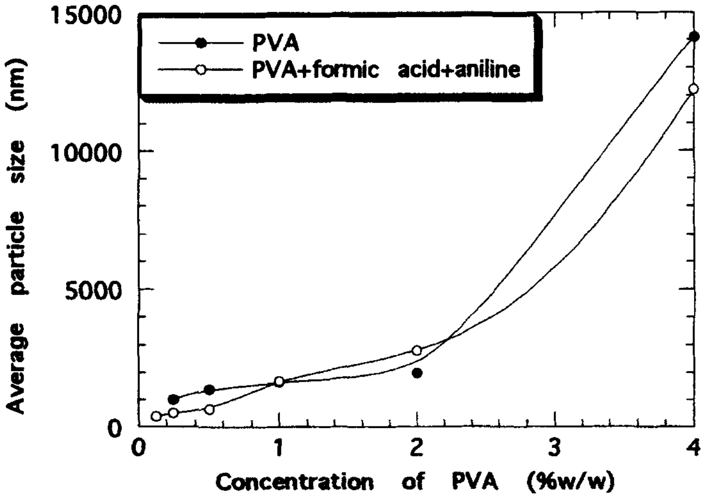

FIGURE 2 Average particle size of the PVA aggregates as a function of the PVA concentration in solutions without and with the addition of components of the aniline polymerization.

PVA aggregates should be lower in the concentrated PVA solutions which should result in higher apparent sizes of the measured aggregates. The substitution of the viscosity of pure water by the bulk viscosity of the PVA solution in the calculations should compensate this error, but the bulk viscosity of the solution includes the contribution of the PVA aggregates whose exact equilibrium concentration is difficult to determine. The input of the bulk viscosity of PVA solution instead of the viscosity of water substantially modified the resulting values of the particle size for the PVA solutions of the highest concentrations, as can be seen in Table I. The conclusion from these measurements is that the concentration of the PVA solutions should be below 2% (w/w) in order to obtain reliable QELS results, independent of the introduced solvent viscosity.

Although the polymerization reaction components have an irregular effect on the QELS measurement of the particle size of PVA aggregates at higher PVA concentrations, the size of the PVA aggregates is systematically lower for the diluted solutions containing the polymerization components (roughly 50% of the average size values obtained for the PVA solutions of the same concentrations but without the polymerization components), as can be seen in Figure 3, which is an enlarged area of the low concentration range in Figure 2.

Investigation of the effect of NaCl on the behavior of PVA solutions indicated that although the relative viscosities were not substantially modified by NaCl (see experimental data in Fig. 1) in comparison with the solutions of the same concentration of the PVA but without the addition of NaCl, the measurement of the PSD by QELS proved the progressive destruction of PVA aggregates with increasing NaCl concentration.[4] These results, see Figure 4, show the variation of the

TABLE I Effect of input viscosity on the average particle size calculated from QELS measurement of PVA solutions

| *Concentration of PVA solution (%w/w)* | *Calculated size (nm) using viscosity of PVA solution* | *Calculated size (nm) using viscosity of water* |
|---|---|---|
| 8 | 220 | 46 196 |
| 4 | 1493 | 14 100 |
| 2 | 1416 | 2035 |

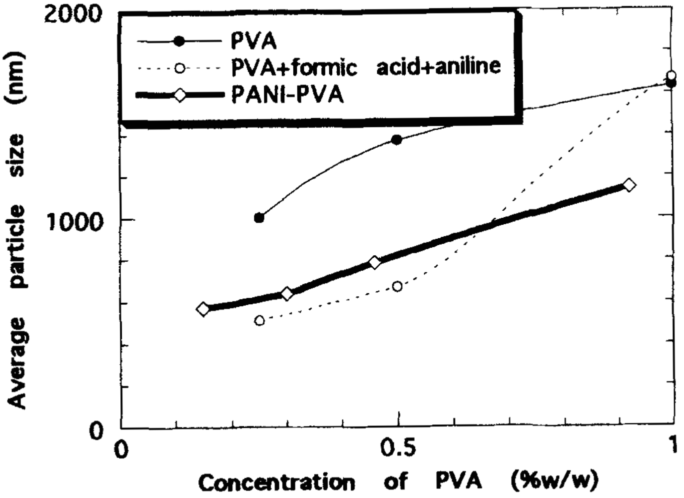

FIGURE 3 Average particle size of the PVA aggregates and of the synthesized PANI-PVA composite particles as a function of the PVA concentration in solutions without and with the addition of the components of the aniline polymerization.

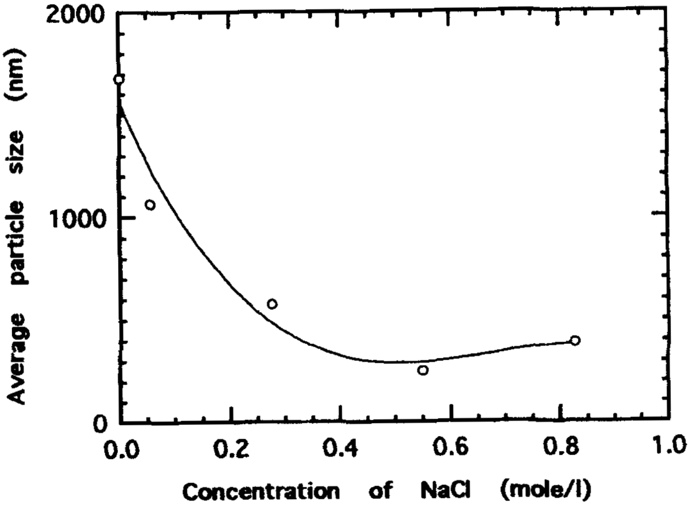

FIGURE 4 Average particle size of the PVA aggregates as a function of NaCl concentration in the PVA solution at a concentration of 1% (w/w).

average size of the PVA aggregates with NaCl concentration in 1% (w/w) PVA solutions. It seems reasonable to explain these results of the QELS measurements by a partial destruction of the PVA aggregates.

## Sedimentation of PVA Aggregates During Centrifugation

In order to elucidate whether the concentration of the PVA in solution varies due to sedimentation of PVA aggregates during centrifugation, two PVA solutions (30 ml each) at 4% w/w without and with the aniline polymerization components were centrifuged during 121 h at 6000 rpm and measured subsequently by QELS and viscometry. A volume of 0.5 ml of each solution was taken near the meniscus for QELS measurement. The average particle size was 157 nm for the PVA solution without polymerization components and 36 nm with components. These results indicate that the largest PVA aggregates can sediment under the conditions of centrifugation because the measured average particle sizes were at least 3 to 10 times lower than the lowest values (see Fig. 2) obtained for the same solutions before centrifugation. Moreover, a small polymer cake was observed at the bottom of the sedimentation tubes after centrifugation. However, the relative viscosities of the initial PVA solutions before centrifugation and of upper fractions (representing 85% of the solution) after the centrifugation were practically identical (see Tab. II) for the PVA solutions with and without the addition of the polymerization components. It indicates that the sedimenting PVA aggregates probably do not significantly influence the viscosity of the PVA solution to their relatively low concentration. More detailed investigation of the sedimentation of the PVA aggregates was not required.

TABLE II Relative viscosities of PVA solutions without and with the polymerization reaction components before centrifugation and of upper fractions after the centrifugation

| | *Relative viscosity before centrifugation* | *Relative viscosity of upper fraction after centrifugation* |
|---|---|---|
| PVA solution without polymerization components | 11.24 | 11.89 |
| PVA solution with polymerization components | 11.68 | 11.98 |

## Size of PANI-PVA Composite Particles Measured by QELS in Diluted Polymerization Products

Three polymerizations of aniline were carried out in PVA solutions. The PSD and the average particle size of the diluted suspensions after polymerizations were determined by the QELS. A typical result is in Figure 3 showing the average particle size measured for one suspension at different concentrations and in Figure 5 which shows the PSD of the PVA aggregates in the initial PVA solution and the PSD of one of the diluted polymerization products. The results demonstrated in Figure 5 represent excellent reproducibility of the polymerization of the aniline under the given conditions because almost the same PSD values were obtained previously.[3] However, with regard to the experimental findings demonstrated, especially in Figure 3, the attribution of the definite PSD to the composite PANI-PVA particles was questionable because almost the same PSD values were obtained for the PVA aggregates in solutions with the addition of the polymerization components. The results of a more detailed investigation of this point are discussed in the following paragraphs.

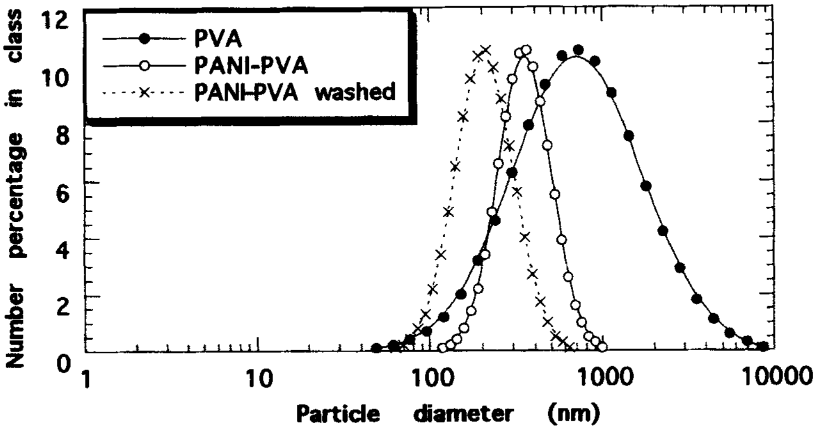

FIGURE 5 Particle size distributions of i. PVA aggregates in solution before polymerization, ii. of the composite PANI-PVA particles in diluted polymerization product, and of iii. the PANI-PVA particles after their separation from excess PVA solution by centrifugation and redispersion of the sediment in water.

## Relative Viscosity of the Suspension After Polymerization and of the Supernatant Solution After Centrifugation

The relative viscosity of the diluted (4% w/w of PVA) suspension of the composite particles PANI-PVA after polymerization of the aniline was $\eta = 15.92$, which is higher (by about 36%) as compared with the relative viscosity $\eta = 11.68$ of the PVA solution with the polymerization reaction components (see Fig. 1) before polymerization. The synthesized composite particles were separated from the PVA solution by centrifugation of 20 mL of suspension. The relative viscosity of the upper fraction of the colorless supernatant PVA solution (after centrifugation) was $\eta = 12.58$ thus comparable with the relative viscosity $\eta = 11.68$ of the initial PVA solution. The volume of the lower fraction was not sufficient to measure the relative viscosity without dilution. The relative viscosities of higher ($\eta = 3.01$) and lower ($\eta = 2.99$) fractions diluted to 2% (w/w) of PVA were identical within the range of experimental errors and only slightly higher than the relative viscosity of the initial solution $\eta = 2.93$ (with the polymerization reaction components) at the same concentration (see Fig. 1). The relative viscosity of the whole suspension diluted to 2% (w/w) of PVA was $\eta = 3.25$. The sedimented PANI-PVA particles were redispersed in 20 mL of water. The relative viscosity of this redispersed suspension was $\eta = 1.03$.

The above relative viscosities imply that only a small part of the PVA is incorporated in the separated and redispersed PANI-PVA particles. The concentration and, consequently, the relative viscosity of the PVA remaining in supernatant solution is only moderately changed by the polymerization of aniline. All viscosity data indicate that the composite PANI-PVA particles behave practically as suspended hard spheres.

## Size of the Composite PANI-PVA Particles After Separation by Centrifugation and Redispersion in Water

The size of the composite PANI-PVA particles redispersed in water after their separation from the PVA supernatant solution by centrifugation was measured by QELS and its constant average value of

220 nm was practically independent on the concentration of the suspension. The standard deviation of the PSD was 86 nm. The entire PSD of the PANI particles separated from the excess PVA solution by centrifugation, repeatedly redispersed and centrifuged in water is shown in Figure 5. The width of the PSD of these particles is almost the same as that measured directly by QELS in diluted suspension after the polymerization; however, the entire PSD and, of course, the average particle size are shifted to lower values, probably due to the reduced contents of the undestroyed PVA aggregates. The average particle size and the standard deviation of the PSD of this sample measured by QELS before the elimination of the PVA solution by centrifugation were 370 nm and 131 nm, respectively. The QELS measurement was performed within the range of PVA concentrations assured to be low enough to suppress the above mentioned concentration effects.

## Scanning Electron Microscopy

The image from the scanning electron microscopy (SEM) of the PANI-PVA particles is shown in Figure 6. It demonstrates that the particles are almost perfectly spherical and their PSD is ultranarrow

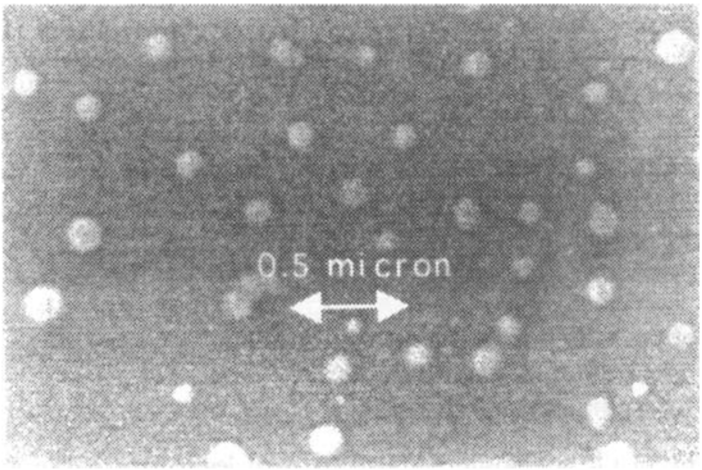

FIGURE 6 Scanning electron microscopy photography of PANI-PVA composite particles.

thus confirming the QELS measurements. Obviously, the average particle size seen on the SEM image is lower in comparison with the QELS measurements because of the substantially reduced thickness of the PVA shell due to the drying of the deposited sample.[4] As the number of the particles in Figure 6 is relatively low, the calculation of the PSD from the SEM image was not done.

## Polymerization of *m*-toluidine

Relatively slow polymerization of *m*-toluidine allows samples to be taken from the polymerization mixture for following the relative viscosity of the intermediate polymerization product, as well as the evolution of the PSD, starting from the PVA aggregates up to the composite particles formed during polymerization. The evolution of the PSD shown in Figure 7 confirmed, in this case too, good reproducibility of *m*-toluidine polymerization. Practically the same result was obtained previously.[3]

Small volume samples of 2 mL each were taken each hour from the polymerizing suspension (whose initial volume was 30 mL) and diluted 10 times with 0.25 M NaOH which immediately stops the polymerization. The relative viscosities of the diluted samples were measured to

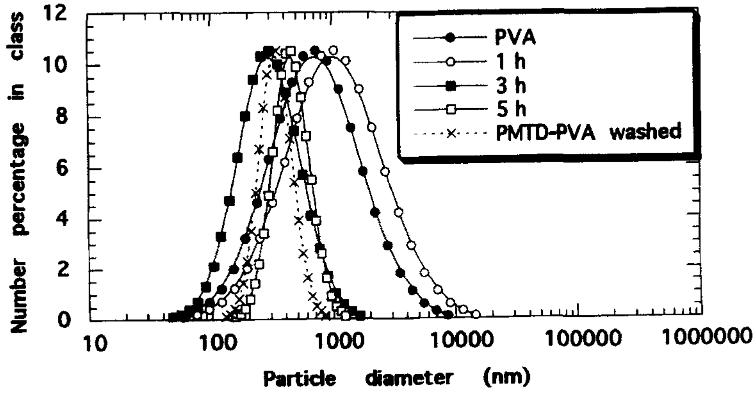

FIGURE 7 Evolution of the particle size distribution of samples taken from the reaction mixture at different stages of the polymerization of *m*-toluidine, starting from the initial PVA solution until the end of the polymerization, and particle size distribution of the poly(*m*-toluidine)-PVA particles after their separation from excess PVA solution by centrifugation and redispersion of the sediment in water.

follow polymerization with time. Thereafter, the diluted samples were centrifuged during 23 h and the relative viscosities of the upper and lower half of the samples diluted 2.5 times further were measured again. The results are shown in Figure 8. It can be concluded that the relative viscosity of the samples does not change significantly during polymerization of *m*-toluidine. Centrifugation does not have significant effect on the distribution of the free PVA in the supernatant solution because no important difference in the relative viscosities between the higher and lower diluted fractions could be detected.

The QELS measurements of the upper and lower fractions after centrifugation provided a series of average particle sizes fluctuating with polymerization time the samples were taken. These results can be seen in Figure 9 which shows, for the sake of comparison, also the average particle sizes measured directly in raw diluted suspensions before the elimination of excess of PVA by centrifugation.

The sediments of poly(*m*-toluidine)-PVA (PMTD-PVA) particles obtained by centrifugation of the samples taken at different polymerization times were redispersed in water and their PSD values measured by QELS at different concentrations. The mean value of

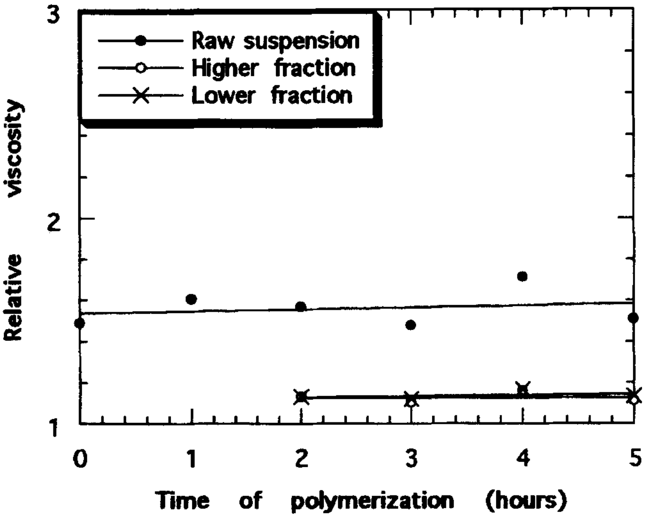

FIGURE 8 Variation of the relative viscosity during the polymerization of *m*-toluidine measured in the raw diluted polymerization product and in upper and lower fractions taken from the sedimentation tubes after centrifugation and additional dilution.

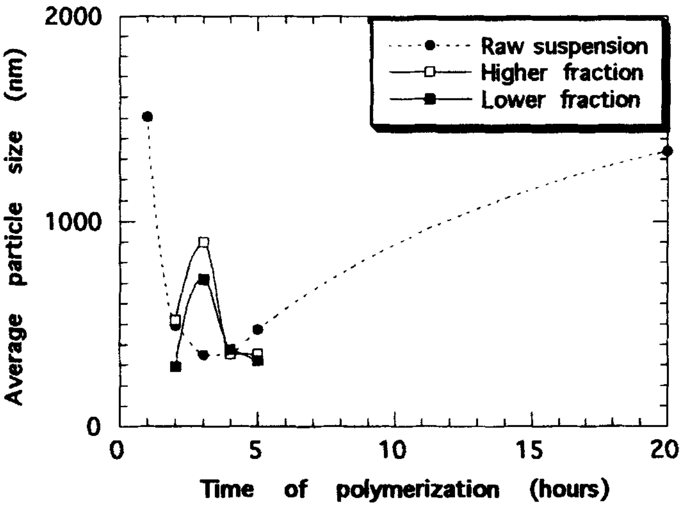

FIGURE 9 Variation of the average particle size during the polymerization of *m*-toluidine measured in the raw diluted polymerization product and in upper and lower fractions taken from the sedimentation tubes after centrifugation and additional dilution.

eleven independent measurements gave an average particle size of 360 nm with a standard deviation of 66 nm. No other than statistical fluctuations of the average particle size has been observed from sample to sample with no systematic correlation as a function of the polymerization time or of the concentration of the particles. A typical PSD of the redispersed PMTD-PVA particles is shown in Figure 7.

Similarly as in the case of the PANI-PVA particles, the width of the PSD of the PMTD-PVA washed and redispersed particles is almost the same as that measured by QELS directly in diluted PMTD-PVA suspension at the end of the polymerization. Nevertheless, the average particle size of the redispersed PMTD-PVA sample is 351 nm, the standard deviation of the PSD is 109 nm, which is shifted, again, to a lower value as well as the entire PSD as compared with the average particle size of 470 nm and the standard deviation of the PSD of 165 nm of the same sample before centrifugation, washing and redispersion. These differences can probably be due to the reduced contents of the undestroyed PVA aggregates in the redispersed sample as well as to the reduced effective size of the washed and redispersed PMTD-PVA particles.

## CONCLUSION

It has been found that 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 from 200 to 600 nm for PANI and from 400 to 3000 nm for poly(*m*-toluidine). The PANI-based colloidal particles synthesized in this work exhibit at least the same but in most cases a narrower PSD as compared with commercially available uniform PS latex standards. Such a comparison was already demonstrated.[3] The determination of the PSD and of the average particle size of the composite PANI-PVA and PMTD-PVA colloidal particles by the QELS is a delicate task. However, accurate values can be obtained provided that conditions of measurement are established in such a manner as to avoid artifacts due to the particular behavior of PVA solutions.

### Acknowledgment

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### References

[1] L. H. C. Mattoso, S. K. Manohar, A. G. MacDiarmid and A. Epstein (1995). *J. Polym. Sci., Polym. Chem.*, **33**, 1227.
[2] Y. Wei, R. Hariharan and S. A. Patel (1990). *Macromolecules*, **23**, 758.
[3] N. Gospodinova and J. Janča (1998). *Int. J. Polym. Anal. Charact.*, **4**, 323.
[4] N. Gospodinova, E. Jančová and J. Janča (1999). *12th Int. Symp. Polym. Anal. Charact.*, La Rochelle, France.