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Structure of Carboxylated Latices As Revealed by Small-Angle X-ray Scattering

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ABSTRACT: An analysis of the radial structure of carboxylated latex particles by small-angle X-ray scattering (SAXS) is given. The latex was prepared by a batch emulsion polymerization of methyl methacrylate and methacrylic acid. The analysis of the SAXS intensities leads to the conclusion that the particles of number-average diameter 90.8 nm exhibit a pronounced core–shell structure, i.e., practically all the carboxyl groups are located within a shell of 13.6 nm thickness.

Introduction

Latices prepared by copolymerization with monomers containing carboxyl groups like acrylic or methacrylic acid have found widespread industrial applications.[1–5] This is mainly due to the fact that carboxylated latex particles exhibit an enhanced stability against flocculation.[4–7] Also, depending on the acid content, the particles will swell upon increasing the pH value, which leads to a marked increase of the viscosity.[1] A question of utmost importance when studying these latices is the location of the carboxyl groups within the particles. Up to now this problem has been studied using mainly titration experiments to distinguish between carboxyl groups sitting directly on the surface and those "buried" in the particles.[1,4–7] Titration experiments, however, will give only rather indirect information about the spatial structure of the particles. Swelling may also disturb the structure of the carboxylated particles since frozen-in nonequilibrium states within the particle will immediately relax.

In this paper we present the first investigation of the internal structure of carboxylated latices by small-angle X-ray scattering (SAXS).[8–10] This technique is well suited for the study of latex particles since the monomers usually employed for the synthesis of such systems differ greatly with regard to electron density. Thus, in recent publications[9,10] it could be demonstrated that the internal structure of core–shell particles consisting of polystyrene and poly(methyl methacrylate) (PMMA) can be studied by SAXS down to minute details of the order of a few nanometers. Here we extend these investigations to PMMA latices containing 5% of methacrylic acid (MAA) prepared by a batch emulsion polymerization. It is the goal of this investigation to show the feasibility of the SAXS technique to elucidate the radial structure of the particles.

Experimental Section

1. **Materials.** Methyl methacrylate (MMA, Fluka) was washed three times with 10% aqueous NaOH and subsequently with H_2O to remove the stabilizer. After careful drying, the monomer was distilled under reduced pressure. Methacrylic acid (MAA, Fluka) was purified by distillation shortly before use. $K_2S_2O_8$ (Fluka) was recrystallized twice from water. The surfactant sodium dodecyl sulfate (SDS, Fluka >99.5%) was used as received. All emulsion polymerizations were carried out in freshly bidistilled water.

2. **Preparation of Carboxylated Latices.** Carboxylated latices were prepared by emulsion polymerization in a four-neck flask at 80 °C under an atmosphere of nitrogen. In a typical experiment the following recipe was used: MMA, 95 parts; MAA, 5 parts; water, 350 parts; SDS, 0.83 parts, $K_2S_2O_8$, 0.4 parts. The flask was charged with water and the SDS and purged with nitrogen. After having reached the temperature of 80 °C, the monomers were added at once and the polymerization was started by adding the initiator dissolved in 20 mL of water. The polymerization was stopped after 6 h by adding hydroquinone and cooling in an ice-cold bath. To remove possible coagulum the latex was filtered over glass wool.

All latices were cleansed by serum replacement.[11–13] The latex was placed in a filtration cell (Sartorius Ultrasart 50) using a cellulose nitrate filter with a nominal pore size of 50 nm (Schleicher & Schuell PH 75). Bidistilled water was pumped through this cell unless the conductance of the filtrate assumed a constant value.

3. **Characterization.** Electron microscopy was done using a Hitachi H700 transmission electron microscope. To avoid errors due to degradation of PMMA in the electron beam, the latices were negative stained with phosphotungstic acid.[14]

The diameter of the latex particles was also determined by turbidimetry.[19,20] For this purpose the turbidity of the diluted latex was measured using a Perkin-Elmer Lambda 2S UV/vis spectrometer.

Titration experiments were conducted according to the method devised by Nishida et al. (cf. ref 1 and further citations given there). Thus the latex cleansed by serum replacement is treated with an excess of aqueous 0.1 N NaOH for 24 h. Back-titration led to the conclusion that only 70% of the carboxyl groups could be titrated by this procedure. In addition to this, it was found that the methacrylic acid is practically fully embodied in the latex; i.e., virtually no carboxyl groups could be detected in the serum.

An important prerequisite for the SAXS analysis of latex particles is the exact knowledge of the breadth of the size distribution,[15] which was determined by a disk centrifuge.[16,17] Thus, the number-average diameter D_n as well as the weight-average diameter D_w of the carboxylated latex was determined with Brookhaven DCP disk centrifuge. The spinning liquid was 10–15 mL of 5% aqueous sucrose. As buffer, 0.8–1 mL of 2% sucrose solution was applied. To avoid a temperature gradient the spinning liquid was covered with 0.4 mL of dodecane. The size of the latex probe analyzed was typically 0.1–0.3 mL. Evaluation of the number- and weight-average diameter of the latices was achieved using the DCP 7.0 software supplied by Brookhaven.

4. **SAXS Measurements.** Measurements of absolute SAXS intensities were done using a Kratky camera equipped with a position-sensitive counter. The details of the measurements as well as of the desmearing procedures applied to the scattering data may be found in ref 10. Prior to the measurement the latices were diluted with pure water to typically 5 wt %. To check the influence of interparticle interference, some measurements were done to much lower concentrations (0.5 wt. %). Since the influence of the structure factor was found to be negligible for the angular region under consideration here (cf. the discussion

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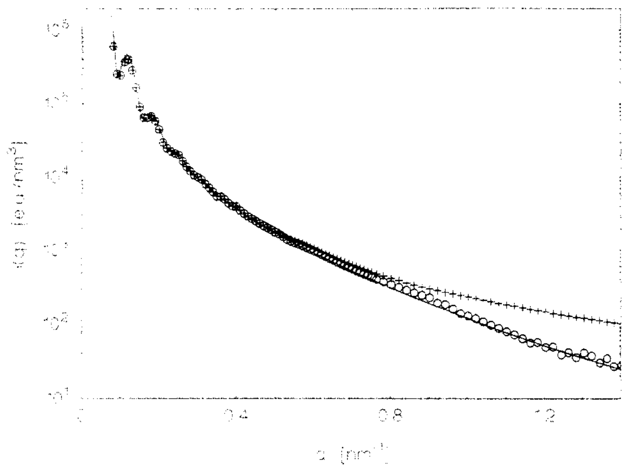

Figure 1. Desmeared SAXS scattering intensity of the carboxylated latex. Crosses, raw data; circles, data after subtraction of the background caused by density fluctuations of polymeric material. The constant background was determined by the Porod plot shown in Figure 2.

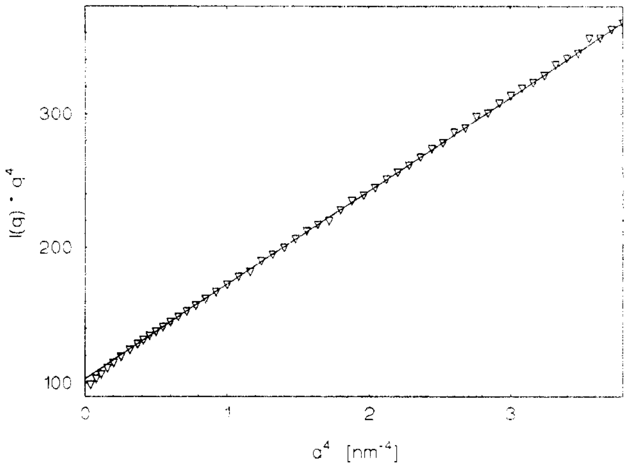

Figure 2. Porod plot (cf. ref 8) of the SAXS intensities given in Figure 1 (crosses). The constant background scattering due to density fluctuations within the particles has been used to correct the SAXS intensities in the region of higher angles (circles, Figure 1).

of this point in ref 9), all measurements could be done at 5 wt % to obtain good counting statistics.

5. Modeling of the SAXS Intensities.[10] The carboxylated particles are assumed to have a concentric structure characterized by a radial electron density $\rho(r)$. For a dilute system of monodisperse particles the intensity normalized to the scattering intensity of a single electron is given by

$$I(q) = NB^2(q) \tag{1}$$

where N is the number of particles per unit volume, $q = (4\pi/\lambda)\sin(\theta/2)$, with θ being the scattering angle, and $B(q)$ is the scattering amplitude. In the case of spherically symmetric particles with radius R, $B(q)$ can be calculated through

$$B(q) = 4\pi \int_0^R [\rho(r) - \rho_m] r^2 \frac{\sin(qr)}{qr}\, dr \tag{2}$$

with ρ_m being the electron density of the dispersion medium. For polydisperse systems

$$I(q) = \sum_i N_i B_i^2(q) \tag{3}$$

where the index i refers to the type of particle under consideration and N_i is the respective number density.

The size distribution of the latices under consideration here could be done assuming either a Gaussian distribution or an unsymmetric distribution found previously by ultracentrifugation[15] for similar latex systems.[9,10] The polydispersity was modeled by adjusting the breadth of the fractions of the histogram given in ref 10 unless the weight-average diameter as well as the standard deviation coincided with the values supplied by disk centrifugation (see ref 10 for further details of this procedure). The average diameter of the latex as well as the breadth of the distribution obtained from the fits can then be compared with experimental data.

Results and Discussion

Figure 1 displays the desmeared SAXS intensities obtained from a 5.1 wt % latex with a number-average diameter D_n = 91.0 nm (electron microscopy: D_n = 90.4 nm) and a weight-average diameter D_w = 97.0 nm. Both values have been determined by disk centrifugation. The diameter determined by turbidimetry was 98 nm, which is close to the respective weight average. To ensure the absence of interparticle interference, the experiment was repeated using a 0.5 wt % suspension. No alterations of the scattering intensity in the region of scattering angles under consideration here were effected through dilution. As already discussed in great detail recently,[9] this finding proves that in the given region of scattering angles the influences of the structure factor is negligible at concentrations around 5 wt %. Therefore all experiments were conducted in this regime of concentration.

Due to the finite width of the size distribution the scattering curves do not exhibit any minima or maxima beyond q = 0.3 nm^{-1}. The background scattering mainly caused by the density fluctuations of the solid polymer could therefore be determined directly by a Porod plot (see the discussion of the subtraction of the background in ref 10). Figure 2 demonstrates good linearity for the high-angle region and the presence of a background intensity independent of the scattering angle. Subtracting this background leads to the corrected scattering curve shown by the circles in Figure 1. It has to be noted, however, that the influence of the background is non-negligible only above 0.6 nm^{-1}. It is thus nearly inconsequential for the comparison of the experimental scattering intensities ($q \leq 0.7$ nm^{-1}) with given models of the radial electron density.

As a first guess, one might assume a homogeneous distribution of both polymeric compounds throughout the particle. The respective fit of a constant electron density $\rho(r)$ shown in the inset of Figure 3a is displayed in Figure 3a. Here the model matches the experimental data in the region of small angles quite well and leads to a number-average radius of the particles of 92.6 nm. There is, however, a clearly visible discrepancy in the region of wider angles which is much higher than the experimental uncertainty.

Another argument against this model may be derived from fact that the model must reproduce the absolute scattering intensities furnished by the experiment. Due to the small amount of PMAA (5%) present in the latex spheres, their average electron density is mainly determined by the electron density of solid PMMA. Taking a slightly higher value as the average electron density of the particles (see inset of Figure 3a), a number density of particles has to be assumed which amounts to a concentration of 8.1 vol % instead of 5.1 vol % used in the SAXS experiment. This figure is certainly out of the range given by experimental uncertainty. Taking the electron density instead as a fit parameter at a fixed number density, a value far above the accessible range will result. It is thus obvious that a homogeneous electron density throughout the particles does not give a proper description of the data.

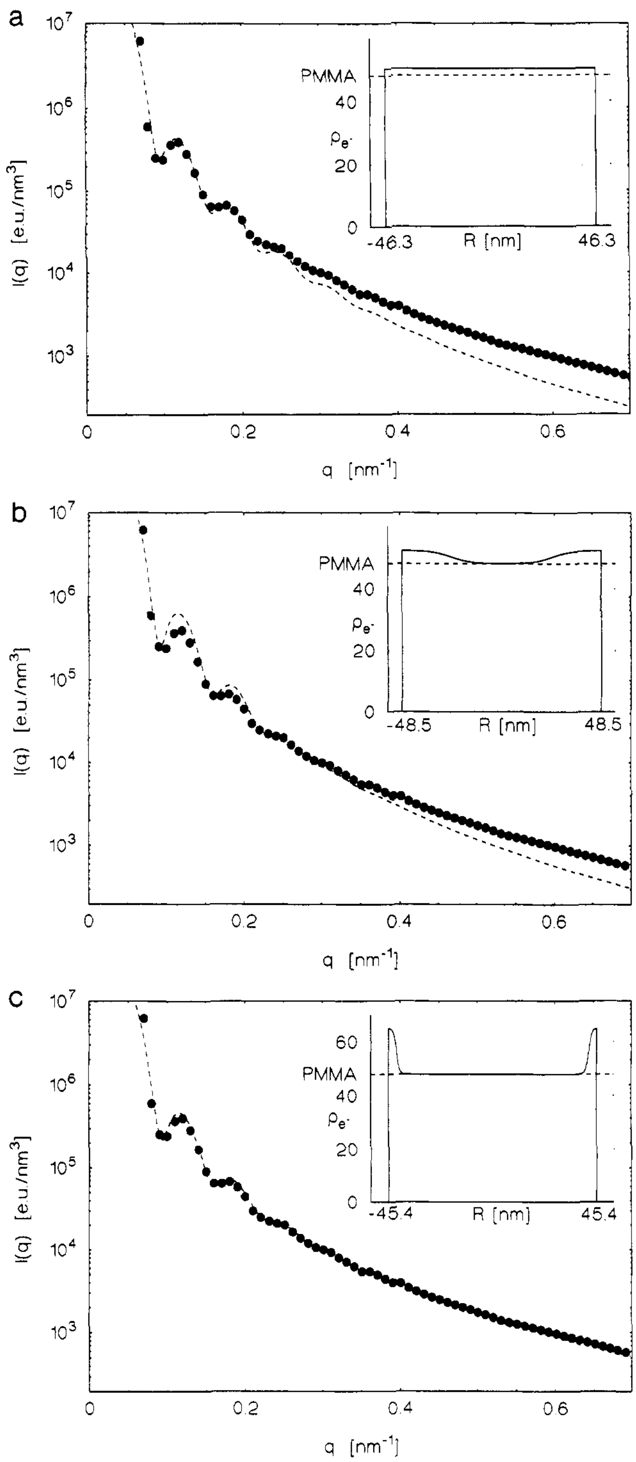

Figure 3. Modeling of the experimental SAXS intensities by the electron densities shown in the inset of the respective figures. The filled circles give the measured intensities whereas the dashed lines refer to the calculated intensities. The dashed lines in the insets give the electron density of solid PMMA with respect to the dispersant water; the solid lines in the inset denote the electron density used for the calculation of the SAXS intensities according to eqs 1–3.

This is expected from other indirect experiments on carboxylated latices reported in the literature.[1]

A more probable distribution is shown in the inset of Figure 3b, where a penetration of the carboxyl groups deep into the particles is assumed. The variation of the radial electron density is modeled using an expression first given by Halfand and Tagami[18] for the interface of immiscible block copolymers:

$$\rho(r) = \rho_{\text{core}} + \frac{\rho_{\text{shell}} - \rho_{\text{core}}}{1 + \exp[c(r_0 - r)]} \qquad (4)$$

where c is a positive constant characterizing the width of the interface between the two polymer phases and r_0 characterizes the radial position of the interface. The resulting electron density is shown in the inset of Figure 3b. In the following fit the width of the shell is defined by the outer radius and the locus within the particle where the electron density is only 0.5% above ρ_{core}. The width thus defined is assumed to be proportional to the diameter of the particles. Here, too, the resulting fit is rather poor since the calculated intensities require again number densities much too high (7.6 vol % instead of 5 vol %). The number-average diameter resulting from this fit is 97 nm, a value also out of the range of experimental uncertainty.

The best fit of the experimental intensities describing the entire range of scattering angles could be achieved by an electron density distribution modeled according to eq 4 (cf. inset of Figure 3c). Here a rather sharp core–shell structure is assumed with a core which exhibits the electron density of pure PMMA. Again the shell as well as r_0 is taken to be proportional to the diameter of the particles, leading to the following results of the fit: number-average diameter = 90.8 nm; weight-average diameter = 96.1 nm. The electron density distribution depicted in the inset of Figure 3c requires a latex concentration of 5.4%. These data are in very good agreement with the figures obtained by independent methods (see above). The modeling shown in Figure 3c therefore allows one to conclude that the average particle has a carboxylated shell with an average width of 13.6 nm.

The present model assuming a steep but not infinitely sharp interface inside the particle is not in contradiction with the fact that the final slope of the scattering curves follows a q^{-4} law. From the above model, the magnitude of $\Delta\rho$ inside the particle amounts to 15 e/nm^3, whereas $\Delta\rho$ at the outer surface toward the dispersant water amounts to 65 e/nm^3. The contribution of the two interfaces is weighted according to the square of the respective difference of the electron densities $\Delta\rho$. It is thus obvious that the scattering intensities at the highest angles are mainly determined by the surface particle/water. In addition to this, the electron density rises rather steeply, and model calculations predict for the q range under consideration here linear Porod plots (cf. the discussion in ref 21). The total surface calculated from the intercept in Figure 2 and $\Delta\rho$ = 65 e/nm^3, however, is higher by ca. 15% than the value derived from the number-average diameter and the outer surface alone. This points to the presence of an additional internal surface, in agreement with the model shown in the inset of Figure 3c.

Up to now the internal structure of the particles could be modeled only in terms of the radial electron density. To calculate the volume fraction of the poly(methacrylic acid) (PMAA) the density of solid PMAA must be known. Unfortunately, no reliable data are available in the literature. Also, the SAXS technique does not allow one to distinguish between a mixture of two polymers and a copolymer, of course. Nevertheless, it is instructive to make a first guess by assuming the volume contraction when going from the monomer MAA to the polymer PMAA to be the same as measured[22] in the case of MMA/PMMA. Thus an electron density of solid PMAA of 75 excess e/nm^3 can be estimated. This figure would give a maximum volume fraction of PMAA in the region near the surface of ca. 55 vol % and an overall volume fraction of PMAA of 5.2%. The latter figure is in agreement with the overall weight fraction of MAA used in the polymerization.

Conclusion

The SAXS analysis of the radial structure of a carboxylated latex particle prepared by a batch process clearly demonstrated the carboxyl groups to be located mainly near the outer surface. The electron density as depicted in the inset of Figure 3c leads to the conclusion that the locus of the polar component is a shell of 13.6 nm thickness. The change of the radial electron density when going from the unpolar core to the polar shell is rather steep. The analysis presented herein thus points to the strong tendency for segregation of polar and nonpolar components during the emulsion polymerization.

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