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ORIGINAL CONTRIBUTION

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Preparation and characterization of well-defined sterically stabilized latex particles with narrow size distribution

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Abstract The synthesis and comprehensive characterization of a purely sterically stabilized latex with narrow size distribution is reported. By use of non-ionic initiators no chemically bound surface charges are generated. Stabilization of the particles is achieved through use of a non-ionic surfactant having a double bond in the hydrophobic part which is chemically bound to the surface. Analysis of the latex particles thus generated by transmission electron microscopy, disc centrifugation, and small-angle X-ray scattering (SAXS) reveals that the size distribution is narrow (standard deviation between 6 and 10%). SAXS furthermore demonstrates that the surfactant is located in a thin layer on the surface. The interaction of the particles is purely repulsive as shown by the analysis of the turbidity of the latex. The systems obtained herein may serve as model systems of water-borne purely sterically stabilized colloid particles.

Key words Latex – steric stabilization – SAXS – turbidity

Introduction

Suspensions of polymer latex particles in water or non-aqueous mediums may be regarded as model systems for condensed matter since these systems allow the study of phase transitions as function of the interaction potential of the particles [1]. Up to now the overwhelming majority of experimental study of aqueous latex dispersions has been devoted to electrostatically stabilized latex particles, i.e., to systems in which stabilization against flocculation has been achieved through chemically bound or adsorbed charges. The interaction of such particles which can be described by a screened Coulomb potential seems to be reasonably well understood by now [1]. Purely sterically stabilized latexes where the stabilization is achieved through polymer chains affixed to the surface have mainly been studied in non-aqueous solvents. Thus, poly(methylmethacrylate) particles stabilized by a chemically bound surface layer of poly(12-hydroxystearic acid) [2–4] have by now become a highly useful model system used for a great number of experimental studies [5–7].

Much less is known about the interaction of purely sterically stabilized latex particles which are dispersed in water. An investigation of such particles bearing no charge with regard to particle interaction and flow behavior is highly interesting because these suspensions can exhibit non-DLVO-type interactions and demixing phenomena as function of temperature [8, 9]. Thus, Zhu and Napper could demonstrate in the course of a number of thorough studies that aqueous poly(*N*-isopropylacrylamide) (PNIPAM)- or poly(ethylenoxide) (PEO) stabilized poly (styrene) (PS) latex particles exhibit attractive interactions as function of the concentration of added salt [10–12]. The flocculation induced by the hydrophobic attraction in these systems was studied by these authors by means of dynamic light scattering.

In the present communication, we describe the synthesis and the characterization of poly(styrene) latex particles dispersed in water which are purely sterically

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stabilized. Starting from the route developed by Ottewill and Satgurunathan [13–15] the preparation of the latex will be described which carefully avoids chemically bound charges. Except from possible small charges acquired by adsorption of ions in solution these particles carry no net charge. The short polymer chains are affixed to the surface by chemical bonds and the systems thus obtained may be regarded as model systems of aqueous sterically stabilized systems.

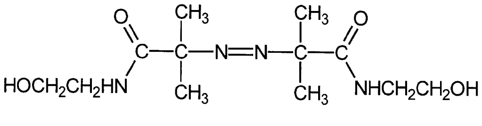
Special care has been taken to obtain particles with a narrow size distribution. It is obvious that a model dispersion must exhibit a narrow distribution of the radii of the particles because a broad size distribution may be followed by a respective chemical polydispersity. In addition to this, studies of particle interaction in model suspensions by scattering methods require narrow size distributions as well. As extensively discussed by D'Aguanno and Klein [16] the polydispersity of sizes will cause an incoherent contribution which may become the main part of the measured scattering intensity at small angles. It is therefore evident that such an incoherent contribution will profoundly disturb studies of particle interaction and must be minimized by a narrow size distribution. A polydispersity of sizes may also be accompanied by a respective polydispersity of the radial structure which would furthermore complicated the analysis of the system by scattering methods.

Experimental

Materials

Styrene was obtained from the BASF AG and purified by washing several times with 3 M NaOH and subsequently with H_2O. After drying with $CaCl_2$ the monomer was distilled in vacuo shortly before use. 2,2′-Azo-*bis*[2-methyl-*N*-(2-hydroxyethyl) propionamide] (VA-086) was obtained from Wako Pure Chemical Industries (see Scheme 1). The surfactants poly(ethyleneoxide) mono sorbitanmonooleat (Tween 80) and poly(ethyleneoxide) sorbitanmonostearat (Tween 60) was obtained from Aldrich and used without further purification. Scheme 2 gives the chemical structure of Tween 80.

Scheme 1



VA-086

Ascorbic acid (Fluka,Bio Chemica >99.5%) and H_2O_2 (Fluka, 35%) were used without further purification. Water was purified by reverse osmosis (Millipore MilliRO) and subsequent ion exchange (Millipore MilliQ).

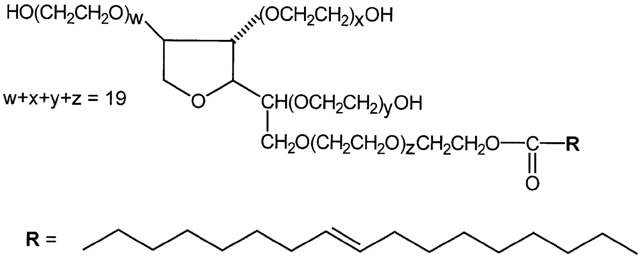
Emulsion polymerization

All PS-latexes were prepared by a batch emulsion polymerization using a 3 L reactor (Büchi) which could be thermostatted by a cooling jacket. The reactor was equipped with a thermometer, a condensor and a stainless-steel stirrer (Büchi). After charging the reactor with water, monomer and surfactant the mixture was degassed by repeated evacuation at 60 °C. To this mixture ascorbic acid dissolved in 10 ml of degassed water was added under an atmosphere of nitrogen. The mixture was stirred with 150 U revolutions/min and the reaction was started by the addition of H_2O_2 at 60 °C.

In the case of VA-086, a temperature of 80 °C was chosen. This initiator was dissolved in 80 ml degassed water and the solution was also added through a septum to start the reaction. During emulsion polymerization the mixture was stirred with 400 revolutions/min for typically 6 h. After this time the latex was filtered through a sieve to remove coagulum. Typical recipes are as follows: 2000 g H_2O, 220 g styrene, 30 g Tween 80, initiated by 0.64 g ascorbic acid together with 1.1 ml H_2O_2 (35%). The mixture is stirred with 150 revolutions/min; or: 2000 g H_2O, 145 g styrene, 15 g Tween 80, initiated by 2.5 g VA-086, stirred with 400 revolutions/min.

All latexes prepared here were purified by serum replacement or dialysis. The ionic strength of all systems was adjusted through exhaustive serum replacement with 0.005 M aqueous KCl solution. The contents of solid polymer was determined gravimetrically. The degree of conversions of all polymerizations was 98%.

Scheme 2



Tween 80

Characterization

The density of the latex particles was determined using a DMA-60 densitometer supplied by PAAR (Graz, Austria). The size of the particles and their size distribution were determined by use of transmission electron microscopy (TEM, Hitachi 700), by a Brookhaven DCP disc centrifuge according to ref. [17] and by dynamic light scattering (Peters ALV 4000). The radial structure of selected latexes was analyzed by small-angle X-ray scattering (SAXS) using a SAXS-camera described elsewhere [18].

The interaction of the particles was investigated using the turbidimetric method presented recently [17, 19, 20]. The specific turbidities τ/c_L of the latexes were obtained using a Perkin–Elmer-Lambda 2S UV/VIS-spectrometer. All suspensions solutions were filtered through a cellulose acetate filter (pore size 0.45 μm, Roth). Further details of the measurements and the procedures used for the evaluation of data may be found in ref. [20].

Results and discussion

As mentioned in the Introduction, the preparation of purely sterically stabilized latexes has been the subject of only a few experimental studies up to now. Ottewill and Satgurunathan [13] have investigated the emulsion polymerization of styrene by use of non-ionic surfactants and macromonomers. The polydispersity found by these workers was 15.5% [14]. More recently, the synthesis of sterically stabilized latexes was the subject of studies by Tauer et al. [21], Vidal et al. [22], Filet et al. [23] and Torii et al. [24]. In several cases, the size distribution of the systems prepared in the course of these studies was rather broad.

As shown by data gathered in Table 1, the systems prepared by the method devised here are in general narrowly distributed. Good agreement between the different methods used herein for determination of the diameter and the polydispersity is seen. The hydrodynamic diameters measured with PCS are slighly larger than those determined by other mentioned methods. This is not surprising because Tween 80 is a polydisperse surfactant. Stenkamp and Berg [25] could recently show that hydrodynamic measurements are sensitive to a very low density of long tails which cannot be detected by static scattering methods.

The initiator was found to play a decisive role for the breadth of the distribution and in general for the reproducibility: The redox initiator ascorbic acid/H_2O_2 leads to less reproducible results than the amphiphilic azo-initiator VA-086. We ascribe the problem of the former initiator to possible side reactions of H_2O_2 with the surfactant Tween 80, e.g. through oxidation of the double bound or hydroxy-groups and subsequent reactions. Hence, the present results show that the azo-initiator is more suitable for the preparation of narrowly distributed latexes. Nevertheless, Table 1 demonstrates that the redox initiator may lead to well-defined dispersions as well.

Figure 1 shows a TEM micrograph of a latex PSTW80 (Table 1). The small breadth of the monomodal size distribution is directly evident and is corroborated by the results obtained through disc centrifugation. Figure 2 demonstrates the good agreement obtained for latex PSTW80 (Table 1) by both methods.

The micrograph displayed in Fig. 1 furthermore suggests the presence of a thin surface layer of the surfactant. As demonstrated recently, the surface of PS latex particles can be studied by SAXS with great accuracy [18]. This is due to the fact that the contrast of the PS core of the particle in water is quite low. The measured SAXS-signal is therefore governed by the scattering by the surface layer of the surfactant. Figure 3 gives an example of such a SAXS-study of latex PSVATW015 together with a fit of a core-shell distribution of the radial electron density. The

Table 1 Characterization of the latexes

Latex	Initiator	D_N (nm)	D_W/D_N	Determined by
PSTW80	H_2O_2/AA	109	1.007	TEM
		110	1.018	DCP
PSTween2	H_2O_2/AA	131	1.023	DCP
		131	1.016	SAXS
PSTW803	H_2O_2/AA	111	1.018	DCP
		112	1.030	SAXS
		$D_{PCS} = 122$ nm	—	PCS
PSVATW015	VA-086	85.1	1.028	SAXS
		85.2	1.011	TEM
		86.5	1.028	Turbidimetry
		$D_{PCS} = 98.3$ nm	—	PCS

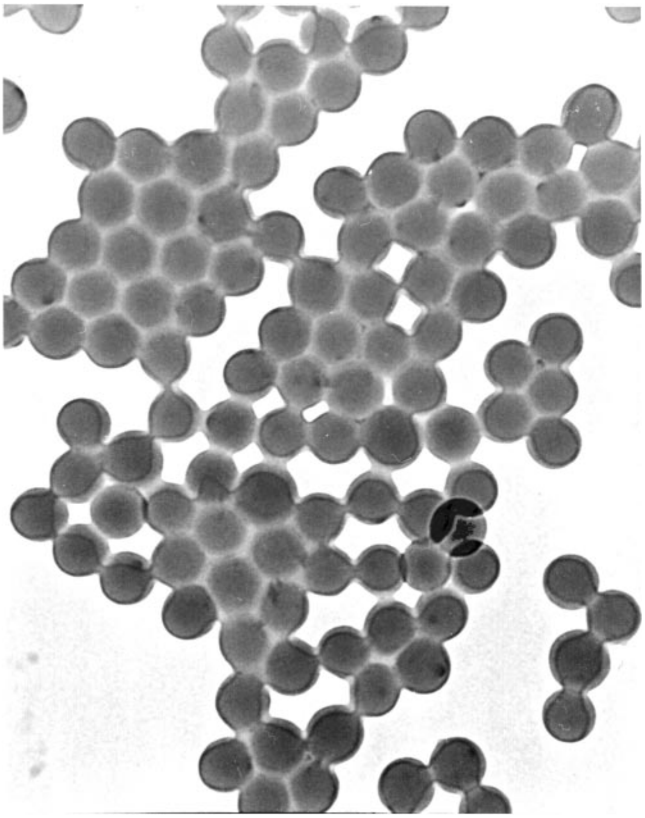


Fig. 1 Transmission electron micrograph of latex PSTW80 (cf. Table 1)

analysis of core-shell systems by SAXS has been described in detail in ref. [18]. The inset of Fig. 3 displays the radial excess electron density resulting from this fit.

The fit of the data shown in Fig. 3 was provided by the following parameters: The core has a diameter of 82.9 nm and an excess electron density of 6.4 nm^3, whereas the thickness of the shell was 1.1 nm with an electron density of 29/nm^3 (cf. inset of Fig. 3). The surface layer expected from the synthetic procedure thus can be proven directly. The deep minima of the scattering curve immediately indicate the narrow size distribution. For the optimal fit a slightly asymmetric distribution derived from ultracentrifugation (cf. ref. [18]) with a standard deviation of 9.7% had to be assumed. This result is in accord with the findings of TEM and turbidimetry and disc centrifugation (cf. Table 1).

As could be expected from the work of Ottewill and Satgurunathan [13] the double bound in Tween 80 leads to some extent to a chemical fixation of this surfactant on the surface of the particles. This can be seen very easily when comparing systems prepared by use of Tween 80 to latexes polymerized by use of Tween 60. Since the latter surfactant contains no polymerizable double bond it is only adsorbed on the surface and can be removed through exhaustive serum replacement or by dilution with or dialysis against a mixture of ethanol and water (1 : 1). Latexes prepared by aid of Tween 60 coagulate rapidly under these

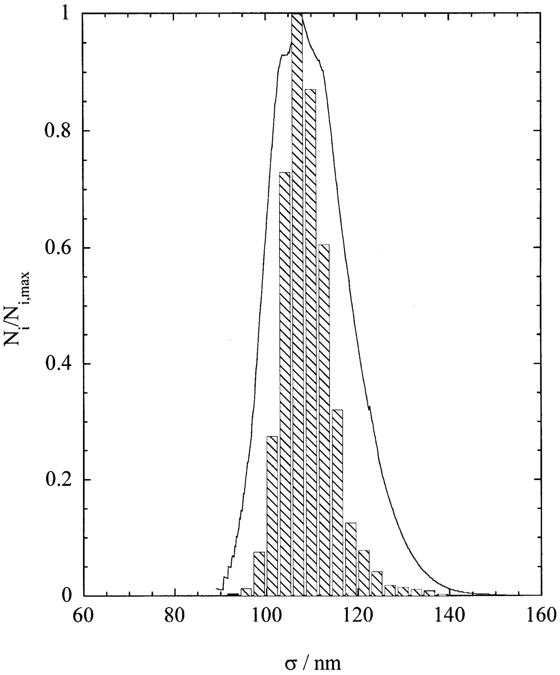


Fig. 2 Comparison of the size distribution determined by electron microscopy (histogram) and by disc centrifugation (solid line)

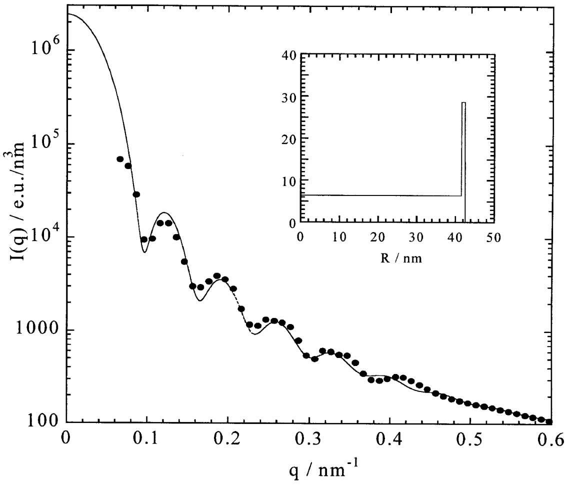


Fig. 3 Analysis of the radial structure of latex PSVATW015 by small-angle X-ray scattering (SAXS): Scattering intensity $I(q)$ as function of the magnitude of the scattering vector $q(q = (4\pi/\lambda)\sin(\theta/2)$; λ is the wavelength of radiation; θ the scattering angle). The inset gives the radial excess electron density resulting from the fit (solid line) of the experimental scattering intensities

conditions, whereas particles with chemically fixed surfactants stay stable [13]. PCS measurements in different KCl solution have shown that the systems become unstable at 1 M KCl at 25 °C which is still a good solvent for PEO. It is well known that systems with thin steric layer may flocculate in dispersion media that are good solvents for the stabilizing moieties [9].

From the synthetic procedure it is obvious that the particles obtained through use of a nonionic initiator are not expected to carry any chemically bound surface charge. Stabilization is thus only achieved through the thin surface layer of the surfactant affixed to the surface by chemical bonds. Such particles should interact in good approximation as hard spheres: only if the short chains of the shell overlap, the particles should feel a hard repulsion, no interaction of longer range as is the case in, e.g. electrostatically stabilized systems is possible. To remove the effect of residual adsorbed charges [26] or from charges formed owing to possible side reactions when studying the particle interaction, an ionic strength of 0.005 was chosen (cf. the discussion of this point below).

Because of the narrow size distribution of the latexes prepared herein, the interaction can be conveniently probed by scattering methods [1, 27]. Turbidimetry is suitable to explore the scattering intensity in the region of smallest scattering vectors $q (q = (4\pi/\lambda)\sin(\theta/2)$; θ is the scattering angle, λ the wavelength of the radiation in the medium) [17, 19, 20, 28–30]. From these data the structure factor $S(q)$ may be obtained and compared with theoretical expressions taking into account particle interaction. For the particles under consideration here $S(q)$ is expected to be described by the structure factor of a system of hard spheres provided by the Percus–Yevick theory [27].

As shown recently [17, 19, 20, 28–30] the turbidity may be factored into an integrated form factor $Q(\lambda^2)$ and an integrated structure factor $Z(\lambda^2, c)$ according to

$$\tau = K^* c_L \left(\frac{n_0 \pi \sigma_L}{\lambda_0}\right)^3 \left(\frac{16\pi}{3}\right) Q(\lambda^2) Z(\lambda^2, c_L) , \qquad (1)$$

where K^* defines the optical constant by

$$K^* = \frac{3n_0}{4\lambda_0 \rho_L} \left(\frac{m^2 - 1}{m^2 + 2}\right)^2 , \qquad (2)$$

with c_L being the weight concentration and ρ_L being the density of the particles, n_L the refractive index of the latex particles and $m = n_L/n_0$ their relative refractive index. Thus, the integrated structure factor $Z(\lambda^2, c)$ can be obtained from the specific turbidities τ/c_L by

$$Z(\lambda^2, c_L) = \frac{(\tau/c_L)}{(\tau/c_L)_0} , \qquad (3)$$

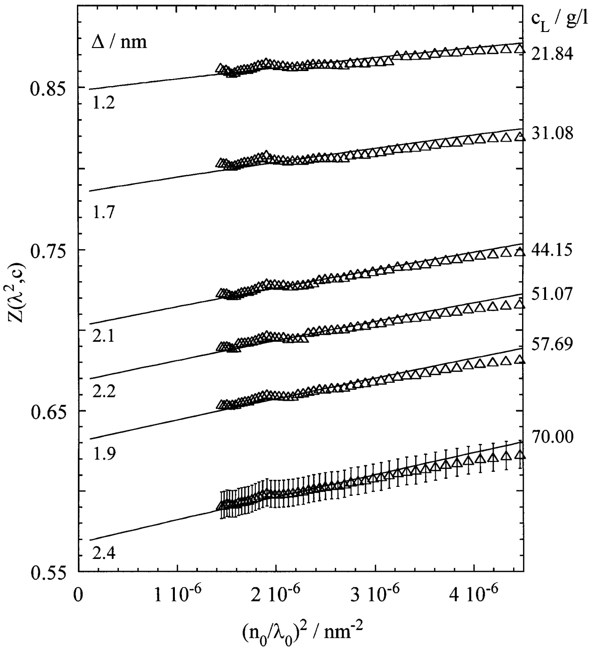
where $(\tau/c_L)_0$ is the specific turbidity extrapolated to vanishing latex concentration c_L. The function $Z(\lambda^2, c_L)$ may be expanded into powers of the size parameter $n_0 \pi \sigma/\lambda_0$ leading to [17]

$$Z(\lambda^2, c_L) = S(0) + 8\alpha \left(\frac{n_0 \pi}{\lambda_0}\right)^2 + B \left(\frac{n_0 \pi}{\lambda_0}\right)^4 + O(\lambda^{-6}) . \qquad (4)$$

Here α is the first coefficient of the expansion of $S(q)$ in powers of q^2, whereas the coefficient B contains factors pertaining to the interaction of the particles as well as to their optical radius of gyration [17, 19, 20]. If the size parameter $n_0 \pi \sigma/\lambda_0$ is not too big, the third and fourth terms in Eq. (4) give only minor contributions. In this case $S(0)$ can be extrapolated from experimental data with very good accuracy [17, 19, 20]. For strongly scattering systems turbidimetry thus furnishes $S(0)$ which is a quantity difficult to measure by other methods.

Figure 4 displays the integrated structure factor $Z(\lambda^2, c_L)$ as function of λ^{-2} for different concentrations c_L together with a fit by the Percus–Yevick-theory for hard spheres. The size distribution of the latex under consideration here is narrow and as outlined in refs. [19, 20] the effect of polydispersity can be dismissed within the the limits of error. The resulting effective diameters from the

Fig. 4 Integrated structure factor $Z(\lambda^2, c)$ (see Eq. (3)) determined experimentally from latex PSVATW015 (circles) together with the optimal fit of the integrated structure factor of a system of hard spheres (cf. text for further explanation) as function of λ^2 (λ the wavelength in medium). The numbers on the right-hand side indicate the concentration of the latex in g/l



fit, calculated from $S(0)$, are identical for all concentrations under consideration here. By comparison with the core diameter determined by the SAXS-measurement it results an effective shell thickness Δ of 2 ± 1 nm (see Fig. 4). This can be attributed to the stabilizing polymer layer and is in good agreement with the shell thickness obtained from the SAXS data.

It must be kept in mind that the ionic strength was chosen to be rather high (0.005) to minimize the effect of the electrostatic repulsion due to adsorbed charges. Further studies have demonstrated that anions adsorbed preferentially onto the surface of the present latex particles may indeed lead to additional repulsion if the ionic strength is of the order of 0.001 [31]. In this case the effective diameter measured by turbidimetry is increased considerably. Hence, even in case of latexes without chemically affixed charges possible effects of adsorbed charges must be considered when discussion the interaction of the particles.

Conclusion

The synthesis of narrowly distributed model latexes has been presented. By use of appropriate initiators and a surfactant containing a double bond in the hydrophobic part, purely sterically stabilized particles are obtained. Analysis by SAXS reveals that the particles exhibit a well-defined core-shell structure in which the surfactant is located in a thin layer on the surface. Turbidimetry furthermore shows that these particles interact as hard spheres as expected for a purely sterically stabilized latex. These latexes may therefore be used as model systems for waterborne colloids without chemically bound charges.

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