Abstract Dynamic properties of monodisperse and bimodal mixtures of electrostatically stabilized polymer latices have been studied at high concentration. Macroscopic properties were measured by rheometry and viscous as well as elastic behavior was investigated. Information on particle diffusion was obtained by means of fiber optical quasi elastic light scattering (FOQELS). In monodisperse systems, short time self-diffusion of particles at high ionic strength could be described by theoretical calculations for hard spheres although shear viscosity showed deviations from hard sphere behavior. Elastic properties were observed by rheology at high volume fractions and the existence of a yield stress could also be optically detected by FOQELS. In bimodal mixtures, a “probe diffusion”, i.e., diffusion of a small number of large spheres in a matrix of small particles could be measured by FOQELS. Probe diffusion was strongly slowed down with increasing volume fraction and the concentration dependence was similar to that of viscosity. Variation of particle size ratio and composition allowed for the possibility to measure diffusion of small and/or large particles in the mixture by FOQELS.

Key words Latex – colloidal dispersion – diffusion – bimodal dispersion – viscosity

Introduction

Concentrated polymer dispersions have been intensely studied with respect to their rheological behavior. In electrostatically stabilized polymer latices the interaction potential depends on the ionic strength and colloidal crystals can be observed at low particle volume fraction and low ionic strength. Sterically stabilized hard sphere systems can be used to investigate the glass transition [1]. Information on microscopic dynamic properties, i.e., the diffusive motion of the particles, is of great interest in order to correlate local dynamics with macroscopic properties of the sample. Diffusion coefficients are usually determined by means of quasi elastic light scattering (QELS), but this technique requires the solution to be optically transparent, which is not the case for concentrated dispersions. Therefore, only dispersions for which index matching of colloidal particles and suspension medium is feasible, can be studied by QELS at high concentrations. A new technique to determine diffusion coefficients in turbid solutions has recently been developed by Horn and coworkers and uses a fiber optical QELS (FOQELS) to detect the back scattered light. Wiese and Horn demonstrated the usefulness of this technique [2].

The objective of this contribution is to compare rheological data and diffusion coefficients of concentrated polymer dispersions. There are only few studies that compare results obtained from the same system. To this end, we investigated i) suspensions of monodisperse electrostatically stabilized polymer latices, and ii) bimodal
mixtures of these monodisperse dispersions at different composition and size ratio of particles.

Theoretical considerations for both rheology and light scattering have been frequently presented in the literature [3–5] and the reader is referred to the indicated references for further information. QELS probes particle movements on a length scale given by \(2\pi/q_{\text{exp}}\) (\(q\) being the scattering vector at the experimental conditions), which has to be compared to the position of the first maximum of the structure factor \(q_m\) [5]. \(q_m\) is related to the distance between particles and their surrounding nearest neighbors in the system and, to a first approximation, is proportional to \(\rho_N^{1/3}\) (\(\rho_N\) being the particle number per volume). If \(q_{\text{exp}} \geq q_m\), FOQELS measures the short time self-diffusion coefficient \(D_{st}\). The particle displacements are small in comparison to the interparticle spacing. If \(q_{\text{exp}} < q_m\) collective diffusion (combined diffusion of many different particles) is measured. In conventional QELS \(q_{\text{exp}}\) is variable due to the different scattering angles, whereas it is fixed in FOQELS experiments.

### Experimental

Synthesis and characterization of monodisperse latices have been described elsewhere [6]. Particle diameters were 304, 164, and 64 nm, respectively. Particle size distributions were narrow. Rheological tests were performed with a Bohlin CS 10 rheometer. A self-constructed FOQELS set-up was used to measure diffusion coefficients at high concentration. The optical set-up is equivalent to that described by Wiese and Horn [2]. Time-correlation functions were measured with an ALV-5000 correlator. A HeNe laser was used as light source, thus defining the experimental scattering vector at \(q_{\text{exp}} = 2.647 \times 10^5\) cm\(^{-1}\).

### Results and discussion

**Monodisperse latices**

Figure 1 shows a comparison of normalized diffusion coefficient and viscosity of concentrated monodisperse polymer latices versus particle volume fraction. The viscosity data are given as inverse relative viscosity at low \(\left(\eta_0/\eta_s\right)^{-1}\) and high shear rate \(\left(\eta_0/\eta_s\right)^{-1}\), respectively, \(\eta_s\) being the viscosity of water. The diffusion data in Fig. 1 agree nicely with theoretical predictions by Beenakker and Mazur [7] for short time self-diffusion of hard spheres. The concentration dependence of the relative viscosities (at high and low shear rate) cannot be satisfactorily be described by the Dougherty-Krieger or Quemada equations [8, 9], which are known to describe hard sphere suspensions. Obviously, deviations from hard sphere interaction influence viscosity, but not short time self-diffusion.

When the particle interaction potential was increased further, with increasing concentration and/or decreasing ionic strength, dispersions became viscoelastic. A transition from liquid like to solid like behavior was found in a narrow concentration range. Elastic properties could be detected by various rheometrical tests:

i) A yield stress was observed when a ramp of increasing shear stresses was applied to the samples.

ii) In constant stress, i.e., creep experiments, a spontaneous recoverable compliance was found.

iii) A plateau modulus was observed in dynamic-mechanical experiments.

iv) Low shear rate viscosity diverged.

The solidification transition could also be detected by FOQELS. Close to the transition, the decay of the time correlation function became much broader. For elastic samples the time correlation function no longer decayed completely and strong count rate fluctuations were observed during the measurements. Figure 2 shows two intensity autocorrelation functions corresponding to a liquid (top) and solid (bottom) sample, respectively, as well as \(G'\) and \(G''\) data of the same samples. The predominantly viscous sample showed elastic properties only at the highest frequencies accessible (\(G'\) and \(G''\) have about the same magnitude there) and was clearly viscous at lower frequencies. The higher concentrated sample showed elastic properties even at the smallest frequency (\(G'\) stayed constant and was always higher than \(G''\)) and the time