*Macromol. Symp.* ***145****, 9–20 (1999)*

# Investigation of the Adsorption of Surfactants on the Poly(styrene) Latex Particles by Small-Angle X-Ray Scattering

S. Seelenmeyer, M. Ballauff*

Polymer-Institut, Universität Karlsruhe, Kaiserstr. 12, 76128 Karlsruhe, Germany

Summary: We present the study of the adsorption of a non-ionic surfactant onto latex particles by small-angle X-ray scattering (SAXS). The analysis of the process of adsorption by SAXS is discussed in detail. It is demonstrated that SAXS allows to monitor the gradual built-up of the surface layer with increasing amount of added surfactant. SAXS also allows to obtain the radial volume fraction of the hydrophilic tails of the surfactant. Possible limitations of this analysis are discussed.

## Introduction

Latex particles possessing spherical symmetry present ideal objects for structural studies by scattering methods as small-angle X-ray scattering (SAXS)[1)] or small-angle neutron scattering (SANS)[2)]. For non-interacting systems, all structural information is embodied in the radial distribution $\rho(r)$ of the scattering length density which determines the scattering amplitude B(q) through[1)]

$$B(q) = 4\pi \int_0^R [\rho(r) - \rho_m] r^2 \frac{\sin(qr)}{qr} dr \qquad (1)$$

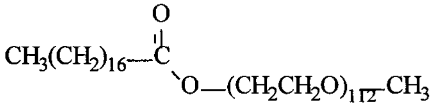
Here R is the radius of the particle whereas $\rho_m$ denotes the scattering length density of the dispersion medium. The scattering intensity I(q) ($q=(4\pi/\lambda)\sin(\theta/2)$; θ: scattering angle; λ: wave length) follows as $I(q)=B^2(q)$ and may thus be directly related to the radial structure of the particles. The forward scattering I(0) is uniquely determined by the overall contrast $\overline{\rho} - \rho_m$ where $\overline{\rho}$ is the average scattering length density defined by

$$\bar{\rho} = \frac{\int_0^R [\rho(r) - \rho_m] r^2 dr}{\int_0^R r^2 dr} \qquad (2)$$

The scattering intensity measured at higher q-values furnishes details of the profile $\rho(r) - \rho_m$. Hence, the structure of polymers or surfactants adsorbed on the surface of core-particles with low contrast $\bar{\rho} - \rho_m$ may be studied in great detail by SANS or SAXS because in this case the measured scattering intensity I(q) originates mainly from the adsorbed layer. The scattering length density profile obtained from this analysis may be converted into the volume fraction profile of the hydrophilic part of the adsorbed surfactant or polymer which extends into the aqueous phase. In principle, scattering methods are therefore capable of furnishing comprehensive information on the structure of the surface layer.

Up to now, adsorption onto the surface of latex particles has been studied by a number of authors using SANS3-7). Using partially deuterated latex particles or mixtures of $H_2O$ and $D_2O$ the contribution of the core particle to the measured scattering intensity can be minimized and the scattering signal is mainly due to the surface layer. The SANS-data thus obtained may be analyzed according to the scheme devised by Auroy and Auvray8-10) for polymers affixed to flat surfaces. An important point of this analysis is the proper treatment of scattering arising from the fluctuations within the layer structure.

Here we wish to discuss the analysis of adsorbed layers of surfactants by SAXS. Previously it could be shown that SAXS allows to follow the process of adsorption of the non-ionic surfactant Triton X-405 and of sodium dodecylsulfate (SDS) on the surface of poly(styrene) (PS) latex particles11,12). PS particles are well suited for studying the process of adsorption because their contrast in water is low ($6.3e^-/nm^3$; ref.13,14)). The scattering curves measured at different concentration of the added surfactant allowed to follow the process of gradual coverage of the surface of the particles. In addition to this, these measurements showed directly the concentration at which saturation of the surface is achieved11,12). The analysis demonstrated clearly that free micelles are formed beyond the saturation of the surface. SAXS furthermore allows to study the competitive adsorption of Triton X-405 and SDS11). Due to the rather short hydrophilic part of Triton X-405 the surface layer was too thin, however, to allow a quantitative analysis of the volume fraction profile by SAXS.



$$CH_3(CH_2)_{16}-\overset{\overset{O}{\|}}{C}-O-(CH_2CH_2O)_{112}-CH_3$$

Scheme 1: Structure of the surfactant $C_{18}E_{112}$

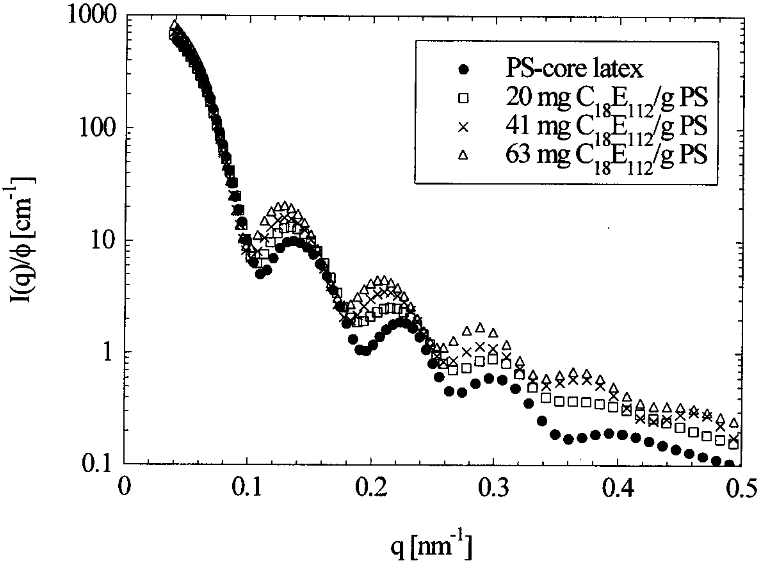
In this paper we present the study of the adsorption of the non-ionic surfactant $C_{18}E_{112}$ (cf. Scheme 1) onto the surface of PS-latex particles. The SAXS-intensity has been measured by using an improved Kratky-camera[15)]. This device allows to extend the measurements of I(q) down to $q=0.03nm^{-1}$ whereas the minimum value achieved by the commercial equipment is ca. $0.08nm^{-1}$ (cf. the discussion in ref.[12,14)]). The improved equipment also gives the opportunity to measure I(q) with increased precision. The main emphasis of the present discussion is laid on the experimental procedure and the method of analyzing the SAXS-data thus obtained. The steps necessary for evaluation the data will be discussed. The resulting structural data are compared to recent data obtained by SANS (cf. ref.[7)] and further literature cited there).

## Experimental

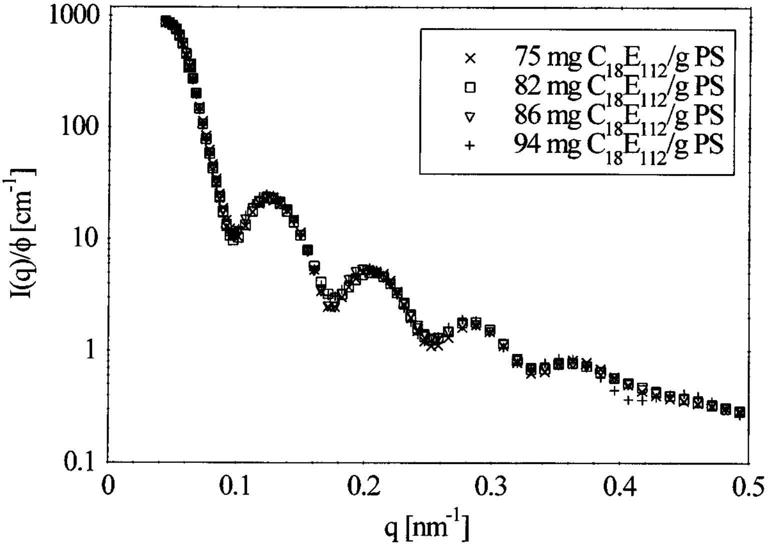
The PS-latex used here has been synthesized as described recently[16,17)]. The particles have no chemically bound surface charges and are solely stabilized by a small amount of SDS. The surfactant $C_{18}H_{112}$ was synthesized and purified carefully by dialysis. Details will be reported elsewhere[18)]. The surfactant was added to the PS-core latex with gentle shaking. Previous measurements had shown that equilibrium is established very quickly in these systems[11,12)]. In the following the concentrations of the surfactant are related to the mass of the core latex. As an example, 60mg/g indicates that the total amount of the surfactant $C_{18}E_{112}$ is 60mg per g PS-particles in the latex.

All SAXS-measurements have been conducted using the improved Kratky-camera described recently[15)]. The raw data have been corrected for the scattering of the serum and of the sample holder. Desmearing of the scattering curves was done as described in reference[14, 15)]. In all cases to be discussed here absolute scattering intensities (in $cm^{-1}$) have been obtained.

As discussed at length in recent reviews[13,14)], the effect of interparticular interference is restricted to the region of smallest q-values. At higher q the influence of S(q) can be safely dismissed. Hence, measurements can be done at finite concentrations (7wt.%) without the necessity of extrapolation to vanishing concentration (cf. the discussion of fig. 7 of ref.[13)]).



**1a**



**1b**

Fig. 1 Comparison of the desmeared SAXS-intensities obtained from the PS-core-latex and from the core latex covered with different amounts of the surfactant $C_{18}E_{112}$. Fig.1a: Data taken up to saturation of the surface; Fig. 1b: Data taken beyond saturation of the surface.

## Results and Discussion

*Process of adsorption:*

As a typical result of the SAXS-analysis of adsorption, fig. 1 displays the comparison of the scattering intensities of the core latex and of the latex to which various amounts of $C_{18}E_{112}$ per gram PS have been added. It is directly obvious that the maxima of the scattering curves are shifted to smaller scattering angle as indicated by the arrow (fig. 1a). Concomitantly, the intensity has raised considerably. Both effects are due to the adsorbed surface layer of the surfactant consisting mainly of poly(ethylene oxide) which has a much higher electron density ($64e^-/nm^3$) than PS ($6.3e^-/nm^3$). Due to the increasing size of the layer the radius of the particles is increased and the maxima of I(q) are shifted towards smaller q-values.

As in references[11,12)] the point at which saturation of the surface of the core particles has been achieved is easily to detect by the constancy of the position of the maxima. This effect is clearly seen in fig. 1b. Further addition of surfactant will not lead to an increase of the thickness of the surface layer but to the formation of free micelles[11,12,18)]. The present results also indicates that the free micelles formed beyond saturation will not stick to the surfaces or form hemimicelles on the surfaces. In this case the scattering intensity measured at small q would increase very much also beyond the point of saturation since the adsorbed micelles would contribute to the coherent scattering of the latex particles. Evidently, the scattering intensities of the surfactant-coated particles virtually superimpose throughout the q-range shown in fig. 1b and the formation of hemimicelles can be ruled out.

From the experimental data it is therefore evident that free micelles are formed beyond saturation of the surface. The scattering intensity of these micelles will add up to the intensity of the latex particles and mainly contribute at high q-values[11,12,18)]. This point must be kept in mind when analyzing I(q) at high scattering angles after the point of saturation has been reached (see below). As stated above the amounts of SDS used for the stabilization of the core particles is small. Therefore the present data do not allow a quantitative analysis whether the residual SDS-molecules are fully replaced by the non-ionic surfactant or whether SDS is built into the layer. The analysis points to the second possibility, however.[18)]

Together with the results presented previously[11,12)] it becomes obvious that SAXS is well-suited to follow the process of adsorption:

i) SAXS allows to follow the gradually built-up of the surface layer;

ii) The point of saturation can be determined which also gives the amount of surfactant adsorbed on the surface;

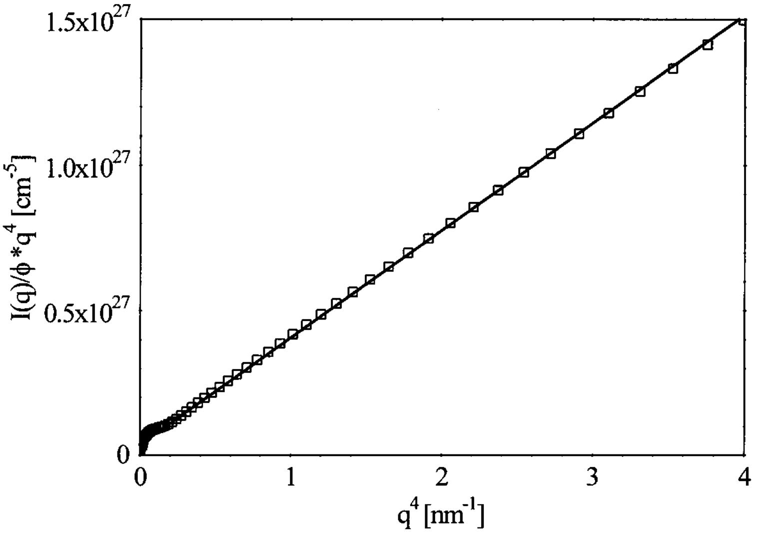


Fig. 2 Determination of $I_{PS}(q)$ by a Porod-plot of I(q) obtained from the PS-core particles.

iii) SAXS can demonstrate that free micelles are formed beyond saturation[11,12,18]; as shown here there is no second layer of the surfactant being built up at higher concentrations of the surfactant. Also, any association of the micelles with the covered latex particle can be ruled out completely.

*Structure of covered particles:*

The analysis of the SAXS-intensity of the core latex using the method devised recently15) gives a number-average radius of 35nm and a polydispersity of 11.8%. The depth of the minima of I(q) (see fig. 1) can be used to obtain the standard deviation of the distribution[15]. The residual SDS-molecules used in the synthesis17) of the core latex leads to a thin shell of higher excess electron density on the surface. This is in accord with recent findings on similar systems11).

As shown above the point of saturation of the surface of the core particles thus characterized is directly evident from the constancy of the maxima of the scattering curves. For the present system the maximum concentration of the surfactant is located at ca. 70mg $C_{18}E_{112}$ per g PS-core. This corresponds to an average area of 10.1nm$^2$ per molecule. Since the interaction between the surfactant and the surface of the PS-core particles is strong (see below), no free micelles will be formed below saturation of the surfaces. The scattering intensity I(q) obtained shortly below saturation may therefore be analyzed for the structure of the surface layer. This point is crucial for a meaningful analysis of I(q) since even a small amount of free micelles would give an additional signal at high q-values which profoundly disturbs the evaluation of I(q).

The scattering intensity I(q) of a particle covered by a polymeric layer can in general be formulated as (see the discussion in ref.[19)] and further literature cited there)

$$I(q) = I_{CS}(q) + I_{fl}(q) + I_{PS}(q) \qquad (3)$$

Here $I_{CS}(q)$ is the part of I(q) due to the core-shell structure of the covered particles. It can be calculated by use of eq.(1) for a spherical particle having a core-shell morphology. In the case discussed here the core has a low electron density whereas the shell consisting of poly(ethylene oxide) chains is characterized by a high electron density, i.e., by a high contrast towards the dispersion medium water.

The term $I_{fl}(q)$ refers to the contribution by the thermal density fluctuations within the adsorbed layer. This term has first been discussed by Auroy and Auvray[8-10)] and may give an appreciable contribution at high q-values if the layer is not too small. For polymeric networks affixed to PS-latex particles it may even become the leading term at highest scattering angles[20]. The third term $I_{PS}(q)$ denotes the scattering intensity which originates from the density fluctuations of the solid PS of the core[13,14]. This term can easily be determined by SAXS-measurements of the core particles and subtracted from I(q) of the covered particles.

It must be noted that all three terms add up independently, there is no cross term. This is due to the fact that these intensities originate from statistically independent fluctuations of the electron density in the scattering volume. Hence, the respective cross terms of the scattering amplitudes related to the three terms in eq.(3) cancel out and solely the intensities of the different contributions add up.

In the following, the analysis of the scattering intensity will be demonstrated using the data which corresponds to nearby saturation of the surface by the surfactant (63mg/g PS; triangle fig. 1a). The evaluation of I(q) proceeds along the following steps:

i) The contribution $I_{PS}(q)$ caused by the PS cores can be obtained by a Porod plot[1)] of the intensity of the core particles. Fig. 2 shows the Porod plot of the core latex. The slope of this plot leads directly to $I_{PS}(q)$ which may be assumed as constant throughout the q-range under consideration here ($q<1 \mathrm{nm}^{-1}$). Substracting this part of I(q) according to eq.(3) gives the

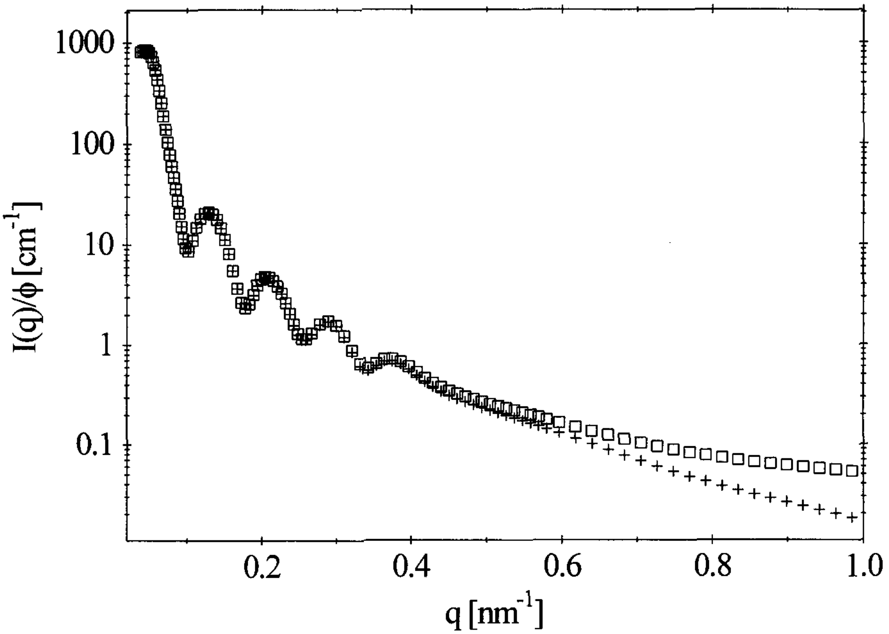


Fig. 3 Subtraction of $I_{PS}(q)$ (see eq.(3)) from the scattering intensity I(q) of particles covered by 63mg $C_{18}E_{112}$ per gram core of the particles. The squares denote the uncorrected intensities whereas the crosses display $I(q)-I_{PS}(q)$ (cf. eq.(3)). $I_{PS}(q)$ has been taken from the slope of the Porod plot of the core particles shown in fig. 2

corrected intensity displayed in fig. 3. Here it becomes obvious that $I_{PS}(q)$ is negligible at small q but becomes an appreciable contribution at $q>0.6 nm^{-1}$.

ii) The radial structure of the covered particle can now be analyzed using these data which refer to $I(q) - I_{PS}(q)$ (cf. eq.(3)) which are shown in fig. 3. This analysis can be done by the method described recently[14,15]. The polydispersity of the core particles is determined from the scattering intensity of the PS-core particles (see above). The width of the size distribution thus obtained is a important parameter[14,15]. It may be assumed in good approximation that the polydispersity of the particles remains the same after adsorption of the surfactant.

iii) The radial excess electron density within the adsorbed layer now may be discussed in terms of models suggested by literature[5]: For a dense layer of polymer chains attached terminally to a hard wall a parabolic profile of the volume fraction is expected (see the discussion in ref.[6]). If attractive interactions between the hydrophilic chains and the particles must be taken into account, an exponential volume fraction profile is expected[6]. Given the

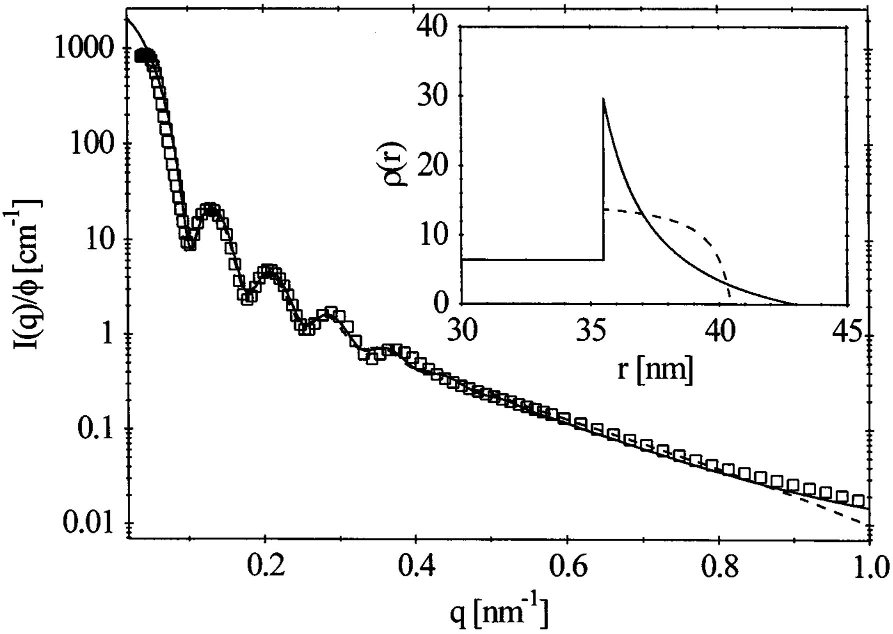


Fig. 4 Analysis of the radial excess electron density of the adsorbed layer. Using the radial profiles shown in the inset the experimental I(q) corrected for $I_{PS}(q)$ (see the discussion of fig. 3) can be fitted by variation of the respective model parameters. The core ($r \leq 35.5$nm; see inset) consists of solid PS having a constant excess electron density of $6e^-/nm^3$. The core comprises also the short hydrophobic part of the surfactant. The radial structure of the hydrophilic tails of the surfactant are modeled in terms of two assumed profiles by fitting two parameters: 1. Parabolic profile (dashed line): Height at surface of particle and maximum extension; 2. Exponential profile (solid line): Height at surface of core particle and maximum extension.

excess electron density of the poly(ethylene) chains in water the volume fractions can directly be converted into the respective radial excess electron densities. Conversely, the profiles $\rho(r) - \rho_m$ obtained from fits of the SAXS-data yield directly the volume fraction profile of the polymer at the surface.

From analyses of similar systems[6,19,20)] it is obvious that $I_{fl}(q)$ may become important at the high q-values. Hence, the profile of the excess electron density can be derived taking into account mainly the intermediate q-range in which the minima and maxima of $I_{CS}(q)$ are clearly visible. Fig. 4 displays the resulting fit for the two possible volume fraction profiles. It is obvious that the present q-range is too small to discern between these two models. The q-range employed here leads to a reliable 0. and 2. moment of the excess electron density of the surface layer, however. There is a slightly better fit by the exponential profile, however, in agreement with previous analyses of comparable systems$^{6)}$ and a previous SANS-study of poly(ethylene oxide) chains adsorbed onto PS-particles$^{20)}$. Moreover, a comparison between the maximum extension of the profile and the hydrodynamic radius measured by viscosimetry gives an additional strong argument in favor of the exponential profile. Here the exponential profile describes correctly the maximal extension of the layer as determined be the hydrodynamic radius$^{17)}$.

The agreement of measured and calculated I(q) is less good if more surfactant is added, i.e., beyond the point of saturation. Here a part of the surfactant which is not adsorbed anymore onto the surface gives a small but non-negligible contribution at high q-values. As discussed previously$^{11,12)}$, this additional contribution arising from free micelles may be compared to the scattering signal measured from micelles of the surfactant $C_{18}E_{112}$: SAXS-measurements of solutions of $C_{18}E_{112}$ in $H_2O$ give the scattering intensity of free micelles at a given concentration of the surfactant. On the other hand, knowing the point of saturation, the amount of free surfactant in the latex may be calculated. After subtracting from I(q) the fitted intensity obtained shortly below saturation (cf. fig. 4), the residual signal may be compared with the signal of free $C_{18}E_{112}$-micelles. This comparison shows that both signal agree within given limits of error$^{18)}$. If there would be an appreciable contribution of $I_{fl}(q)$ at high q-values, the excess signal observed from the latex would be higher because of this contribution is not present in solutions of free micelles.

The profiles $\rho(r)-\rho_m$ thus obtained for different coverage of the surface may be used to determine the normalized zeroth moment $M_{0,\text{layer}}$ of the surface layer according to

$$M_{0,layer} = 4\pi \int_{Rc}^{\infty} [\rho(r) - \rho_m] r^2 dr \qquad (4)$$

where $R_c$ denotes the radius of the core particle. Given the excess electron density of poly(ethylene oxide) this quantity may directly be converted into the amount of the surfactant adsorbed onto the surface. Plots of $M_0$ vs. the concentration of the surfactant in the system proved to be linear below the point of saturation$^{18)}$. This indicates that the adsorption of the surfactant $C_{18}E_{112}$ onto the surface of the PS-core latex is strong as discussed above. The same conclusion has been drawn from the fact that latexes covered by surfactants of the type studied here are stable against high shear rates up to high volume fractions$^{21)}$. The adsorption of such tenside molecules is so strong that the steric stabilization of the particles remains operative even when the latex is subjected to high shearing forces.

## Conclusion

The above discussion together with previous results[11,12)] show that SAXS is an excellent tool to study the process of adsorption onto the surface of latex spheres. In particular, the analysis by SAXS demonstrates that

i) The point of saturation can be seen directly from the scattering curves;

ii) Free micelles are formed beyond saturation; there is no second layer of the surfactant being built up at higher concentrations of the surfactant;

iii) Any association of the micelles with the covered latex particle can be ruled out;

iv) A quantitative analysis of the built-up of the layer can be done in terms of the 0. moment of its excess electron density distribution[18)].

Acknowledgment: Financial support by the Bundesministerium für Bildung und Forschung, Projekt "Konzentrierte Kunststoffdispersionen", and of the AIF is gratefully acknowledged.

## Literature

1. O. Glatter, O. Kratky, Eds. *Small Angle X-Ray Scattering,* Academic Press, London 1982
2. J. S. Higgins, H. C. Benoit, *Polymers and Neutron Scattering*, Clarendon Press, Oxford, 1994
3. R. H. Ottewill, *Progr. Colloid Polym. Sci.* **1992**, *88*, 49; and further references given there
4. N. M. Harris, R. H. Ottewill, J. W. White, in *Adsorption from Solution*, R. H. Ottewill, C. H. Rochester, A. C. Smith, eds., Academic Press, London, 1983
5. R. H. Ottewill, E. Sinagra, I. P. MacDonald, J. F. Marsh, R. K. Heenan, *Colloid Polym. Sci.* **1992**, *270*, 602, and further references given therein
6. G. J. Fleer, M. A. Cohen Stuart, J. M.H. M. Scheutjens, T. Cosgrove, B. Vincent, Polymers at Interfaces, Chapman and Hall, London 1993
7. P. C. Griffiths, T. Cosgrove, J. Shar, S. M. King, G.-E. Yu, C. Booth, M. Malmsten, *Langmuir* **14**, 1779 (1998)
8. P. Auroy, L. Auvray, *J. Phys. II* **3**, 227 (1993)
9. P. Auroy, L. Auvray, *Langmuir* **10**, 225, (1994)
10. P. Auroy, L. Auvray, *Macromolecules* **29**,337 (1996)
11. J. Bolze, K. D.Hörner, M. Ballauff, *Langmuir* **12**, 2906 (1996)
12. J.Bolze, K. D. Hörner, M. Ballauff, *Colloid Polym. Sci.* **274**, 1099 (1996)
13. M. Ballauff, J. Bolze, N. Dingenouts, P. Hickl, D. Pötschke, *Macromol Chem. Phys.* **197**, 3043 (1996)
14. N. Dingenouts, J. Bolze, D. Pötschke, M. Ballauff, *Adv. Polym. Sci.* **144**, 1 (1999)
15. N. Dingenouts, M. Ballauff, *Acta Polym.* **49**, 178 (1998)
16. R. H. Ottewill, R. Satguranthan, *Colloid Polym. Sci.* **265**, 845 (1987)
17. A. Weiss, N. Dingenouts, M. Ballauff, H. Senff, W. Richtering, *Langmuir* **14**, 5083

(1998)

18. S. Seelenmeyer, M. Ballauff, in preparation
19. N. Dingenouts, Ch. Norhausen, M. Ballauff, *Macromolecules* **31**, 8912 (1998)
20. S. T. Mears, T. Cosgrove, T. Obey, L. Thomson, I. Howell, *Langmuir* **14**, 4997 (1998)
21. see the discussion of this point in ref.[17] and further references given there.