Dilational Viscoelasticity of Polyelectolyte/Surfactant Adsorption Films at the Air/Water Interface: Dodecyltrimethylammonium Bromide and Sodium Poly(styrenesulfonate)

B. A. Noskov,[†] G. Loglio,[‡] and R. Miller*,[§]

Department of Colloid Chemistry, St. Petersburg State University, Universitetsky pr. 2, 198904 St. Petersburg, Russia, Dipartimento di Chimica Organica, Universita degli Studi di Firenze, Via della Lastruccia 13, 50019 Sesto Fiorentino, Firenze, Italy, and MPI für Kolloid- und Grenzflächenforschung, Wissenschaftspark Golm, D-14424 Golm, Germany

Received: August 1, 2004; In Final Form: September 21, 2004

The dynamic surface elasticity of mixed aqueous poly(styrenesulfonate)/alkyltrimethylammonium bromide solutions has been measured by the oscillating barrier, oscillating drop, and capillary wave methods as a function of time and surfactant concentration. At low surfactant concentrations (<0.3 mM) the surface viscoelastic behavior is close to that of relatively concentrated pure PSS solutions. The classical Goddard et al. model cannot explain all the experimental results in this concentration range, and a modification of this model is proposed. At intermediate concentrations the real part of the dynamic surface elasticity drops abruptly by almost 1 order of magnitude. This feature can be connected with the formation of a heterogeneous surface film in accordance with recent results by Monteux et al. (*Langmuir* **2004**, *20*, 57). At high surfactant concentration (>2 mM) the modulus of the dynamic surface elasticity is low and the adsorbed film is viscoelastic.

Introduction

It is well-known that the addition of small amounts of conventional surfactants to aqueous polymer solutions leads to drastic changes of their properties. These systems find numerous industrial applications, for example, in oil recovery, pharmaceutical formulations, and film coating, and have been intensively studied.[1−6] For the past 30 years special attention has been paid to mixtures of oppositely charged surfactants and polyelectrolytes.[3−8] In this case strong electrostatic interactions between the components lead to complex formation in the solution at surfactant concentrations orders of magnitude below the critical micellar concentration of the pure surfactant system.

Although the surface properties of mixed polyelectrolyte/surfactant solutions are of tremendous practical importance, studies have focused for many years mainly on the bulk properties.[4−8] Only the surface tension was measured rather frequently as a function of the surfactant concentration c_s at a constant polyelectrolyte content.[2−6] Such dependencies display usually a few break points. The first one is followed by a plateau region, where the surfactant monomer activity is almost constant, and is attributed by some authors to a critical aggregation concentration (cac) in the solution bulk.[5,6,9−16] At c_s < cac the surface tension of the mixed solution is significantly lower than the values of the solutions of the surfactant or polyelectrolyte separately. This fact gives evidence to the formation of complexes of high surface activity between the solutes in the surface layer. Goddard et al. proposed a simple model of the surface structure for dilute polyelectrolyte/surfactant solutions (Figure 1).[3−6] The surfactant ions form a monolayer at the liquid surface and attract electrostatically the charged macromolecules.

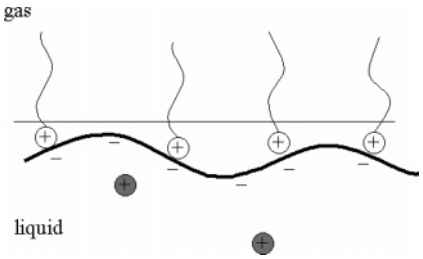

Figure 1. Schematic representation of polyelectolyte−surfactant interaction at the liquid surface according to Goddard et al.[3−6]

The charged groups of the polymer play a role of counterions. Note that, although this picture seems rather natural, it cannot be examined by means of the surface tension measurements only. More elaborate methods of surface chemistry, however, were not applied to the systems under consideration for a long time.

The current situation is somewhat different. Recently mixed adsorbed films of polyelectrolytes and surfactants have been studied by measurements of the dynamic surface tension[13,16] and elasticity,[13−15,17] ellipsometry,[9,18−20] Brewster angle microscopy,[14,15] X-ray analysis,[10] and neutron reflectivity.[11,12] The most important results correspond probably to concentrations higher than the first break point in the surface tension isotherm, where microgel[18] and sandwich-like[11,12] structures were discovered in the surface layer. At lower concentrations the polymer chains have an extended conformation due to electrostatic repulsion and in accordance with the model of Goddard et al.[10−12] Also polyelectrolytes with different intrinsic persistence lengths and degrees of charge have been studied.[10,13−15] Although the number of experimental techniques is rather large, some of them have been applied only to a very few particular systems so far. For example, among adsorbed films of anionic polyelectrolytes and cationic surfactants only the system of poly(styrenesulfonate)/alkyltrimethylammonium bromide (PSS/

* To whom correspondence should be addressed.
[†] St. Petersburg State University.
[‡] Universita degli Studi di Firenze.
[§] MPI für Kolloid- und Grenzflächenforschung.

10.1021/jp046560s CCC: $27.50 © 2004 American Chemical Society
Published on Web 11/06/2004

ATAB) has been studied by neutron reflectivity.[11,12] The surface dynamic elasticity has been measured at different concentrations, frequencies, and degrees of charges only for solutions of polyacrylamide methylpropanesulfonate (PAMPS) and ATAB by using the capillary wave[14,15,17] and oscillating bubble[13] methods. Reference 17 also contains some results for xanthan/dodecyltrimethylammonium bromide (xanthan/DTAB) films. The surface dilational viscoelastic behavior proved to be rather complicated and cannot be described by simple rheological models.[13−15,17] The concentration dependence of the dynamic surface elasticity was nonmonotonic. The authors were able to correlate their surface rheological data with results from other methods assuming that the films were incompressible layers.[13−15] This assumption, however, can be accepted only as a first approximation because the surface elasticity of PAMPS/ATAB films depends on the frequency.[14,17]

In this work we applied various methods of surface dilational rheology (oscillating barrier, oscillating drop, and capillary wave methods) to adsorbed films of PSS/DTAB. The main aim was to study the range of low surfactant concentrations where other experimental techniques indicated a relatively simple surface structure and where the Goddard at al. model allowed inferring some general conclusions on the surface dilational viscoelasticity. The interpretation of the surface rheological data for PSS/DTAB films can be facilitated in comparison with PAMPS/ATAB adsorbed films. Indeed, apart from the X-ray technique,[10] PSS/DTAB films have been recently investigated in detail by neutron reflectivity[11,12] and ellipsometry.[18−20] Besides, the dilational surface viscoelasticity of PSS adsorbed films has been studied by the same methods in broad frequency and concentration ranges,[21] and the surface rheology of DTAB solutions is also well-known.[17,22]

Experimental Section

All experimental relaxation methods used in this work are based on subtle mechanical perturbations of the equilibrium at the liquid surface and subsequent measurement of the system response.[23−29] Small harmonic changes of the liquid surface area δS are usually induced, and the resulting changes in the surface tension $\delta\gamma$ or the characteristics of surface waves are measured directly. For small perturbations, linear relationships describe the system and the surface tension perturbation is proportional to the area perturbation. In this case the dilational dynamic surface elasticity ϵ, which is the proportionality factor, does not depend on the perturbation amplitude:

$$\epsilon(\omega) = \delta\gamma/(\delta \ln S) \tag{1}$$

In the general case, the dynamic surface elasticity can depend on the angular frequency of the perturbations ω. Using the irreversible thermodynamics, one can determine the general form of the function $\epsilon(\omega)$ and relate the parameters of this dependence (the relaxation times and relaxation strengths) to both the equilibrium surface properties and the kinetic coefficients of the relaxation processes.[27] If the surface film is viscoelastic, the oscillations of surface tension and surface area proceed out of phase and the surface elasticity proves to be a complex quantity, $\epsilon = \epsilon_r + i\epsilon_i$.

The setups for measuring the surface wave characteristics and surface tension oscillations together with the corresponding experimental procedures have been described in detail elsewhere,[23−26,28,29] so that we represent here only some basic principles of the employed techniques. At the lowest frequencies ($<\sim$0.1 Hz) one can measure the dynamic surface elasticity by the oscillating drop method.[25] We used a commercial instrument (PAT1 from Sinterface Technologies, Germany). The pendant drop was created at the tip of a capillary by a computer-driven dosing system in a closed glass cuvette, where a small portion of the solution under investigation was placed at the bottom to reduce drop evaporation. The software (National Instruments LabView) allows controlling the surface area of the drop as a function of time. Although any function is possible, in this work we used only harmonic oscillations of the drop surface area. The software ensured the control of the drop parameters on line during the measurement and calculation of the surface area and the surface tension based on these images (according to the Gauss−Laplace equation) as a function of surface age. The elasticity modulus was determined from the amplitude ratio of the oscillations of the surface tension and surface area, while the phase shift between the oscillations of the two parameters (surface tension and surface area) determined the phase angle of the dynamic surface elasticity. The accuracy of the results depended on the relative surface area amplitude. Amplitudes $\leq\pm10\%$ ensure that the data were precise enough and at the same time the influence of nonlinear effects was negligible.

Most of the results in this work were obtained by the oscillation barrier method.[24,29] In this case a moving PTFE barrier induced low-frequency oscillations of the liquid surface area in a PTFE Langmuir trough. A mechanical generator transformed the rotation of an electromotor to a translational motion with reversion and gave the possibility to control the frequency and amplitude. The relative amplitudes applied were between 0.4% and 4%. The corresponding surface tension oscillations were measured by the Wilhelmy plate method using a roughened glass plate. As in the case of the oscillating drop technique, the measured dependencies $\delta S(\omega)$ and $\delta\gamma(\omega)$ allowed the determination of the dynamic surface elasticity. At frequencies of less than 0.2 Hz, the length of the surface longitudinal waves far exceed the length of the Langmuir trough and the surface tension oscillations in the trough are homogeneous. At higher frequencies, the surface tension oscillations are inhomogeneous and other methods have to be used.

The characteristics of capillary waves were measured by means of an electromechanical method based on the dynamic condenser principle.[21,23,26,28] One condenser plate was a thin metal plate with the thickness less than half of the wavelength. The second plate was the liquid surface under investigation in the Langmuir trough. A mechanical generator excited the capillary waves. The propagation of the waves caused capacitance oscillations of the dynamic condenser, and as a result an alternating electric current appeared in the circuit. Measurements of the amplitude and phase of the electric signal allowed us to determine the damping coefficient and the length of the transverse capillary waves. The dynamic surface elasticity can be calculated from the capillary wave characteristics according to the corresponding dispersion equation.[23,28] Note that, although the specific energy dissipation in the surface layer exceeds the specific dissipation in the bulk solution, the energy of the waves dissipates mainly in the bulk solution because the wavelength (the penetration depth of the motion into the bulk liquid) exceeds the thickness of the surface layer by about 6 orders of magnitude. The surface viscoelasticity influences the wave characteristics only as a result of alterations of the boundary conditions for the equations of liquid dynamics. Therefore, the damping coefficient of surface waves is a complicated function of both components of the dynamic surface elasticity.[23,26] If $|\epsilon| > 0.14\gamma$, the capillary wave characteristics are almost independent of the surface elasticity and are mainly determined by the surface tension.[22,23] For most of the PSS/DTAB solutions under

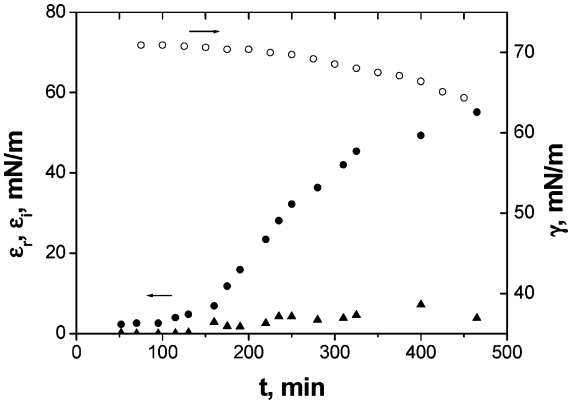

Figure 2. Kinetic dependencies of the dynamic surface tension (open circles) and the real (closed circles) and imaginary (closed triangles) parts of the dynamic surface elasticity at $c_p = 0.01$ wt % and $c_s = 0.02$ mM.

investigation the surface elasticity modulus meets this condition, and consequently, the capillary wave method can give only rough values of the surface elasticity. Nevertheless, the results are useful for the estimation of the frequency dependence of the elasticity.

PSS with a molecular weight of 70000 (Aldrich) was used as received. DTAB samples were obtained from Aldrich and Merck. Some of them were purified by double recrystallization from an ethyl acetate/ethanol mixture. However, the experimental results did not depend on the used DTAB sample, which can be explained by solubilization of impurities in the aggregates formed in the solution. Fresh twice-distilled water was used for the preparation of the solutions. An all-Pyrex apparatus and alkaline permanganate were employed in the second stage of distillation. All solutions were carefully stirred before the measurements.

Results

All measurements in this work were performed at two PSS concentrations of $c_p = 0.01$ wt % and $c_p = 0.05$ wt %, and various DTAB concentrations. Figures 2−7 show some dynamic surface tension and dynamic surface elasticity dependencies, determined by the oscillating barrier method at a frequency of 0.14 Hz. Note that, although eq 1 is strict only for oscillations around equilibrium, one can use it as a definition of the dynamic surface elasticity for a system far from equilibrium as well, if changes of any surface property are negligible during one period, i.e., the system is in a quasi steady state.

Loss of solution in the Langmuir trough due to evaporation allowed oscillating barrier measurements only up to about 8 h. One can see from Figures 2 and 3 that this time was insufficient to reach the equilibrium at low concentrations ($c_s \leq 0.3$ mM). At higher concentrations the surface properties change faster, but the rate of equilibration increases with DTAB concentration only in the range of very dilute solutions ($c_s \leq 0.2$ mM). At $c_s \approx 0.3$ mM ($c_p = 0.01$ wt % PSS, Figure 4) and at $c_s \approx 1$ mM ($c_p = 0.05$ wt % PSS, Figure 5) the surface tension and dynamic surface elasticity take equilibrium values (within the error limits) in less than 1 h. However, at even higher concentrations the establishment of equilibration can be slowed again (Figures 6 and 7). The relaxation times of surface tension and surface elasticity are similar but not always equal. At higher concentrations (Figure 6) sometimes one can observe changes of the real part of the dynamic surface elasticity while the surface tension is constant in the error limits (about ±0.2 mN/m). A reverse situation is possible at lower concentrations (Figure 2); i.e., the

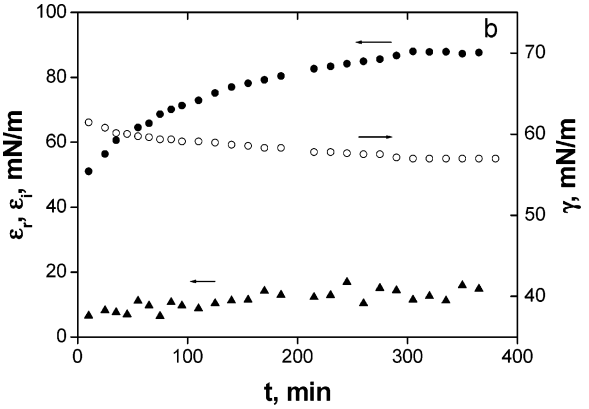

Figure 3. Kinetic dependencies of the dynamic surface tension (open circles) and the real (closed circles) and imaginary (closed triangles) parts of the dynamic surface elasticity at $c_p = 0.05$ wt % and $c_s = 0.1$ mM.

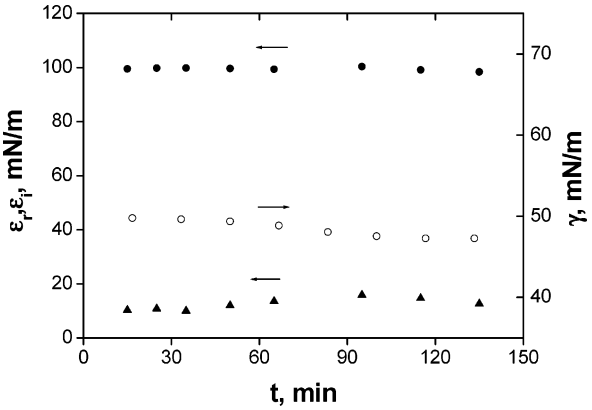

Figure 4. Kinetic dependencies of the dynamic surface tension (open circles) and the real (closed circles) and imaginary (closed triangles) parts of the dynamic surface elasticity at $c_p = 0.01$ wt % and $c_s = 0.3$ mM.

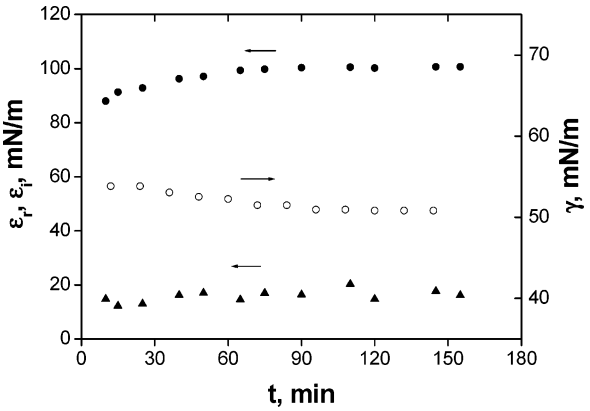

Figure 5. Kinetic dependencies of the dynamic surface tension (open circles) and the real (closed circles) and imaginary (closed triangles) parts of the dynamic surface elasticity at $c_p = 0.05$ wt % and $c_s = 1$ mM.

real part of the surface elasticity is constant within ±2 mN/m, but the surface tension continues to decrease. The latter distinctions in the equilibration rates were also observed for PSS solutions without DTAB.[21] These peculiarities of the kinetic dependencies of the dynamic surface properties reflect the complicated nature of the system under investigation where various aggregates can exist in the surface layer at different concentrations (see below). Note that, although the final equilibrium surface properties were quite reproducible, the difference in the kinetic dependencies sometimes exceeded the

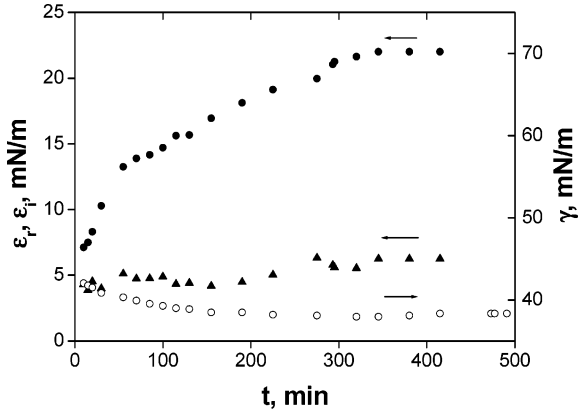

Figure 6. Kinetic dependencies of the dynamic surface tension (open circles) and the real (closed circles) and imaginary (closed triangles) parts of the dynamic surface elasticity at $c_p = 0.01$ wt % and $c_s = 2$ mM.

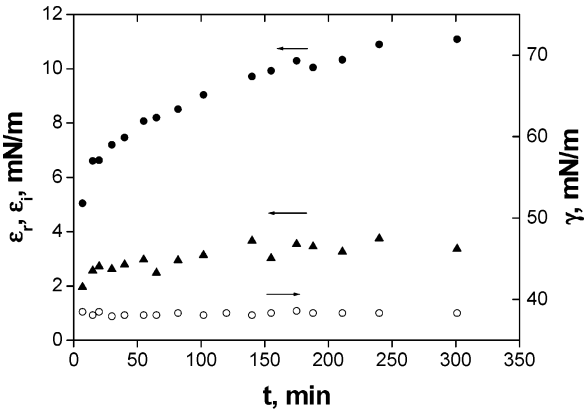

Figure 7. Kinetic dependencies of the dynamic surface tension (open circles) and the real (closed circles) and imaginary (closed triangles) parts of the dynamic surface elasticity at $c_p = 0.05$ wt % and $c_s = 10$ mM.

corresponding error limits. In particular, the oscillating drop method usually led to slower kinetic dependencies in comparison with the oscillating barrier method. This can be explained by the influence of convection in the solution on the measurements of the dynamic surface properties. Obviously, the convection is stronger in the Langmuir trough than in a small drop. The duration of the surface oscillations also influenced the kinetic curves. Another reason for the slower adsorption rate in drop shape experiments is the restricted reservoir of surface active molecules in the small drop volume.[30]

It is well-known that the creation of a fresh surface in polyelectrolyte solutions is accompanied by extremely slow changes of the surface properties with time.[21,31,32] This is usually explained by the formation of an electrostatic adsorption barrier.[31] However, it has been shown recently that this is not the only reason for the slow relaxation of the surface properties.[21] One can assume that the slow changes of the surface properties in the system under investigation and in pure polyelectrolyte solutions (without conventional surfactants) have the same mechanism. The characteristic time of the diffusion to the surface τ_D can be estimated from the following relation:[23]

$$\tau_D = \frac{1}{D}\left(\frac{\Gamma}{c}\right)^2 \qquad (2)$$

where Γ is the adsorbed amount, D is the diffusion coefficient in the bulk phase, and $c = c_p$ or c_s.

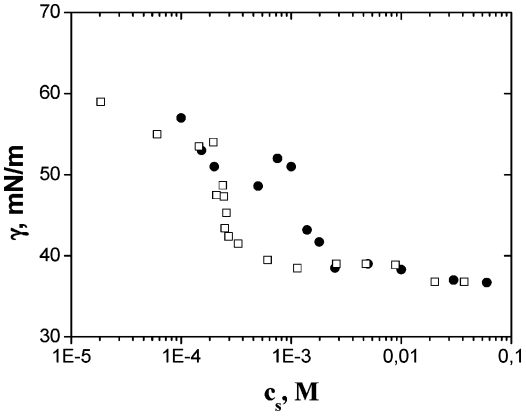

Figure 8. Surface tension of the mixed PSS/DTAB solutions versus DTAB concentration at $c_p = 0.01$ wt % (open squares) and $c_p = 0.05$ wt % (closed circles).

Taylor et al. determined the adsorption of DTAB at the air/water interface from a mixed PSS/DTAB solution by neutron reflectivity.[11] This quantity was almost independent of the PSS concentration and depended only slightly on the DTAB concentration with the exception of a narrow concentration range where it increased abruptly from about 3×10^{-6} to 9×10^{-6} mol/m^2. Using the latter value and $D = 4 \times 10^{-10}$ m^2/s given in ref 13 yields $\tau_D = 500$ s at $c_s = 0.02$ mM, which decreases rapidly for higher concentrated solutions. Taylor et al. also determined the PSS volume fraction in the adsorbed film and the film thickness, which depended also only slightly on the solution composition.[11] These data lead to an adsorbed amount of 10^{-8} mol/m^2 (for a molecular weight of 70000). The diffusion coefficient of the polyelectolyte depends in general on the concentration of both solutes. However, as a rough estimate one can take a value of 2×10^{-11} m^2/s, which follows from the correlations between D and the PSS molecular weight at various salt concentrations.[33] This gives $\tau_D = 2.5$ s for PSS. Therefore, the experimental characteristic times of the surface equilibration exceed the estimates by a few orders of magnitude. Note that PSS practically does not adsorb from its pure solutions at concentrations lower than about 0.1 wt %.[21] For pure DTAB solutions the deviations of the surface properties from the values for pure water begin at $c_s \approx 1$ mM.[18,22] Even if we take into account that only interactions between PSS and DTAB lead to their adsorption at low concentrations, the estimated τ_D shows that the slow changes of the surface properties cannot be explained only by the surfactant and polymer diffusion from the bulk phase to the surface. Other evidence of the nondiffusional adsorption kinetics is given by the nonmonotonic dependence of the characteristic time on the DTAB concentration.

Figure 8 shows the dependencies of γ vs c_s at two concentrations of the polyelectolyte. At $c_s < 0.3$ mM the data correspond to nonequilibrium adsorbed films at about 5 h after the creation of the fresh interface. This can be a reason for the high scatter and sometimes even nonmonotonic changes of the experimental data in this concentration range. At higher concentrations the obtained results are similar to those obtained by other authors for a surface age of 1 h.[11,18] The differences in the surface lifetimes lead to different surface tension isotherms at $c < 0.3$ mM. At higher surface age, the concentration dependence is weaker than reported earlier[11,18] and one can expect that the surface pressure deviates from zero at significantly lower concentrations than those studied in this work (≥ 0.02 mM, Figure 8). On the other hand, the surface tension drop at $c_s \approx 0.3$ mM ($c_p = 0.01$ wt %) and $c_s \approx 1$ mM ($c_p = 0.05$ wt %) is

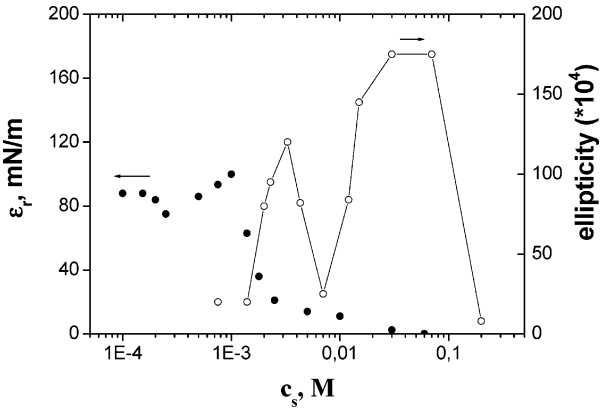

Figure 9. Real part of the dynamic surface elasticity (closed circles) and the ellipticity (data redrawn from ref 18, open circles) of the mixed PSS/DTAB solutions versus DTAB concentration at $c_p = 0.05$ wt %.

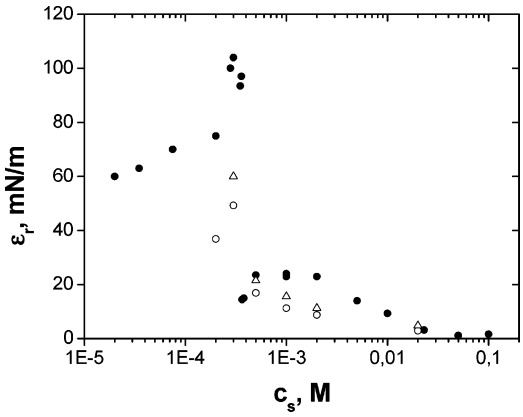

Figure 10. Real part of the dynamic surface elasticity of the mixed PSS/DTAB solutions versus DTAB concentration at $c_p = 0.01$ wt % and the frequencies 0.14 Hz (the oscillating barrier method, closed circles), 0.08 Hz (the oscillating drop method, open triangles), and 0.02 Hz (the oscillating drop method, open circles).

smaller and more abrupt in comparison with the previous results.[11,18] Nevertheless, this drop and the subsequent quasi-plateau are real features of the equilibrium surface tension isotherm. Note that the beginnings of the quasi-plateaus for both dependencies in Figure 8 correspond to the case when approximately 80% of the PSS sulfonate groups are neutralized by DTAB in the bulk solution. This is in agreement with the results of Monteux et al. on the same system and indicates that the surfactant/polymer ratio is a key parameter in controlling the surface properties of solutions of oppositely charged surfactant/polyelectrolyte mixtures.[20]

The traditional explanation of the plateau in the γ vs c dependence consists of aggregation in the bulk phase, leading to an approximately constant monomer activity. Many authors connected the abrupt change of the slope in the surface tension−concentration dependence for the mixed polymer/surfactant solutions with the cac.[2,5,6,9−16] However, this concept cannot be applied to PSS/DTAB solutions. Recently, Monteux et al. have shown by using a DTAB specific electrode that the cac ≈ 0.02 mM at $c_p = 0.05$ wt %.[18] One can assume that for $c_p = 0.01$ wt % the cac is also much lower than the beginning of the quasi-plateau in the surface pressure isotherm. The same authors showed that a strong increase of the ellipsometric signal accompanied the abrupt change of the slope of the surface tension−concentration curve and connected these peculiarities with the formation of microgel particles in the surface layer.[18]

It is well-known that the surface tension is not very sensitive to conformational changes in adsorbed polymer films.[26,28,34] In contrast, the dynamic surface elasticity responds significantly stronger to any changes in the surface structure. Figure 9 shows indeed that the abrupt drop of the surface tension by about 30% (Figure 8) is accompanied by a 1 order of magnitude decrease of the real part of the dynamic surface elasticity. This figure also contains data on the ellipticity (ratio of the reflection coefficients r_p/r_s of the incident beam at the air/water interface close to the Brewster angle for two different states of polarization) published recently.[18] The increase of the adsorbed film thickness, which leads to an increased ellipticity, begins almost simultaneously with the strong changes in the mechanical film properties and, consequently, of the adsorbed film structure. According to Monteux et al., large aggregates form in the surface layer and the surface layer becomes highly heterogeneous.[18] The data on the dilational surface viscoelasticity show that changes in the surface structure cannot be reduced just to the formation of microgel particles but the adsorbed film between them, which influences the dynamic surface properties, undergoes strong changes as well. The appearance of a microgel phase at the surface precedes the corresponding event in the bulk phase: at $c_s > 4$ mM (close to the point where the charges brought by PSS and DTAB are equal) the solution becomes opalescent and then turbid. A similar succession of the microgel formation (first at the interface and after that in the bulk phase) was also observed for an entirely different polymer system—with increasing temperature of aqueous solutions of poly(*N*-isopropylacrylamide).[35]

For $c_p = 0.01$ wt %, again the surface tension drop (Figure 8) is accompanied by strong changes in the dynamic surface elasticity, which was measured by the oscillating drop and the oscillating barrier methods at different frequencies (Figure 10). The dilational viscoelastic behavior is similar to that at higher PSS concentrations (Figure 9). As in the case of the γ vs c dependencies, the scatter of the experimental data in Figures 9 and 10 at $c_s \leq 0.3$ mM is larger because the system is far from equilibrium. This is probably the main reason for the distinction between the results of the two experimental methods at approximately the same surface ages. The surface tension relaxation proceeds slower in the case of the drop, which oscillates only for about 5 min every hour. The barrier oscillates continuously, and the volume of the Langmuir trough is larger than the drop volume by a few orders of magnitude. This leads to stronger convection in the former case. At $c_s > 0.3$ M the difference between the data of the two methods is smaller, however, and cannot be explained only by the differences in the applied frequencies. One can assume that the hydrodynamics of the system still has some influence on the results.

When the system approaches equilibrium, the surface elasticity increases for $c_s < 0.3$ mM (Figures 2 and 3), and one can expect that the limiting values are higher than those presented in Figures 9 and 10. At $c < 0.02$ mM measurements at equilibrium are impossible because of the too slow equilibration. However, even a rough extrapolation to small DTAB concentrations leads to high dynamic surface elasticity values. Therefore, one can assume that the interaction of PSS and DTAB in the surface layer proceeds in the range of extremely low concentrations, probably less than the cac in the bulk phase. On the other hand, both components of the complex dynamic surface elasticity at low concentrations are close to the values of relatively concentrated pure PSS solutions.[21] At concentrations preceding the abrupt drop of the surface elasticity ($c_s \approx 0.3$ mM at $c_p = 0.01$ wt % and $c_s \approx 1$ mM at $c_p = 0.05$ wt %) one can observe a local maximum of the surface elasticity (Figures 9 and 10). Beyond the range of fast changes the real part is

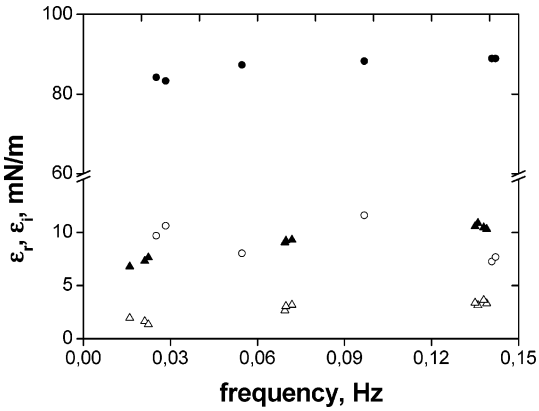

Figure 11. Frequency dependence of the real (closed symbols) and imaginary (open symbols) parts of the dynamic surface elasticity at $c_p = 0.05$ wt % and $c = 0.2$ mM (circles) and 10 mM (triangles).

about 20 mN/m. This rather small value indicates a looser surface structure. At the subsequent concentration increase the dynamic surface elasticity slowly decreases further, reaching zero at $c_s > 0.02$ M. For higher concentrations the low-frequency relaxation methods do not show any surface viscoelasticity as in the case of pure PSS and DTAB solutions at the same concentrations. Unlike other surface properties (Figure 9), the dynamic surface elasticity does not display any peculiarities after the abrupt drop. One can assume that the nonmonotonic concentration dependence of the ellipticity in this concentration range is connected mainly with changes in the number and/or size of microgel particles at the surface,[18] whereas the surface viscoelasticity is not sensitive to these parameters but mainly to the properties of the adsorbed film between the particles.

The relative accuracy of the imaginary part of the dynamic surface elasticity is less in comparison with the real part. At low concentrations ($c_s < 0.3$ mM at $c_p = 0.01$ wt % and $c_s < 1$ mM at $c_p = 0.05$ wt %) ϵ_r exceeds ϵ_i by 1 order of magnitude (Figures 2 and 3) and one can consider the adsorbed film to be purely elastic. At higher concentrations the phase angle of the dynamic surface elasticity increases and the ratio ϵ_i/ϵ_r can reach about 50% (Figure 5), thus indicating significant energy dissipation in the surface layer. The adsorbed film proves to be viscoelastic. Figure 11 shows that at low concentrations the frequency dependence of both components of the dynamic surface elasticity is weak and the surface elasticity is almost constant within the error limits. At concentrations beyond the abrupt changes in the surface properties both components of the elasticity depend on frequency, indicating the relaxation of surface stresses. Measurements of capillary wave characteristics show that in this concentration range the surface elasticity continues to increase at higher frequencies. At $\omega > 100\ s^{-1}$ the experimental results lead to the estimate of $|\epsilon| \gg 0.14\gamma$.

Discussion

Probably the most unexpected result of this work consists of a high real part of the dynamic surface elasticity at low DTAB concentrations ($c_s < 0.3$ mM at $c_p = 0.01$ wt % and $c_s < 1$ mM at $c_p = 0.05$ wt %). Obviously, the surface elastic and viscous properties must disappear when either c_s or c_p tends to zero. However, Figure 10 shows that even at $c_s = 0.02$ mM there is no indication of this behavior. Consequently, strong interactions between PSS and DTAB in the surface layer persist at extremely low concentrations, probably less than the cac in the solution bulk.

Let us summarize the main features of the surface dilational viscoelasticity for PSS/DTAB solutions at low DTAB concentrations: (1) a high real part of the dynamic surface elasticity in the range of 60−100 mN/m; (2) a low imaginary part of the surface elasticity ($\epsilon_i/\epsilon_r < 10$); the adsorbed film is elastic; (3) a very slow equilibration; i.e., the relaxation time significantly exceeds the characteristic time of the solute diffusion from the bulk phase to the surface.

Exactly the same dynamic surface properties have been discovered recently for relatively concentrated PSS solutions ($c_p > 0.5$ wt %) in absence of conventional surfactants.[21] This behavior is entirely different from that of the adsorbed films of nonionic polymers[26,28] and surfactants of low molecular weight.[23,36] Therefore, the mechanical surface properties in this concentration range are determined only by the interactions between the charged stretched PSS chains. DTAB has no direct influence on the surface viscoelasticity. Its role can be seen just as keeping the macromolecules in the surface layer.

The high surface elasticity in general does not contradict the model of Goddard et al.[3−6] (Figure 1). If not all sulfonate groups are neutralized by surfactant molecules and the chain bears some charge, it still possesses an effective rigidity of electrostatic origin and must be stretched at the surface. Ellipsometry,[18] X-ray analysis,[10] and neutron reflectivity[11] show indeed that the thickness of the adsorbed film is small (≤2 nm) in the range of low concentrations and the polyelectolyte does not form long loops and tails from the surface into the bulk. In this case, the mechanism of surface stress relaxation at the expense of segment exchange between the proximal and middle regions of the surface layer[26,28] cannot be in operation and strong repulsion between neighboring segments must lead to a high dynamic surface elasticity.

However, these ideas cannot explain the slow relaxation of surface properties. If the balance of the electrostatic energy and the entropic factor mainly determines the equilibrium concentration of complexes in the surface layer, molecular diffusion must also be responsible for the relaxation of surface stresses. Then the aforementioned calculations of τ_D also give also estimates from above of the main relaxation times, which are by orders of magnitude lower than the experimental results.

The model of Goddard et al. cannot explain the observations of the high surface elasticity at extremely low concentrations either. In the bulk phase mainly a balance between the electrostatic enthalpic contribution and the opposite contribution from the loss of translational entropy governs the formation of an ion doublet and the combination of the counterion with a charged micelle or macromolecule.[37] The absolute value of the latter term quickly increases with dilution, and the equilibrium shifts in the direction of free ions. Although other factors for the polyelectrolyte/surfactant complex formation in a surface layer must be taken into account, for example, hydrophobic effects, which are responsible for the surfactant adsorption, one could also expect a decrease of the PSS/DTAB complex concentration at dilution. This should lead to a faster decrease of the dynamic surface elasticity than we observed (Figures 9 and 10).

The model of Goddard[3−6] also disagrees with the neutron reflectivity results on the PSS/DTAB adsorption films at the air/water interface.[11] It follows from the model and the similarity between the surface rheological data for PSS/DTAB solutions and pure PSS solutions that only a part of the sulfonate groups can be screened by DTAB molecules (cf. above). However, at low concentrations the number of surfactant molecules exceeds the number of polymer segments in the surface layer by a factor of almost 2.[11] The excess of free surfactant seems improbable if we take into account that the driving force for the DTAB

adsorption in pure surfactant solution is negligible at $c_s < 1$ mM. Moreover, the large number of free DTAB molecules in the surface layer should lead to a fast relaxation of surface stresses, which is not the case.

At last, the classical model does not take into account the chemical nature of the polyelectrolyte backbone chain. The peculiarity of the polystyrene chain consists of its high hydrophobicity. The solubility of polystyrene in water is negligible, and these macromolecules form compact globules at the air−water interface.[38] PSS is hydrophilic due to its sulfonate groups, but if the degree of sulfonization is not high ($\ll 1$), the polymer can form intramolecular globules in aqueous solutions, and the whole structure is described as a pearl necklace.[39,40] The decrease of the sulfonization degree leads to a fast increase of the PSS surface activity.[41] Another way to increase the PSS surface activity is to increase the ionic strength of the solution. The hydrophobicity of the PSS chain increases upon decreasing the degree of ionization, and the polyelectrolyte can form two-dimensional aggregates in the surface layer.[21] The hydrophobic nature of the PSS backbone chain becomes clear also in the PSS/DTAB complex formation in the solution bulk. It was shown that in these systems a compact structure is formed where one PSS chain is associated with several DTAB micelles in such a way that the hydrophobic aromatic rings of the polyion are embedded in the micellar interior.[7,8] Hydrophobic effects are also responsible for the cooperative nature of the PSS/DTAB complex formation, "where surfactants tend to bind to adjacent sites of the polymer as they maximize hydrophobic interactions between the hydrophobic chains of the surfactant".[20]

These considerations indicate that the hydrophobic nature of the polystyrene backbone should be taken into account in the description of the PSS/DTAB complex at the air/solution interface too. In the following we will describe a slight modification of the classical model, which is in agreement with the experimental results of this work and literature data on the DTAB surface concentration,[11] the adsorption film thickness,[11,18] and, most important, the dilational viscoelasticity of the PSS adsorption films.[21] On the other hand, the complexity of the surface properties of DTAB/PSS solutions and the limited number of applied methods indicate that the proposed explanation is only tentative. Further work on the clarification of the model is in progress now.

One can assume that the role of ion pair formation between the dodecyltrimethylammonium cation and the sulfonate anion is mainly limited to the local neutralization of free charges at the polymer chain. Then the hydrophobic effect leads not only to the surfactant adsorption but also to the attraction between segments of the polystyrene backbone and hydrocarbon tails of the surfactant, between the segments themselves, and probably between the surfactant tails. As a result the adsorbed film may contain small regions of low effective charge with high hydrophobic interactions between the components. These almost two-dimensional aggregates are characterized by surface activity as a single whole and can contain segments of different PSS chains. The charge of PSS trains between the aggregates is not completely compensated, and they are rigid and strongly repulse each other as they do in the system without surfactant. The whole adsorption film is rigid due to the entanglements of different polyelectrolyte chains and strong cohesion between hydrophobic entities inside the two-dimensional aggregates. This system must be characterized by a high modulus of surface dilational elasticity. On the other hand, the entanglements between different polymer chains can lead to long relaxation times. Figure 12 shows a sketch of this structure. Probably a rather similar structure exists also in PSS adsorbed films if the ionic strength of the solution is high enough.[21] Note that the key element of the proposed concept is the hydrophobic nature of the polyelectrolyte backbone chain. If the chain is hydrophilic, the structure sketched in Figure 12 is hardly possible. For example, the dynamic surface elasticity of the mixed solutions of DTAB and sulfonated polyacrylamides with the hydrophilic backbone is a few times less than that for the PSS/DTAB system.[13−15,17] In this case the experimental data are better described by the classic model.

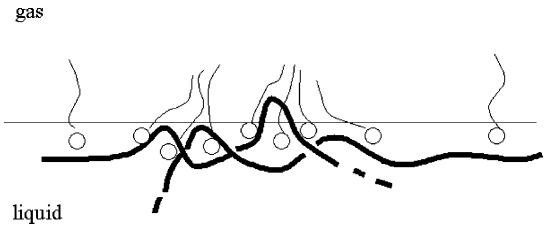

Figure 12. Schematic representation of the aggregate formation in the surface layer at low DTAB concentration.

The increase of the DTAB concentration leads to the formation of microgel first at the surface and after that in the bulk phase.[18−20] The structure depicted in Figure 12 collapses, and the surface properties change rather abruptly (Figures 9 and 10). The process in the surface layer can be described then as a transition from the two-dimensional nanogel to a three-dimensional microgel. The dynamic surface elasticity drops and changes only slightly after that, unlike the ellipsometric signal[18] and the neutron reflectivity profile.[11] This means that the dynamic surface elasticity is not sensitive to the formation of a sandwich-like structure and to the strong changes of the number of microparticles at the interface, which were discovered by other methods.[11,18] In this concentration range ($c_s > 0.5$ mM at $c_p = 0.01$ wt % and $c_s > 2$ mM at $c_p = 0.05$ wt %) measurements of the surface dilational viscoelasticity give too scarce information on the organization of the adsorbed PSS/DTAB film. Low values of the surface elasticity indicate a looser package of the components than at low concentrations. The PSS chains are not stretched even between the microparticles and contain fewer ionized groups. In this case one has to consider a three-dimensional film structure. This picture is in agreement with the faster mechanical relaxation in the adsorbed film. Figure 11 shows indeed that the main relaxation time is comparable with the oscillation period; i.e., it is on the order of 10 s.

The slow decrease of the dynamic surface elasticity with increasing DTAB concentration (Figures 9 and 10) probably indicates the gradual transition of the PSS chains from the surface layer to the bulk phase. At $c_s > 0.02$ M the surface tension and the surface elasticity are close to the values of micellar DTAB solutions; in particular, the elasticity is zero at a frequency of 0.14 Hz. Although traces of PSS can possibly exist in the surface layer, however, their surface concentration is low and they do not influence the surface viscoelasticity. The relaxation of surface stresses proceeds at the expense of DTAB monomer exchange between the adsorbed film and the bulk phase.

Conclusions

We have measured the dynamic surface elasticity of mixed PSS/DTAB solutions as a function of DTAB concentration and surface age at two PSS concentrations (0.01 and 0.05 wt %). The whole concentration range of the surfactant (0.02−100 mM) can be divided into two large regions with different types of the dilational surface viscoelasticity, and a narrow zone between

them with abrupt changes of the surface properties. At low (micromolar) concentrations the surface elasticity increases extremely slowly with time and can reach high values (60−100 mN/m), thus indicating that strong interactions between DTAB and PSS in the surface layer are possible. In this concentration range the surface viscoelastic behavior almost coincides with that of relatively concentrated pure PSS solutions and disagrees in some respects with the expectations based on the model of Goddard et al. A modification of this model is proposed, which takes into account the hydrophobic nature of the polystyrene chain. This modified model assumes that the abrupt decrease in the dynamic surface elasticity in a narrow concentration range is connected with the formation of a microgel in the surface layer, which is in accordance with recent ellipsometric results.[18−20] At higher concentrations the surface elasticity is low and gradually decreases to zero. The adsorbed film is characterized by a loose structure with a main relaxation time on the order of 10 s.

Acknowledgment. This work was financially supported by ESA (FASES, Grant MAP AO-99-052) and the Russian Foundation of Fundamental Research (Project No. RFFI 03-03-32366). Ms. Lina Vachitova is gratefully acknowledged for help in the dynamic surface elasticity measurements.

References and Notes

(1) Saito, S. *Kolloid-Z.* **1957**, *154*, 19.
(2) Jones, M. N. *J. Colloid Interface Sci.* **1967**, *23*, 36.
(3) Goddard, E. D.; Phillips, T. C.; Hannan, R. B. *J. Soc. Cosmet. Chem.* **1977**, *26*, 461.
(4) Goddard, E. D. *Colloids Surf.* **1986**, *19*, 255.
(5) Goddard, E. D. *J. Am. Oil Chem. Soc.* **1994**, *71*, 1.
(6) Goddard, E. D.; Ananthapadmanabhan, K. P. In *Polymer−surfactant systems*; Kwak, J. C. T., Ed.; Surfactant Science Series, Vol. 77; Marcel Dekker: New York, 1998; p 21.
(7) Kogej, K.; Skerjanc, J. *Langmuir* **1999**, *15*, 4251.
(8) Kogej, K.; Theunissen, E.; Reynaers, H. *Langmuir* **2002**, *18*, 8799.
(9) Asnasios, A.; Klitzing, R.; Langevin, D. *Colloids Surf., A* **2000**, *167*, 189.
(10) Stubenrauch, C.; Albouy, P.-A.; Klitzing, R.; Langevin, D. *Langmuir* **2000**, *16*, 3213.
(11) Taylor, D. J. F.; Thomas, R. K.; Penfold, J. *Langmuir* **2002**, *18*, 4748.
(12) Taylor, D. J. F.; Thomas, R. K.; Li, P. X.; Penfold, J. *Langmuir* **2003**, *19*, 3712.
(13) Ritacco, H.; Kurlat, D.; Langevin, D. *J. Phys. Chem. B* **2003**, *107*, 9146.
(14) Jain, N. J.; Albouy, P.-A.; Langevin, D. *Langmuir* **2003**, *19*, 5680.
(15) Jain, N. J.; Albouy, P.-A.; Klitzing, R.; Langevin, D. *Langmuir* **2003**, *19*, 8371.
(16) Ritacco, H. A.; Busch, J. *Langmuir* **2004**, *20*, 3648.
(17) Bhattacharyya, A.; Monroy, F.; Langevin, D.; Argillier, J.-F. *Langmuir* **2000**, *16*, 8727.
(18) Monteux, C.; Williams, C. E.; Meunier, J.; Anthony, O.; Bergeron, V. *Langmuir* **2004**, *20*, 57.
(19) Monteux, C.; Llauro, M.-F.; Baigl, D.; Williams, C. E.; Anthony, O.; Bergeron, V. *Langmuir* **2004**, *20*, 5358.
(20) Monteux, C.; Williams, C. E.; Bergeron, V. *Langmuir* **2004**, *20*, 5367.
(21) Noskov, B. A.; Nuzhnov, S. N.; Loglio, G.; Miller, R. *Macromolecules* **2004**, *37*, 2519.
(22) Stenvot, C.; Langevin, D. *Langmuir* **1988**, *4*, 1179.
(23) Noskov, B. A. *Adv. Colloid Interface Sci.* **1996**, *69*, 63.
(24) Miller, R.; Wüstneck, R.; Krägel, J.; Kretzschmar, G. *Colloids Surf., A* **1996**, *55*, 75.
(25) Loglio, G.; Pandolfini, P.; Miller, R.; Makievski, A. V.; Ravera, F.; Ferrari, M.; Liggieri, L. In *Novel methods to study interfacial layers*; Möbius, D., Miller, R., Eds.; Studies in Interface Science, Vol. 11; Elsevier: Amsterdam, 2001; p 439.
(26) Noskov, B. A.; Akentiev, A. V.; Bilibin, A. Yu; Zorin, I. M.; Miller, R. *Adv. Colloid Interface Sci.* **2003**, *104*, 245.
(27) Noskov, B. A.; Loglio, G. *Colloids Surf., A* **1998**, *143*, 167.
(28) Noskov, B. A.; Akentiev, A. V.; Loglio, G.; Miller, R. *J. Phys. Chem. B* **2000**, *104*, 7923.
(29) Akentiev, A. V.; Noskov, B. A. *Colloid J.* **2002**, *64*, 129.
(30) Miller, R.; Fainerman, V. B.; Makievski, A. V.; Leser, M.; Michel, M.; Aksenenko, E. V. *Colloids Surf., B* **2004**, *36*, 123.
(31) Cohen-Stuart, M. A.; Hoogendam, C. W.; de Keizer, A. *J. Phys.: Condens. Matt.* **1997**, *9*, 7767.
(32) Babak, V. G.; Desbrieres, J. *Mendeleev Commun.* **2004**, *N 2*, 66.
(33) Wang, L.; Yu, H. *Macromolecules* **1988**, *21*, 3498.
(34) Richardson, R. M.; Pelton, R.; Cosgrove, T.; Zhang, J. *Macromolecules* **2000**, *33*, 6269.
(35) Lee, L. T.; Jean, B.; Menelle, A. *Langmuir* **1999**, *15*, 3267.
(36) Noskov, B. A. *Adv. Colloid Interface Sci.* **2002**, *95*, 236.
(37) Konop, A. J.; Colby, R. H. *Langmuir* **1999**, *15*, 58.
(38) Bijsterbosch, H. D.; de Haan, V. O.; de Graaf, A. W.; Mellema, M.; Leermarkers, F. A. M.; Cohen Stuart, M. A.; van Well, A. A. *Langmuir* **1995**, *11*, 4467.
(39) Essafi, W.; Lafuma, F.; Williams, C. E. *J. Phys. II* **1995**, *5*, 1269.
(40) Dobrynin, A. V.; Rubinstein, M.; Obukhov, S. P. *Macromolecules* **1996**, *29*, 2974.
(41) Theodoly, O.; Ober, R.; Williams, C. E. *Eur. Phys. J. E* **2001**, *5*, 51.