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Dynamic Surface Properties of Sodium Poly(styrenesulfonate) Solutions

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ABSTRACT: We present experimental results on the dynamic surface properties of aqueous solutions of sodium poly(styrenesulfonate). The dynamic surface elasticity at frequencies from 0.01 up to 500 Hz and at concentrations exceeding 0.1 wt % proved to be significantly higher than the corresponding data for solutions of nonionic polymers. Another peculiarity consisted in extremely slow changes of the surface properties with time. The addition of salt did not lead to significant changes of the surface elasticity, which was in disagreement with the expectation from the SCF theory. The obtained results can be explained if one assumes aggregate formation in the surface layer.

Introduction

Polyelectrolytes are of fundamental importance in biology and biochemistry and widely used to control the stability of dispersions in various industrial processes. In many cases the application of polyelectrolytes is determined by the unique properties of their interfacial films. Significant efforts have been spent recently on the study of surface properties of natural polyelectrolytes.[1,2] Although the adsorbed films of strong synthetic polyelectrolytes with simpler molecular structure have been studied for more than 50 years,[3] the progress in this field is significantly slower.

The understanding of the surface layer structure is still rather limited even for the most studied solutions of sodium poly(styrenesulfonate) (PSS).[4−8] Moreover, on a first glance the surface tension results obtained by different authors are contradictory for this system. Thus, Taylor et al. in their study of PSS−surfactant complexes claim that “water-soluble polymers are not normally surface-active at all”.[9] Okubo did not manage to determine any deviations of the surface tension of PSS solutions from the value for pure water at all.[4] At the same time, Theodoly et al. describe a surface pressure increase up to 20 mN/m for solutions of 55% sulfonated PSS and up to 10 mN/m for 90% sulfonated PSS.[8] Caminati and Gabrielli observed an even stronger increase for solutions of PSS with low molecular weight.[5] The reason for this discrepancy is connected with the peculiar behavior of the polyelectrolytes at the liquid−gas interface. The surface tension isotherms are different for aqueous solutions of nonionic polymers and synthetic polyelectrolytes. While in the former case the surface tension deviates from the value of water even at concentrations less than 0.0001 wt %, the surface tension of polyelectrolyte solutions begins to decrease only at relatively high concentrations when the ionic strength is high enough and the lateral repulsion of charged groups is screened to a great extent. This behavior allowed Okubo to introduce the critical polymer concentration c^* when the surface pressure starts to increase.[4,10]

Another peculiarity of adsorbed polyelectrolyte films consists of extremely slow kinetic dependency of the surface tension. For example, Theodoly et al. noted that even 24 h is not enough to reach the equilibrium for solutions of both 55% and 90% sulfonated PSS.[8] Slow surface tension changes were also observed for adsorbed films of hydrophobically modified polyelectrolytes[11] and charged block copolymers.[12] This slow equilibration of the surface layer significantly complicates the determination of the equilibrium surface tension isotherm and probably c^* value. On the other hand, the surface tension is not sensitive enough to polymer conformational transitions in the surface layer.[13,14] Recently, Yim et al. have also discovered that the surface tension cannot be correlated with the adsorbed amount of PSS.[7] These authors also did not find the time dependence of surface tension for rather concentrated PSS solutions at 0.01 g/mL and KCl concentrations of 1.7 and 2.5 M. The latter conditions, however, correspond to fast changes of the surface properties when the equilibrium can be established within a few minutes after creating the interface (cf. our discussion of the dynamic surface tension of PSS solutions below).

Significantly more informative are the measurements of neutron reflectivity, which allow the determination of not only the adsorption value but also the segment distribution perpendicular to the surface.[6,7,9] In this case one can compare the experimental results with calculations of the segment profile according to the self-consistent-field (SCF) theory.[15−18] While qualitative changes of the adsorption and the adsorbed film thickness with the salt concentration proved to be consistent with the theoretical predictions, quantitative agreement was not achieved. Unlike the predicted monotonical segment profile, the experimental one consisted of two distinct layers with different segment concentrations.[6] More recently, Yim et al. have discovered that the concentration dependences of adsorption at different salt contents have maxima at concentrations correlating with the overlap polymer concentrations.[7] This finding cannot be explained by the SCF theory of polyelectrolyte adsorption either.

Most of the studies published so far on surface properties of PSS solutions have been aimed at the determination of equilibrium data. Recent results of

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Theodoly et al.[8] brought some doubts about the possibility to solve this problem. First, the equilibration process proved to be extremely slow. The equilibrium surface tension of relatively concentrated PSS solutions was not reached within a few days. Second, the surface state of a given solution was not unique, but a number of metastable structures were discovered. Consequently, investigations of the nonequilibrium surface properties of PSS solutions turn out to be especially important.

This task is not easy because of a limited number of suitable experimental techniques. In general, information on polymer chain dynamics at different interfaces is rather scarce. This is a conclusion, for example, of a recent discussion in the *European Physical Journal E*.[19−22] For the liquid−gas interface one usually measures the dynamic surface tension of polymer solutions. However, interpretation of the monotonic kinetic surface tension curves is difficult and not always unequivocal. Besides, the creation of a fresh interface is usually accompanied by complicated liquid flows, which is difficult to take into account.[23−25] Another approach is based on small perturbations from the equilibrium and subsequent measurement of the system response (mechanical relaxation spectrometry of the surface layer). For small perturbations linear relationships describe the system, and the surface tension $\delta\gamma$ perturbation is proportional to the area perturbation δA[26]

$$\delta\gamma = \epsilon(\omega)\delta A \qquad (1)$$

The proportionality factor ϵ (the dilational dynamic surface elasticity) is a complex quantity in the general case and depends on the angular frequency of perturbations ω.

Although first studies of the dilational surface viscoelasticity go back to the 1960s,[27,28] the crucial influence of the complex dynamic surface elasticity on the dynamics of various colloid systems, for example, on the stability of foams and emulsions has been realized much later.[29−32] Up to now many authors studied the dynamic surface elasticity of adsorbed and spread films of conventional surfactants[23−25,28−30] and proteins.[1,31−34] Solutions of nonionic homopolymers have been investigated in the low frequency range (below 1000 Hz) by surface relaxation methods only recently.[13,14,35,36] The results were in agreement with the theory of dilational surface viscoelasticity proposed for solutions of linear flexible polymer chains.[37] These studies allowed a determination of not only the relaxation mechanism but also the polymer conformation in the surface layer. To the best of our knowledge, solutions of synthetic polyelectrolytes have not been studied by these methods at all. Only Bhattacharya et al. measured the dynamic surface elasticity of solutions of complexes between some polyelectolytes and conventional ionic surfactants.[38]

The main aim of this work is to compare the dynamic surface properties of solutions of polymers with ionized groups with properties of nonionic polymer solutions. We chose PSS as a representative of strong polyelectrolytes. The main emphasis will be made on the dilation surface viscoelasticity. After a brief description of the experimental methods the results will be represented and discussed.

Experimental Section

The surface tension of PSS solutions was measured by the Wilhelmy plate method with a roughened glass plate attached to an electronic balance. The measurements began in 2 min after the solution was poured in a Teflon Langmuir trough and cleaned by a moving Teflon barrier. The surface tension of PSS solutions changed for many hours, and the intervals between the consecutive surface tension readings usually significantly exceeded 2 min. The whole setup was placed in a lucid cabinet together with a beaker containing water and filter paper to decrease solution evaporation from the trough.

The experimental setups for measurements of the dynamic surface elasticity together with the corresponding experimental procedures were described in detail elsewhere.[13,14,24,39,40] We represent below only the basic principles of the employed experimental techniques. At frequencies less than 0.2 Hz the dynamic surface elasticity was measured by the oscillating barrier method.[40] The surface area of the solution in the Langmuir trough changed periodically with the given frequency and amplitude by oscillations of the Teflon barrier sliding along the polished brims of the trough. If the frequency of oscillations is less than 0.2 Hz, the surface tension of the solution in the trough turns out to be homogeneous. In this case the surface tension measurements by the Wilhelmy plate method allow direct determination of the surface elasticity. The elasticity modulus is determined from the amplitude ratio of the oscillations of the surface tension and surface area according to eq 1. The phase shift between the oscillations of two measured parameters (surface tension and surface area) determines the phase angle of the dynamic surface elasticity.

At higher frequencies we used the capillary wave method. The wave characteristics were measured by means of the electromechanical method based on the principle of a dynamic condenser.[13,14,24,39] 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. Propagation of the waves caused capacity 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 transverse capillary waves. The dynamic surface elasticity can be calculated from the capillary wave characteristics according to the dispersion equation[13]

$$\begin{aligned}\epsilon &= \epsilon_r + i\epsilon_i \\ &= \{\rho\omega^2[\rho\omega^2 - (\gamma k^3 + \rho g k)\tanh(kh)] + 4i\rho\mu\omega^3k^2 + 4\mu^2\omega^2k^3[m\tanh(kh) - k]\}/\{mk^2[\rho\omega^2 - (\gamma k^3 + \rho g k)\tanh(kh)] + k^3(\gamma k^3 + \rho g k)\} \qquad (2)\end{aligned}$$

where $k = 2\pi/\lambda + i\alpha$ is the complex wavenumber, α is the damping coefficient, λ is the wavelength, g is the gravitational acceleration, $m^2 = k^2 - i\omega\rho/\mu$, μ is the viscosity, ρ is the density, and h is the depth of the liquid in the trough.

Equation 2 can be considered to be a complex algebraic equation relative to k. The two main roots of this equation correspond to transversal and longitudinal surface waves. Both wave modes arise as a result of spontaneous thermal fluctuations at the liquid surface or can be excited by a wave generator. In this work we used only the excited transverse surface waves. Note that although the specific energy dissipation in the surface layer, where the monomer concentration is higher, exceeds the specific dissipation in the bulk solution, the energy of waves dissipates mainly in the bulk solution because the wavelength (the penetration depth of the motion into the bulk liquid, between 1 and 3 mm in our case) 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.[14,24] Therefore, the damping coefficient of surface waves is a function of both components of the dynamic surface elasticity. Even if the imaginary part of the surface elasticity is zero (pure elastic film), the damping coefficient can be a complicated (nonmonotonic) function of the elasticity modulus. If $|\epsilon| > 0.14\gamma$, the capillary wave characteristics are almost independent of the

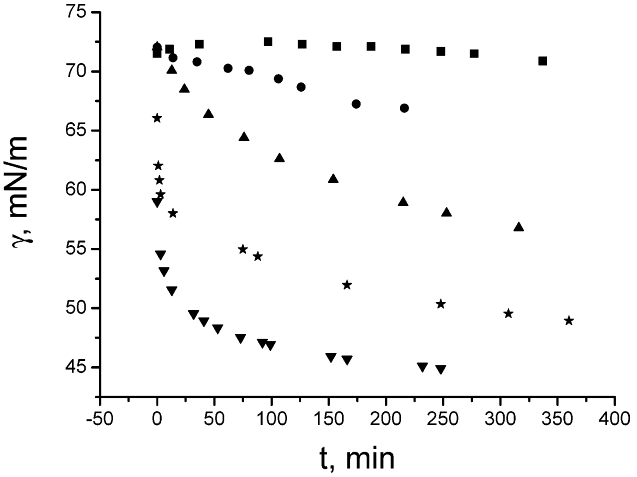

Figure 1. Time evolution of the surface tension of PSS solutions at the concentrations 0.11 wt % (squares), 0.2 wt % (circles), 0.35 wt % (triangles up), 1 wt % (asterisks), and 1.5 wt % (triangles down).

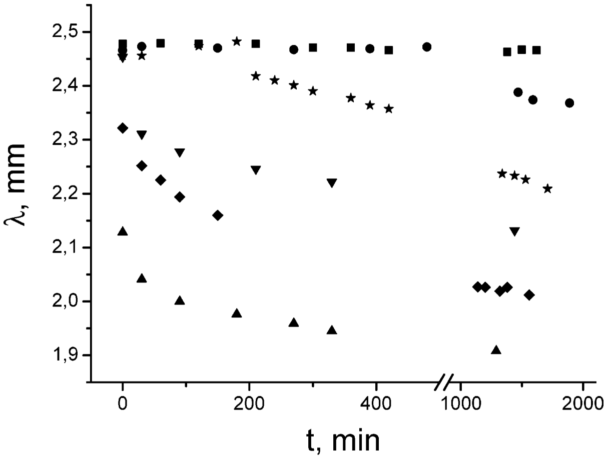

Figure 2. Kinetic dependencies of the length of capillary waves at the frequency 180 Hz for PSS concentrations 0.01 wt % (squares), 0.056 wt % (circles), 0.11 wt % (asterisks), 0.51 wt % (triangles down), 1 wt % (rombs), and 3.4 wt % (triangles up).

surface elasticity and are mainly determined by the surface tension. The surface elasticity modulus of most PSS solutions under investigation meet this condition, and consequently, the capillary wave method can give only rough estimates of the surface elasticity. Nevertheless, we used this supplementary method in order to compare experimental data of both methods at low $|\epsilon|$. Besides, the capillary wave characteristics are less sensitive to possible changes of the liquid level in the trough due to evaporation as the surface tension measured by the Wilhelmy plate method. This is important for long time measurements.

PSS with the molecular mass 70 000 was received from Aldrich and purified by dialysis through a cellulose membrane (Sigma) with a cutoff molecular mass of 12 000. However, this procedure led only to insignificant changes within the error limits of the experimental results, and PSS was also used as received in the course of some measurements. The dialysis gives us some confidence that our sample at least did not contain oligomers with a molecular weight $M < 12\,000$, i.e., in the most dangerous range. The results of Caminati and Gabrielli show some influence of the molecular weight of the PSS on surface tension for $M < 18\,000$.[5] This is almost the same range where we observed the molecular weight dependence of the dynamic surface elasticity for solutions of nonionic polymers.[13,36] At higher M the elasticity almost did not depend on the molecular weight. It is reasonable to assume that the same will be true for PSS solutions.

The elemental analysis of our sample on sulfur gave a degree of sulfonization of 95%, but the real degree can be even a little bit higher because the sample could contain some traces of water.

Sodium chloride from Vecton (St. Petersburg) was purified from organic impurities by heating in an oven up to 800 °C. Fresh twice-distilled water was used for the preparation of solutions. An all-Pyrex apparatus and alkaline permanganate were employed in the second stage of distillation.

Results and Discussion

The surface tension of PSS solutions changes with time and concentration only in the range of relatively concentrated solutions where PSS behaves as a typical surfactant (Figure 1). For example, at a concentration of $c = 1.53$ wt % the surface tension reaches a value of about 45 mN/m after several hours. On the other hand, the surface pressure remains close to zero for several hours after surface formation at concentrations lower than about 0.1 wt %. This behavior, as shown by Okubo,[4,10] is characteristic for various synthetic and natural polyelectrolytes and different from that of neutral surface active polymers with a molecular mass higher than about 10 000. In the latter case the surface pressure has a finite and almost constant value at all concentrations accessible to investigation.[13,14,35,36] It follows from the data of Figure 1 that $c^* \approx 0.1$ wt %. However, longer measurements show that this critical concentration can depend on the duration of measurements (cf. below), and one can obtain only a rough estimate.

Another peculiarity of the data of Figure 1 in comparison with the results for neutral polymers is the very slow equilibration process. The PSS adsorption proceeds for more than 5 h for all concentrations, while for solutions of neutral polymers[13,14,35,36] the equilibrium surface tension is reached for less than 1 min at concentrations higher than 0.0001 wt %. The slow adsorption kinetics of polyelectolytes is well-known and generally attributed to the electrostatic adsorption barrier.[8,41] The first macromolecules arriving at the interface create a local surface charge and thus hinder further adsorption of charged chains.

Note that addition of a small amount of a conventional cationic surfactant (dodecyltrimethylammonium bromide, even at an overall concentration of 0.01 mM) to the solution led to significantly faster changes of the surface tension, thus indicating another adsorption mechanism and probably different structure of the surface layer. On the other hand, this observation can explain why Ahrens et al. did not observe time effects of the adsorption of PSS at the aqueous surface covered by a dioctadecyldimethylammonium bromide.[42]

Measurements of the capillary wave characteristics allow monitoring of the surface properties at longer times. The capillary wavelength is approximately proportional to the cubic root of surface tension and depends only slightly on the dynamic surface elasticity.[24,39] Slow changes of the wavelength with time for PSS solutions are a consequence of the corresponding decrease of the surface tension (Figure 2). For most of the solutions even 20 h is not enough to reach equilibrium. At longer time scales the surface tension decreases even at $c < 0.1$ wt %, and the results in Figure 2 lead to a critical concentration c^* lower than 0.1 wt %.

It follows from the dispersion eq 2 that the damping coefficient of capillary waves α, unlike the wavelength, is determined by both the surface tension and the

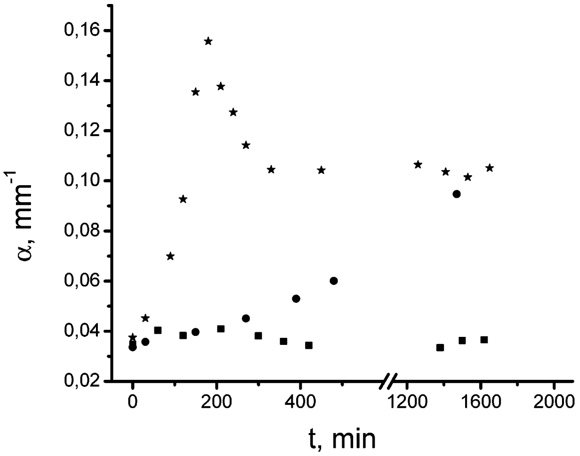

Figure 3. Kinetic dependencies of the damping coefficient of capillary waves at the frequency 200 Hz for the PSS concentrations 0.01 wt % (squares), 0.06 wt % (circles), and 0.11 wt % (asterisks).

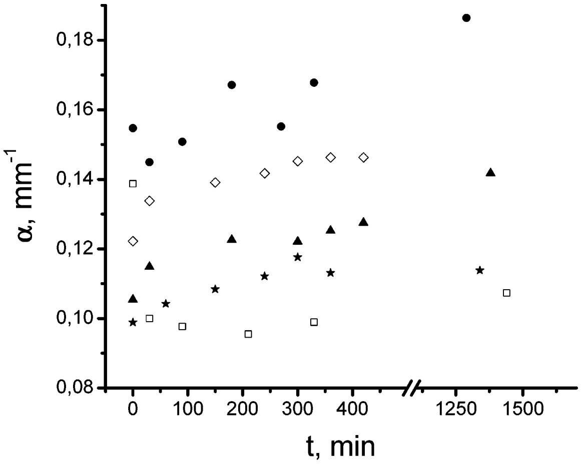

Figure 4. Kinetic dependencies of the damping coefficient of capillary waves at the frequency 200 Hz for PSS concentrations 0.51 wt % (squares), 1 wt % (asterisks), 1.5 wt % (triangles), 2.3 wt % (rombs), and 3.4 wt % (circles).

dynamic surface elasticity. This leads to more complicated kinetic dependencies (Figures 3 and 4). At $c \leq 0.01$ wt % the damping coefficient was almost constant and equaled roughly to the value for pure water. At higher concentrations but less than about 0.1 wt % α increased monotonically as a consequence of the corresponding increase of the dynamic surface elasticity. At concentrations higher than 0.1 wt % a distinct maximum of damping was observed (Figure 3). The local maximum of the damping coefficient of capillary waves as a function of the surface elasticity modulus is described by the dispersion equation and is a consequence of the resonance between the transverse and longitudinal wave modes at the condition $|\epsilon| \approx 0.14\gamma$.[24,43] Therefore, the maximum in Figure 3 only means that the modulus of the dynamic surface elasticity increases with time and crosses the critical value of about 10 mN/m, corresponding to the mentioned condition. The nonmonotonic kinetic dependence of the damping was observed at all frequencies under investigation in the range from 70 up to 500 Hz, and the maximal α was about 7 times larger than the value for water. At last, at concentrations higher than about 0.5 wt % the kinetic dependencies become monotonic again. In this concentration range the modulus of dynamic surface elasticity is significantly higher than 0.14γ and almost does not influence the damping coefficient. The damping coefficient is high and increases slowly, mainly due to the decrease of surface tension. Note also that at $c > 1$ wt % the damping coefficient significantly increases with concentration. This is a consequence of the increase of the bulk phase viscosity in the range of semidilute solutions.

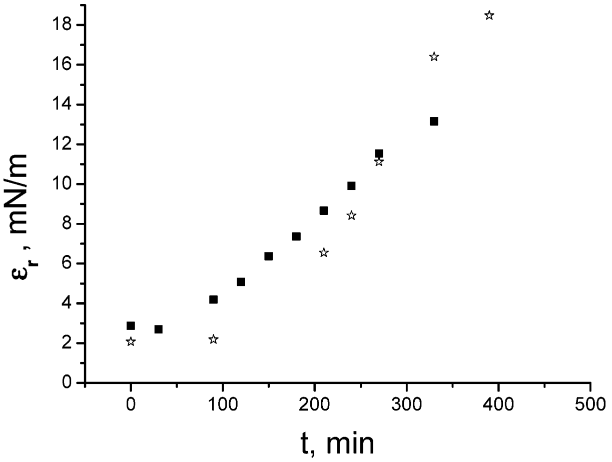

Figure 5. Kinetic dependencies of the dynamic surface elasticity real part of PSS solutions at the frequency 200 Hz and concentrations 0.042 wt % (asterisks) and 0.11 wt % (squares).

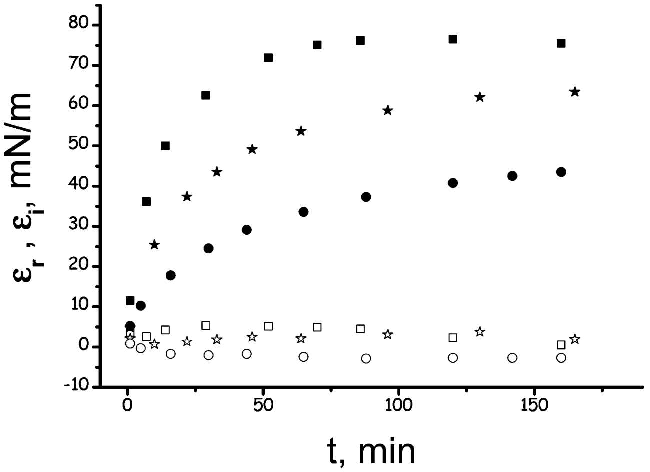

Figure 6. Kinetic dependencies of the real (solid symbols) and imaginary (empty symbol) parts of the dynamic surface elasticity of PSS solutions at the frequency 0.12 Hz for concentrations 0.1 wt % (circles), 0.5 wt % (asterisks), and 0.8 wt % (squares).

If the surface elasticity is low enough, it can be calculated directly from the wave characteristics according to eq 2. Figure 5 shows the real part of the dynamic surface elasticity at a frequency of 200 Hz as a function of time for two relatively small PSS bulk concentrations. The imaginary part is close to zero. The surface elasticity modulus increases with time, reaching values exceeding 0.14γ for about 5 h. At longer times and higher bulk concentrations it increases further, the accuracy of the surface elasticity determination decreases fast, and the capillary wave method leads only to very rough estimates. At the same time high surface elasticity can be easily measured by the oscillating barrier method. Figure 6 shows the corresponding kinetic dependencies at a frequency of 0.12 Hz and the barrier oscillation amplitude of 4 mm calculated from the amplitude and phase of surface tension and surface

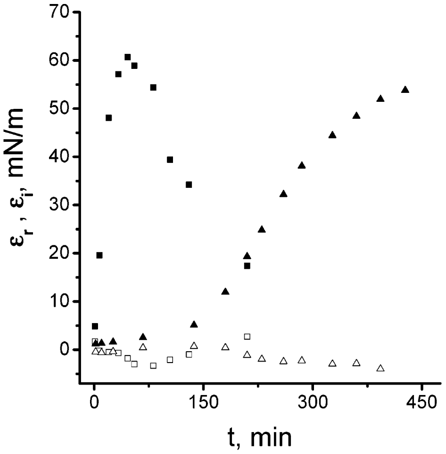

Figure 7. Kinetic dependencies of the real (solid symbols) and imaginary (empty symbol) parts of the dynamic surface elasticity of PSS solutions at the frequency 0.12 Hz for concentrations 0.000 32 wt % (triangles) and 0.16 wt % (squares).

area oscillations according to eq 1. The imaginary part of the surface elasticity is again zero in the error limits. Note that the relative error of the imaginary part is mainly determined by the accuracy of the phase angle measurement and is about 5%, thus leading to the increase of the absolute error at the increase of the surface elasticity modulus. The real part of the dynamic surface elasticity increases with time and bulk concentration. The rate of changes also increases with the concentration although some kinetic curves violate this rule. Some deviations from the general behavior can be attributed to the insufficient control of the natural convection in the Langmuir trough, but other peculiarities of the dynamic surface properties of PSS solutions indicate also more fundamental reasons (cf. below). The surface elasticity reaches a plateau value at concentrations higher than about 0.2 wt % within a few hours, and at $c > 0.3$ wt % this value is approximately constant and amounts to about 73 mN/m. At $c > 0.5$ wt % the solution reaches an almost constant surface elasticity within about an hour, which is significantly faster than the establishment of the equilibrium surface tension (Figure 1). Thereby the surface tension changes while the elasticity is almost constant. This behavior is also opposite to that observed for solutions of nonionic polymers where the surface elasticity proved to be more sensitive to conformational changes in the surface layer than the surface tension.[13,14]

We also applied the oscillating barrier method to relatively dilute solutions at $c < 0.01$ wt %. In this concentration range the surface tension and the surface elasticity are mainly close to zero, but this value is not reproducible to a sufficient extent. Sometimes the surface tension decreased with time even at low concentrations, and the real part of the dynamic surface elasticity changed, too. Figure 7 shows two characteristic kinetic curves when $|\epsilon|$ deviates from zero. The surface elasticity can go through a local maximum and gradually tends to zero afterward (curve I). In other more rare cases the surface elasticity and the surface pressure began to increase slowly after a rather long (few hours) induction period (curve II). These results can be explained if one assumes the inhomogeneity of the solution. A multimacroion domain can encounter the surface, thus leading to adsorption and subsequent slow equilibration. This effect should depend on the preparation conditions of the solution, but we were unable to find any correlation with the time of stirring of the freshly prepared PSS solution. It is more probable that insufficient reproducibility of the results at low concentrations is a consequence of the spontaneous formation of submicron size domains in dilute polylectrolyte solutions. Although these domains have been discovered 25 years ago[44] and since that time studied by various techniques,[45,46] the mechanism of their formation is still not entirely clear.[47]

Note that the kinetics dependencies of type I (Figure 7) were observed in few cases even at higher concentrations up to about 0.2 wt %. Although at $c > 0.01$ wt % the "ordinary" curves of the type shown in Figure 6 are significantly more frequent, the kinetic dependencies of the dynamic surface elasticity of both the ordinary and "anomalous" types were sometimes obtained at the same concentrations and approximately the same kinetic curves of the surface tension. These results are in agreement with the findings of Theodoly et al., who showed that the surface state of a given PSS solution is not unique and different metastable configurations can be realized.[8] Our data show that these different states can correspond to the same surface tension but different surface elasticities. The influence of the bulk heterogeneity on the surface properties of strong polyelectrolyte solutions and the transitions between different states of the surface layer deserve further investigation. This work is now in progress, but in the present study we concentrate our discussion mainly on the surface viscoelasticity of relatively concentrated solutions where the shape of the kinetic curve is entirely reproducible (at $c > 0.2$ wt % for PSS solutions without salt).

If a polyelectrolyte adsorbs at an uncharged surface, the compensation of strong repulsion between neighboring charges is possible only in the case of high affinity between polymer segments and the surface and only in a narrow proximal layer. The SCF theory shows then that the polyion has an almost flat conformation, and the adsorbed film can be considered as a monolayer at a first approximation. This conclusion follows from numerical calculations using different versions of the lattice model[15−17] and also from a simple analytical theory of Fleer.[18] It was confirmed by neutron reflectivity,[6] X-ray reflectivity, and ellipsometry.[8] Neutral polymers have also an almost flat conformation at an early stage of adsorption when the surface excess is relatively low and the real part of the dynamic surface elasticity is relatively high (about 60 mN/m for poly(*N*-isopropylacrylamide) and about 7 mN/m for poly(vinylpyrrolidone)).[13,14,36] Further adsorption leads to the formation of loops and tails protruding into the bulk phase (the distal layer). The relaxation of surface stresses can proceed at the expense of segment exchange between the proximal and distal regions, and the surface elasticity decreases to lower values of about 1 or 2 mN/m in accordance with the theory.[37] The relaxation time depends on the molecular mass and for short chains is comparable with the period of capillary waves (~0.1 s).[13] This mechanism cannot be applied to polyelectolyte solutions without salt where the adsorbed film is mainly a monolayer, and one can neglect any deviations from a flat polymer conformation like loops and tails. In the case of PSS solutions the segment concentration in the surface layer is determined by a balance between the attraction to the surface of strongly hydrophobic styrene

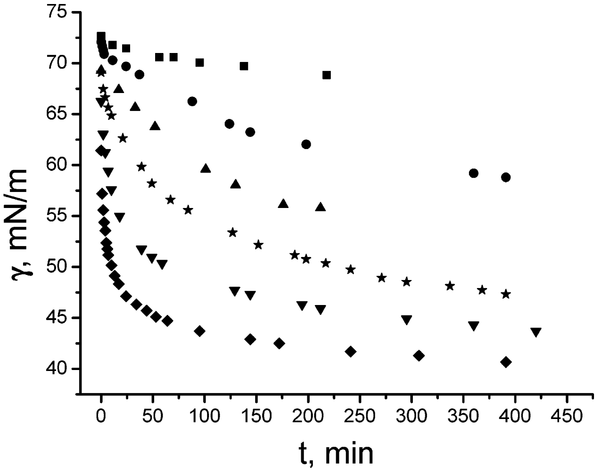

Figure 8. Kinetic dependencies of the surface tension of PSS solutions in 1 M NaCl at the polymer concentrations 0.001 wt % (squares), 0.02 wt % (circles), 0.05 wt % (triangles up), 0.11 wt % (asterisks), 0.51 wt % (triangles down), and 2 wt % (rombs).

groups and the mutual repulsion of the ionized sulfonate groups. The second contribution depends on the ionic strength, which is the main reason for the adsorption increase at the increase of polyelectrolyte concentration. One can assume that the dynamic surface elasticity of PSS solutions is mainly determined by the lateral electrostatic repulsion of the charged groups in the monolayer and thus also have to increase with concentration. At high concentrations the monolayer structure is relatively stable, thus leading to the almost constant real part of the surface elasticity of about 73 mN/m. The static surface elasticity of any solution must be zero. However, the relaxation of surface stresses proceeding at the expense of the formation of long loops and tails or the whole chain desorption is too slow in comparison with the oscillation periods in this work. This results in an effective elastic behavior of the adsorbed PSS film at the frequencies under investigation. Indeed, we observed no changes of the real part of the surface elasticity and zero imaginary part down to a frequency of 0.01 Hz.

The addition of salt to polyelectrolyte solutions leads to a screening of the Coulomb interactions. The SCF theory predicts adsorption increase at the increase of the salt concentration and gradual formation of the distal layer consisting of loops and tails.[15−17] The results on the neutron reflectivity of PSS solutions confirm these qualitative conclusions.[6] At high salt concentrations the surface layer structure has to approach that of neutral polymers, and one can assume that the surface viscoelastic behavior will be approximately the same. Simultaneously, the increase of the salt concentration has to decrease the electrostatic adsorption barrier. Calculations of Cohen-Stuart et al. according to the SCF and Kramers rate theories under the assumption of only electrostatic interactions between polymer segments and using the numerical procedure proposed by Scheutjens and Fleer[17] predict an adsorption rate increase by several orders of magnitude at high salt content.[41] However, to the best of our knowledge the latter conclusions have not been compared so far with experimental results for the liquid−gas interface.

Figure 8 shows the kinetic dependencies of the surface tension of PSS solutions in 1 M NaCl. The corresponding dependencies at $c = 0.1$ wt % and different salt concentrations are shown in Figure 9. The addition of salt leads to lower surface tension, and the earlier beginning of the surface tension decreases with concentration (lower c^* value) according to the conclusions of the SCF theory. However, one can observe a significant increase of the adsorption rate only during the first adsorption stage (for less than an hour) where the electrostatic adsorption barrier seems to be important. At longer times the rate of surface tension decrease is comparable with that for solutions without salt (Figure 1). This contradicts the conclusions of the work[41] and indicates that the electrostatic barrier is not the only reason for the slow PSS adsorption. The same conclusions also follow from measurements of the length and damping coefficient of capillary waves. Note also that the rate of surface tension change strongly increases with the increase in polyelectrolyte and salt concentrations. This may be the reason why Yim et al. did not observe surface tension changes a few minutes after creating the interface.[7]

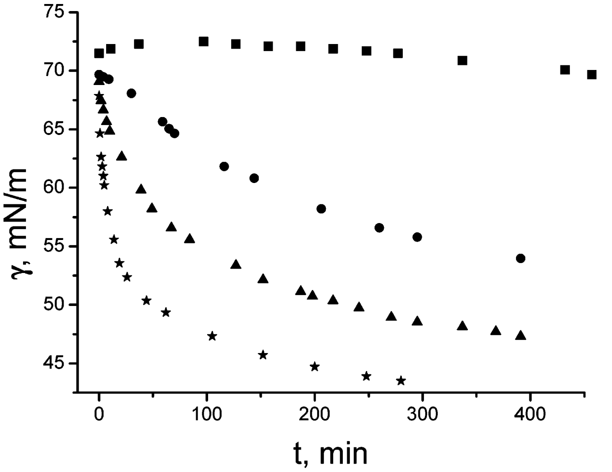

Figure 9. Kinetic dependencies of the surface tension of 0.1 wt % PSS solutions at the NaCl concentrations 0 (squares), 0.1 M (circles), 1 M (triangles), and 3 M (asterisks).

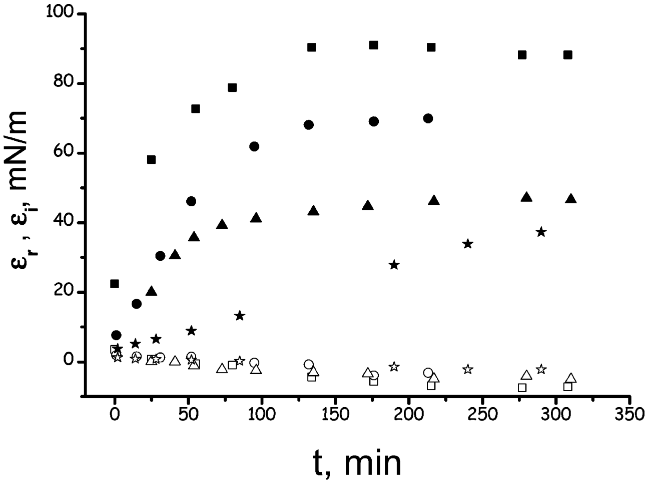

Figure 10. Kinetic dependencies of the real (solid symbols) and imaginary (empty symbol) parts of the dynamic surface elasticity of PSS solutions in 1 M NaCl at the frequency 0.12 Hz and polymer concentrations 0.005 wt % (asterisks), 0.01 wt % (triangles), 0.05 wt % (circles), and 0.11 wt % (squares).

Figure 10 shows the kinetic dependencies of the dynamic surface elasticity of PSS solutions in 1 M NaCl at a frequency of 0.12 Hz. Note that the reproducibility of the results is significantly better even at $c < 0.1$ wt

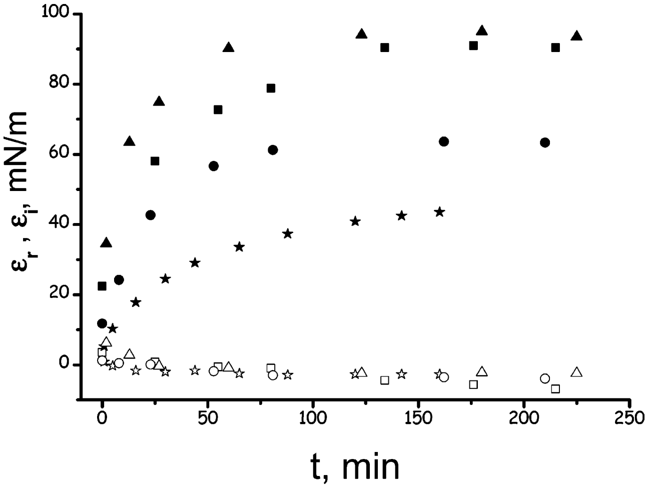

Figure 11. Kinetic dependencies of the real (solid symbols) and imaginary (empty symbol) parts of the dynamic surface elasticity of PSS solutions at the frequency 0.12 Hz and NaCl concentrations 0 (asterisks), 0.1 M (circles), 1 M (squares), and 3 M (triangles).

% than for solutions without salt. The rate of the surface elasticity increase in comparison with the system without salt changes again only at the first period of adsorption. The imaginary part of the surface elasticity is close to zero. At $c > 0.1$ wt % the real part of the surface elasticity reaches an almost constant value of about 85 mN/m, which practically does not change at further increase of the PSS concentration. This plateau value is only slightly higher than that for solutions without salt. The increase of the salt concentration leads mainly to the gradual increase of the real part of the dynamic surface elasticity (Figure 11). Unlike the expectations, the surface elasticity does not decrease with the increase of salt concentration. We did not observe any indication of loop and tail formation, which could lead to a surface stress relaxation. The adsorbed film is elastic, and the whole viscoelastic behavior is similar to the case without salt and again is different from that of nonionic polymer films.[13,14,36]

One can assume that it is the proximal region of the surface layer that mainly determines the measured dynamic surface elasticity. The increase of the polymer and salt concentrations in a broad range leads only to gradual structural changes in this region and, consequently, to a moderate increase of the surface elasticity. For example, the strong changes of the adsorption and the surface layer thickness observed by neutron reflectivity upon addition of salt at a PSS concentration of about 0.1 wt %[6] are accompanied only by an approximately 2-fold increase of the surface elasticity (Figure 11). At higher PSS concentrations the observed effect is even smaller (Figure 10). The rise of adsorption at increasing ionic strength can be mainly connected with the formation of the distal region of the surface layer. At the same time, unlike the case of nonionic polymer solutions,[13,14] the latter region almost does not contribute to the relaxation of surface stresses. This can be possible if the tails and loops are not dangling freely into the water but develop interactions between each other and are included into a more or less rigid structure with mechanical relaxation times exceeding the period of oscillations. In other words, PSS forms aggregates or structured microdomains in the surface layer. Theodoly et al. also assumed strong interaction between neighboring chains in the surface layer in order to explain the properties of spread PSS films, for example, the nonspecular scattering of X-rays.[8] On the other hand, neutron reflectivity studies are unable to determine the two-dimensional microheterogeneity of the surface layer and give only an averaged segment profile. This can be also a reason for the discrepancy between the experimentally determined segment profile and the results of calculations according to the SCF theory of polyelectrolyte adsorption, which does not assume strong attraction between the chains.[6,8]

Another argument in favor of the microheterogeneity of adsorbed PSS films stems from the extremely slow surface tension relaxation even at high salt content. This also contradicts the SCF calculations[41] and can be connected with the strong cohesion between the chains. The slow relaxation is characteristic for heterogeneous surface films, and some authors consider it as an indirect evidence of surface aggregation.[8,48] The slow polymer adsorption can be also connected with a quasi-brush formation when the polymer coils have to be stretched so that the hydrophobic moieties contact the air phase (to overcome the steric barrier).[11,49] However, this adsorption mechanism seems to be improbable for PSS solutions because neutron reflectivity does not indicate a quasi-brush formation, especially for systems without salt.[6,7]

The nature of the attraction forces between PSS chains in aqueous solutions is still an open question. The styrene groups are highly hydrophobic, which leads to a compact conformation of partially sulfonated polystyrene chains in the bulk phase[50] while entirely sulfonated chains, as in this work, are extended. The significant decrease of the dielectric constant in the surface layer can lead to enhanced Coulomb interactions and to stronger counterion condensation and, consequently, to lower effective charge.[7] In its turn this can lead to stronger inter- and intrachain hydrophobic attraction. On the other hand, the forces leading to microdomain formation in the bulk phase, which are not fully understood yet,[44−47] can be also responsible for surface aggregation.

Summary

We have investigated the dynamic surface properties of PSS solutions and compared them with recent data for solutions of nonionic polymers.[13,14,35,36] Unlike the latter systems, the dynamic surface tension of PSS solutions at concentrations up to 1.5 wt % did not reach equilibrium value for more than 1 day. The dynamic surface elasticity changed faster and exceeded the corresponding values for solutions of nonionic polymers studied so far. The imaginary part of the dynamic surface elasticity was close to zero in the frequency range under investigation, and the surface films were elastic. The addition of salt to the PSS solutions accelerated only the first stage of the adsoption process in contradiction with the calculations according to the SCF and Kramers rate theories under the assumption of only electrostatic interactions between the segments.[41] Another salt effect consisted in a moderate increase of the real part of the dynamic surface elasticity. This result also does not agree with the predictions of the SCF theory. Calculations according to the theory indicate the formation of loops and tails freely dangling into the bulk phase when salt addition screens electrostatic interactions.[15−17] The corresponding chain conformation is close to the case of nonionic polymers and characterized by a low dynamic surface elasticity.[13,14] The obtained experimental results can be explained if one assumes that the dynamic surface elasticity is determined mainly by lateral electrostatic interactions between the ionized sulfonate groups in the proximal region and the chain motion in the surface layer is restricted by the formation of aggregates. The strong cohesion between the chains in the distal region of the surface layer is probable if one takes into account the microdomain formation in polyelectrolyte solutions[44−47] or the increase of hydrophobic interactions at the enhanced counterion condensation close to the surface.[7]

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References and Notes

(1) *Proteins at Liquid Interfaces*; Möbius, D., Miller, R., Eds.; Studies in Interface Science Vol. 7; Elsevier: Amsterdam, 1999.
(2) Food Colloids. Fundamentals of Formulation; Dickinson, E., Miller, R., Eds.; Royal Society of Chemistry: Cambridge, 2001.
(3) Katchalsky, A.; Miller I. R. *J. Phys. Colloid Chem.* **1951**, *55*, 1182.
(4) Okubo, T. *J. Colloid Interface Sci.* **1988**, *125*, 386.
(5) Caminati, G.; Gabrielli, G. *Colloids Surf. A* **1993**, *70*, 1.
(6) Yim, H.; Kent, M. S.; Mathewson, A.; Ivkov, R.; Satija, S.; Majewski, J.; Smith, G. S. *Macromolecules* **2000**, *33*, 6126.
(7) Yim, H.; Kent, M. S.; Mathewson, A.; Stevens, M. J.; Ivkov, R.; Majewski, J.; Smith, G. S. *Macromolecules* **2002**, *35*, 9737.
(8) Theodoly, O.; Ober, R.; Williams, C. E. *Eur. Phys. J. E* **2001**, *5*, 51.
(9) Taylor, D. J. F.; Thomas, R. K.; Penfold, J. *Langmuir* **2002**, *18*, 4748.
(10) Okubo, T.; Kobayashi, K. *J. Colloid Interface Sci.* **1998**, *205*, 433.
(11) Millet, F.; Perrin, P.; Merlange, M.; Benattar, J.-J. *Langmuir* **2002**, *18*, 8824.
(12) Milling, A. J.; Richards, R. W.; Baines, F. L.; Armes, S. P.; Billingham, N. C. *Macromolecules* **2001**, *34*, 4173.
(13) Noskov, B. A.; Akentiev, A. V.; Loglio, G.; Miller, R. *J. Phys. Chem. B* **2000**, *104*, 7923.
(14) Noskov, B. A.; Akentiev, A. V.; Bilibin, A. Yu.; Zorin, I. M.; Miller, R. *Adv. Colloid Interface Sci.* **2003**, *104*, 245.
(15) Papenhuijzen, J.; Van der Schee, H. A.; Fleer G. J. *J. Colloid Interface Sci.* **1985**, *104*, 540.
(16) Bohmer, M. R.; Evers, O. A.; Scheutjens, J. M. H. M. *Macromolecules* **1990**, *23*, 2288.
(17) Fleer, G. J.; Cohen-Stuart, M. A.; Scheutjens, J. M. H. M.; Cosgrove, T.; Vincent, B. *Polymers at Interfaces;* Chapman & Hall: London, 1993.
(18) Fleer, G. J. *Ber. Bunsen-Ges. Phys. Chem.* **1996**, *100*, 936.
(19) Raviv, U.; Klein, J.; Witten, T. A. *Eur. Phys. J. E* **2002**, *9*, 405.
(20) Johner, A.; Semenov, A. N. *Eur. Phys. J. E* **2002**, *9*, 413.
(21) Sommer, J.-U. *Eur. Phys. J. E* **2002**, *9*, 417.
(22) Granick, S. *Eur. Phys. J. E* **2002**, *9*, 421.
(23) Dukhin, S. S.; Kretzschmar, G.; Miller, R. In *Dynamics of Adsorption at Liquid Interfaces*; Möbius, D., Miller, R., Eds.; Studies in Interface Science Vol. 1; Elsevier: Amsterdam, 1995.
(24) Noskov, B. A. *Adv. Colloid Interface Sci.* **1996**, *69*, 63.
(25) Noskov, B. A. *Adv. Colloid Interface Sci.* **2002**, *95*, 237.
(26) Noskov, B. A.; Loglio, G. *Colloids Surf. A* **1998**, *143*, 167.
(27) Goodrich, F. C. *J. Phys. Chem.* **1962**, *66*, 1858.
(28) Lucassen, J.; Hansen, R. S. *J. Colloid Interface Sci.* **1967**, *23*, 319.
(29) Langevin, D. *Curr. Opin. Colloid Interface Sci.* **1998**, *3*, 600.
(30) Langevin, D. *Adv. Colloid Interface Sci.* **2000**, *88*, 209.
(31) Wilde, P. J. *Curr. Opin. Colloid Interface Sci.* **2000**, *5*, 176.
(32) Bos, M. A.; van Vliet, T. *Adv. Colloid Interface Sci.* **2001**, *91*, 437.
(33) Gau, C.-S.; Yu, H.; Zografi, G. *J. Colloid Interface Sci.* **1994**, *162*, 214.
(34) Jiang, Q.; Chew, Y. C. *Colloids Surf. B* **2001**, *20*, 303.
(35) Noskov, B. A.; Akentiev, A. V.; Loglio, G.; Miller, R. *Mendeleev Commun.* **1998**, *N2*, 190.
(36) Noskov, B. A.; Akentiev, A. V.; Miller, R. *J. Colloid Interface Sci.* **2002**, *255*, 417.
(37) Noskov, B. A. *Colloid Polym. Sci.* **1995**, *273*, 263.
(38) Bhattacharya, A.; Monroy, F.; Langevin, D.; Argiller, J. *Langmuir* **2000**, *16*, 8727.
(39) Noskov, B. A.; Grigoriev, D. O. *Langmuir* **1996**, *12*, 3399.
(40) Akentiev, A. V.; Noskov, B. A. *Colloid J.* **2002**, *64*, 129.
(41) Cohen-Stuart, M. A.; Hoogendam, C. W.; de Keizer, A. *J. Phys.: Condens. Matter* **1997**, *9*, 7767.
(42) Ahrens, H.; Baltes, H.; Schmitt, J.; Möhwald, H.; Helm, Ch. A. *Macromolecules* **2001**, *34*, 4504.
(43) Earnshaw, J. C.; McCoo, E. *Langmuir* **1995**, *11*, 1087.
(44) Lin, S. C.; Lee, W. I.; Schurr, J. M. *Biopolymers* **1978**, *17*, 1041.
(45) Förster, S.; Schmidt, M.; Antonietti, M. *Polymer* **1990**, *31*, 781.
(46) Matsuoka, H.; Schwahn, D.; Ise, N. *Macromolecules* **1991**, *24*, 4227.
(47) Sedlák, M. *J. Chem. Phys.* **2002**, *116*, 5236, 5246, 5256.
(48) Vollhardt, D. *Adv. Colloid Interface Sci.* **1993**, *47*, 1.
(49) Johner, A.; Leibler, L. *J. Phys. (Paris)* **1990**, *23*, 5299.
(50) Essafi, W.; Lafuma, F.; Williams, C. E. *J. Phys. II* **1995**, *5*, 1269.

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