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Aqueous Micellar Solutions of Hydrophobically Modified Polyelectrolytes

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ABSTRACT: Aqueous micellar solutions of ionic/neutral block copolymers have been studied by static light scattering, photon correlation spectroscopy, small-angle neutron scattering, and surface tension measurements. The polymers used have short poly(*tert*-butylstyrene) (PtBS) neutral segments and long sodium poly(styrenesulfonate) (NaPSS) segments. The scattering studies that were performed are all compatible with the existence of spherical micelles, with highly extended NaPSS coronas, at low salt concentrations (10^{-4} M). Aggregation numbers of 30−40 were found. As the salt (NaCl) concentration is increased, the micelles decrease in size, although the salt dependence is weaker than that predicted by existing theories. The aggregation number does not appear to depend on NaCl concentration over the range of 10^{-4}−10^{-2} M, but decreases to values of 15−20 at high salt (0.1−0.5 M). The addition of NaPSS/PtBS to water decreases the surface tension above a threshold concentration of around 10^{-3} g/mL.

Introduction

Micelles are formed when block copolymers are dispersed in selective solvents, i.e., solvents that will dissolve one block but not the other. These micelles are generally "starlike", with the insoluble component forming a dense core. The soluble blocks are tethered to this core, forming a diffuse corona. The underlying physics of polymer micelles is closely related to the physics governing the formation of polymer brushes by the adsorption of block copolymers on solid surfaces from selective solvents.[1] In both cases, the reduction in enthalpy due to the creation of the interfacial structure balances the loss of entropy by the constrained chains.

A great number of studies on micelle formation by neutral block copolymers have appeared and been reviewed.[2,3] In contrast, relatively fewer detailed studies on micelle formation by charged/neutral block copolymers have been reported.[4−18] Block copolymers with a highly charged polyelectrolyte block are the polymeric analogues of typical low molecular weight surfactants. These systems have considerable potential for use in stabilizing colloidal suspensions, such as those encountered in paints, pharmaceuticals, cosmetics, etc.,[19] and in particular they can bring the advantages of block copolymer stabilizers to bear in aqueous media. Despite recent theoretical[11,14,16] and experimental studies[4,5,7−10,12,15,17,18] on aqueous solutions of micelles of neutral/ionic diblocks, much of their behavior is still not understood. Indeed, the behavior of charged homopolymers (polyelectrolytes) in aqueous solution is still a matter of intense investigation.[20−23]

The present work differs from previous efforts to examine the association behavior of hydrophobically modified polyelectrolytes in at least two respects. In our case, the polyelectrolyte block is always fully charged, both in the sense of having nearly every monomer bearing a charge and in the fact that none of the charged monomers are neutralized with pH. Second, we have avoided the use of mixed solvents by choosing block copolymers that dissolve in pure water.

In this paper, we report the results of neutron and light scattering measurements on aqueous solutions of sodium poly(styrenesulfonate)/poly(*tert*-butylstyrene) (NaPSS/PtBS) diblock copolymers. These diblocks have a fully ionized segment (NaPSS) and a hydrophobic segment (PtBS) and, thus, resemble surfactant molecules where the polar head is replaced by an ionized chain. These polymers might be expected to show behavior intermediate to that of small-molecule, ionic surfactants and polymers. Rheological,[5] adsorption,[24] and surface forces measurements[25] have been previously reported for aqueous solutions of NaPSS/PtBS diblocks. The presence of "aggregated species" was noted in each investigation.[5,24,25] In the present work, we confirm the existence of micelles in aqueous solutions. The structure, shape, and interactions of these micelles are reported and compared with prior work on related systems. Special care has been taken in the zero added salt case where, for the homopolymer NaPSS, features such as the so-called "slow mode" in dynamic light scattering, the origins of which are unclear but which may resemble in some ways the diffusion of aggregated species, are observed. To determine whether there is a difference between our block copolymers and the NaPSS homopolymer, comparative experiments have been carried out. Surfactant properties of NaPSS/PtBS diblocks are discussed. Finally, some recommendations for future work are made.

Experimental Section

Materials. The synthesis and characterization of NaPSS/PtBS diblock copolymers were previously reported.[25] The synthesis involved sulfonation of the polystyrene (PS) components of PS/PtBS diblocks made by anionic polymerization. The resulting poly(styrenesulfonic acid) blocks were neutralized by using sodium methoxide, and percent sulfonation was determined by elemental analysis for sulfur content. Molecular characteristics of the NaPSS/PtBS diblocks are summarized in Table 1. For comparison we also used a NaPSS sample from Polysciences with molecular weight (94 600) similar to that of the MT-2 diblock.

The water used was purified by distillation, deionization, and reverse osmosis (Water Prodigy). Sodium chloride was obtained from Baker Inc. and used as received. Polymer stock solutions were prepared at various concentrations by dissolving polymer into water that had been filtered through 0.02

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μm pore size filters. Solutions were allowed to equilibrate for 1 week prior to measurements. Concentrations suitable for scattering experiments were prepared by serial dilution with filtered water or filtered salt solutions. Polymer solutions were filtered through 0.2 or 0.45 μm pore size filters (Nucleopore) directly into the scattering cells.

Scattering Experiments. Light scattering experiments were performed by using a goniometer from Malvern Instruments. An argon ion laser at a wavelength (λ) of 488 nm was used. The alignment of this instrument was confirmed by measuring scattering intensity (I) as a function of angle (θ) for the dust-free vat fluid (toluene). The product $I \sin \theta$ was observed to be independent of θ over the range 30−140°, confirming proper alignment. Photon correlation spectroscopy (PCS) measurements employed a Brookhaven Instrument Company correlator with 256 channels and a multiple sample time feature (homodyne mode). Results were analyzed on separate computers by nonlinear regularized inverse Laplace transformation techniques (CONTIN[26] or MEXDLS,[27] see text).

Static (time-average intensity) light scattering (SLS) measurements were calibrated on the basis of the known scattering characteristics of toluene. The specific refractive index increments (dn/dc) were measured using an Otsuka double-beam differential refractometer.

Small-angle neutron scattering (SANS) experiments were performed at the Cold Neutron Research Facility at the National Institute of Standards and Technology. An incident wavelength of 5.5 Å ($\Delta\lambda/\lambda = 0.14$) and a sample to detector distance of 14.3 m were employed to probe solutions of NaPSS/PtBS in deuterium oxide.

Surface Tension Measurements. Surface tension measurements were made by the Wilhelmy method[28] using a paper filter plate. Prior to each run, which was always repeated 2−3 times over several days, the surface tension of pure water was measured. After each run with polymer solution, the surface tension of pure water was measured using the same plate to determine whether polymer had absorbed on the plate. The surface tension was always within 1% of that expected for pure water, indicating that negligible adsorption had occurred.

Results

Shape and Size of the Micelles in Water. Direct evidence for micelle formation may be obtained from measurements of size and mass, by comparison with values obtained for the corresponding unimer. Additional evidence concerning micellar structures may be obtained from other methods, including size exclusion chromatography, viscometry, ultracentrifugation, and various fluorescence techniques.[29] Furthermore, for the samples of this work, which have very short hydrophobic PtBS segments and long NaPSS segments, insight into micellar structure may also be gained by comparison with the solution behavior of NaPSS homopolymer. The homopolymer will normally be in its unimeric form in solution (barring the addition of high salt concentrations, etc.), and a great deal of data is available on NaPSS in solution.[23,30−35]

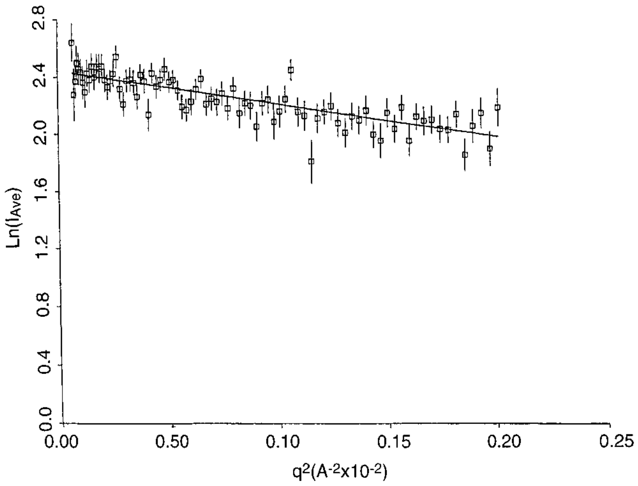

Figure 1. Guinier plot of the SANS data in the q range of the core of the micelles. The solid line is the best linear fit, giving $R_c = 2.64$ nm.

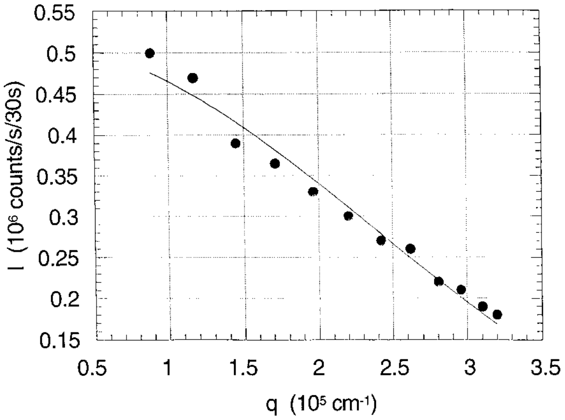

Figure 2. Total scattered light intensity versus the wavevector q for a sample of polymer concentration 2.5×10^{-5} g/mL in pure water. The solid line is the best fit to the form factor of a sphere, giving $R_g = 70$ nm.

SANS experiments were conducted on sample MT-2 in D_2O. A Guinier plot of the natural logarithm of the average excess scattering intensity ($\ln I$) versus q^2, where q is the momentum transfer, is shown in Figure 1. These data indicate a radius of gyration of the core (R_c) of 2.64 ± 0.1 nm. We interpret this value to be the radius of the core of a micelle, which is a "melt" of PtBS segments in collapsed conformations. This interpretation is made possible because the relevant q range to determine R_c ($qR_c \sim 1$) does not overlap the q range where the form factor of the arms and the structure factor between micelles are dominant ($qL \sim 1$, where L is the extension of the corona of a micelle). For R_c, by knowing the density of PtBS homopolymer, we can calculate the aggregation number, P, which is found to be on the order of 30. Light scattering results show that the total radius of a micelle is around 80 nm (see the following). In contrast, SANS experiments on molecular solutions of NaPSS homopolymers in water required isotopic labeling to measure the R_g of individual chains.[32] In contrast, several groups[34] have shown that NaPSS solutions of this precise molecular weight at this precise concentration exhibit a visible correlation peak in this q range. Such a peak is clearly missing from our spectrum. We have also simulated the form factor of a micelle constructed from a hard core and a shell of symmetrically arranged rods (using the measured values of R_c and L).[36] The result is in good agreement with Figure 1 and even predicts a large increase in I in the low q regime, which was observed experimentally but is not shown in Figure 1.

Light scattering experiments provide additional evidence of micelle formation. SLS measurements on dilute solutions provide the form factor and the radius of gyration of the micelles in the solution. A typical SLS result obtained for sample MT-2 in water is presented in Figure 2, where the solid curve is the best fit to the form factor of a sphere. These results provide strong evidence for the presence of spherical objects having R_g values of about 70 nm. A more definitive analysis of the particle shape would require measurements over a broader range of q and would take into account polydispersity and the inhomogeneous refractive indices of the micelles. All of the scattering plots (Guinier, Zimm, or Kratky plots) are sensitive to polydispersity.[37] For

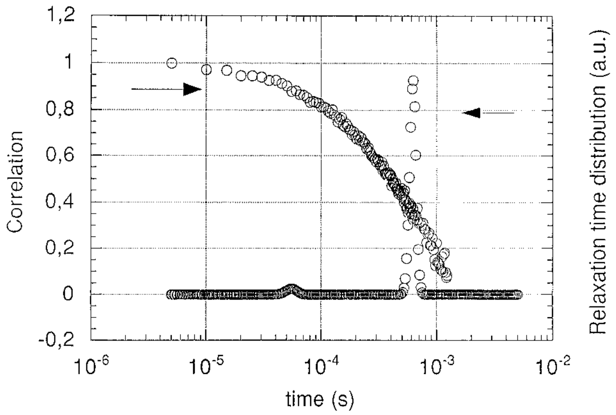

Figure 3. Typical correlation function plotted versus time and its inversion by the MEXDLS method, which provides the distribution of the relaxation times of the system.

hard spherical objects, Guinier plots exhibit linearity over a larger range of q than do Zimm plots. More precisely, for hard spheres Guinier plots should be linear up to $qR_g = 1.4$, which we observe. Recently, Gao and Eisenberg[16] found that, even for block copolymers with polydispersity indices as low as 1.03 (the value measured for MT-2), the molecular weight distribution of the diblock has a profound effect on its micellization behavior. Furthermore, they showed that micelles formed from such diblocks would also be polydisperse.

Comparison of our results in Figure 2 with those obtained on NaPSS of 780 000 molecular weight in water by Drifford and Dalbiez[31] is revealing. The polymer concentration used in each experiment was 2.5×10^{-5} g/mL. Drifford and Dalbiez[31] observed a strong peak in the plot of I versus q (centered around $q = 2.3$). We observe no such peak. This suggests that the micelle aggregates are not as highly charged as comparably sized linear chains. This is due to the fact that each micelle is neutralized by a "sea" of counterions trapped within the corona, indicating that the loss of entropy experienced by these ions is compensated by the gain in Coulomb energy. In addition, our results show that, at the same concentration, NaPSS solutions scatter much less than MT-2 solutions (typically an order of magnitude when studying the less concentrated samples). This tends to confirm that MT-2 solutions are composed of larger and more weakly repulsive objects.

The PCS signals that we observed for MT-2 in water could not be fit by a single exponential, i.e., the ratio of the second cumulant over the square of the first cumulant is always larger than 5×10^{-2}. We therefore utilized special inverse Laplace transform routines (CONTIN[26] and MEXDLS[27]) in data interpretation. A representative distribution of the correlation times is shown in Figure 3. This plot shows the existence of a slow mode that we interpret as being due to translational diffusion of the micelles. A weak dependence of the apparent diffusion coefficient, D, on q^2 was observed, and the limiting value of D was obtained by extrapolating to infinitely small q. R_H was evaluated by use of the Stokes–Einstein equation:

$$R_H = \frac{kT}{6\pi\eta_o D}$$

where k is Boltzmann's constant, T is absolute temperature, and η_o is the solvent viscosity. A value for R_H of 80 nm was obtained, which is in good agreement with the R_g value of 67 nm determined from SLS. For spheres, theory[38] gives $R_g/R_H = 0.775$. Thus, the value $R_g/R_H = 0.84$ computed from our light scattering provides additional support for the existence of spherical or near-spherical micelles. From the N value of the PS segment (Table 1), we calculate a contour length for the NaPSS segment of ca. 100 nm (assuming tetrahedral bond angles in the backbone). This indicates that the radius of the micelle approaches that of an extended chain in the absence of added salt.

It must be noted that PCS experiments on NaPSS homopolymers in low salt[35] also show a slow mode that is nondiffusive, varies with the polymer concentration,[31] and disappears upon the addition of electrolyte. We reconfirmed this on our sample of NaPSS (see the following). In contrast, our data show that the mode attributed to the diffusion of micelles is fairly insensitive to the polymer concentration and varies only gradually when electrolyte is added, without disappearing (see the following).

In principle, PCS data should also provide information on polydispersity. In practice, with micellar solutions of polyelectrolytes such an analysis is not prudent. The positions of the slow modes obtained by CONTIN and MEXDLS are in agreement, but a systematically larger value of D (less than 10%) was obtained from CONTIN. Thus, we employed average values of D in evaluating R_H. These analysis methods (see refs 26 and 27 for details) must be considered approximate for the analysis of such a complex polymer system. Furthermore, the PCS results systematically indicate the existence of a small fast mode, which could be responsible for the high values of the cumulant ratios. Qin and coworkers[17] recently investigated the polydispersity of micelles composed of polystyrene/poly(methacrylic acid) diblocks in dioxane/water mixtures. They concluded that the micelles were polydisperse on the basis of sedimentation velocity experiments and combined measurements of R_g and the hydrodynamic radius R_H.

Effect of Added Salt. Values of R_H and R_g for MT-2 in aqueous NaCl solution are plotted in Figure 4. Conductivity measurements made on our solutions showed that without added electrolyte a residual concentration of 10^{-4} M in salt can be detected. This leads us to assign this value to all measurements made where no salt was added. As salt concentration, S, is increased, a decrease in the size of the micelles is noted. This effect is due, at least in part, to electrostatic screening of the charges in the NaPSS corona of the micelle. At 0.5 M NaCl, an R_H of only 26 nm is measured. It is interesting to note that the dependence of size on salt concentration depicted in Figure 4 is weaker than expected from theoretical models for polyelectrolyte brushes and micelles with polyelectrolyte coronas.[14,39–42] On the other hand, the dependence of R_H and R_g on S is similar to the variation in interaction range with S observed experimentally for adsorbed NaPSS/PtBS brushes.[25]

The variation in the ratio R_g/R_H with S is also shown in Figure 4. At 10^{-4} M NaCl, $R_g/R_H = 0.84$ is measured; this result, as noted earlier, suggests the presence of spherical particles. As S is increased, R_g becomes larger than R_H, with values of $R_g/R_H \cong 1.45$ at 0.3 and 0.5 M NaCl. Also, as S is increased above 10^{-2} M, there is a decrease in the degree of aggregation, with P values (determined by SLS) ranging from around 40 at low salt (10^{-4} and 10^{-2} M) to a value of 15 at 0.5 M NaCl (Figure 5). Thus, the larger R_g/R_H values at higher S may be due to the smaller P values. Furthermore, the larger R_g/R_H values at high salt may reflect the increase in flexibility of the polyelectrolyte coronas due to the addition of salt. We do not believe that the increasing

Table 1. Molecular Characteristics of NaPSS/PtBS Copolymers

sample	N(NaPSS)[a]	M_w(NaPSS)	N(PtBS)	M_w(PtBS)	M_w/M_n[b]	% sulfonation[c]
MT-2	4.13	83,000	26	4,200	1.03	89
MT-6	612	126,000	15	2,400	1.04	84

[a] N = weight-average degree of polymerization. [b] M_w/M_n = polydispersity ratio. [c] Based on sulfur content analysis.

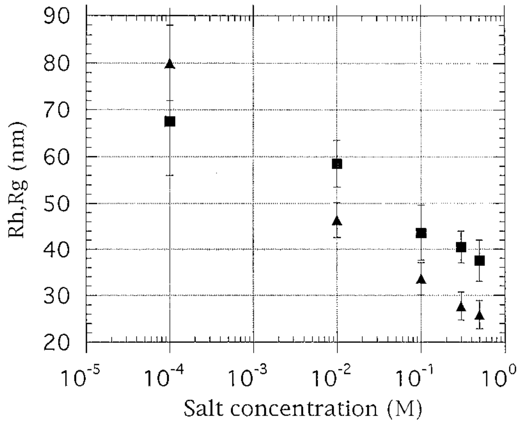

Figure 4. Plots of R_H (▲) and R_g (■) as a function of NaCl concentration.

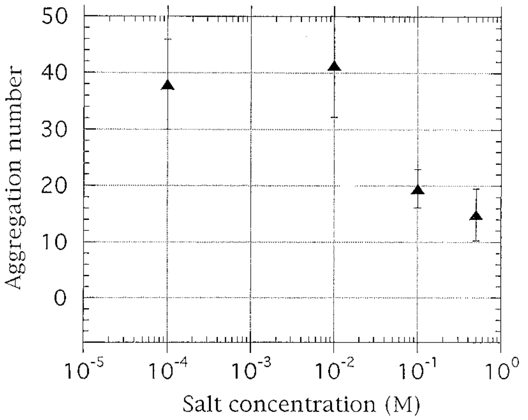

Figure 5. Aggregation number as a function of salt concentration (determined by SLS).

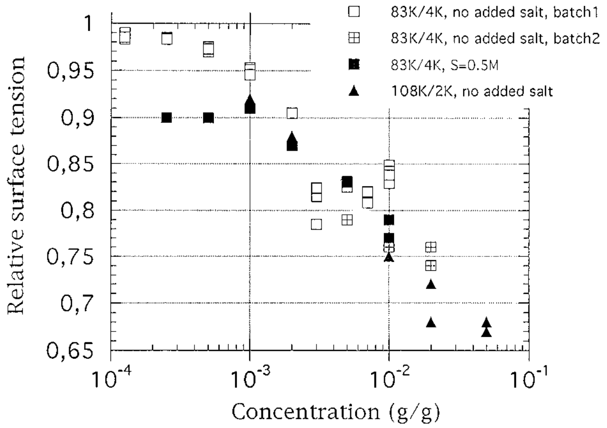

Figure 6. Surface tension of solutions of polymer divided by surface tension of pure water for MT-2 in pure water, MT-6 in pure water, and MT-2 at 0.5 M NaCl.

R_g/R_H values with increasing S indicate any dramatic changes in shape of the micelles because I versus q plots suggest spherical shapes over the entire range of S investigated.

Finally, we noted that the slow mode observed via PCS in the low-salt limit is the same as that observed in the high-salt range. In other words, a continuous change in size, with no apparent discontinuities, is noted in the R_H data of Figure 4. We again directly confirmed that, upon the addition of salt (0.1 M), the slow mode shown by a NaPSS solution changes abruptly by more than 1 order of magnitude, in contrast to the gradual evolution of the MT-2 signals upon salt addition. This fortifies the interpretation (in the previous section) that the slow mode data correspond to translational diffusion of the micelles.

Air/Water Interfacial Properties. We have investigated how the surface tension of aqueous solutions of NaPSS/PtBS in contact with air varies with polymer concentration and with S. The results of surface tension measurements on solutions of MT-2 and MT-6 are summarized in Figure 6. The results show that, in a range of polymer concentrations where micelles are always observed by light scattering (10^{-4}–10^{-3} g/mL), no substantial reduction in surface tension is noted. This reduction is only observed when the polymer concentration is higher than 10^{-3} g/mL; this is some 3 orders of magnitude above the CMC.[42] Very similar behavior was observed for solutions of MT-2 and MT-6 despite their different architectures (Table 1). As a control experiment, we examined solutions of NaPSS homopolymer and found no reduction in surface tension at any concentration. The behavior of the diblocks is quite different from the behavior generally observed for solutions of low molecular surfactants, where surface tension is reduced for any concentration lower than the CMC and then saturates.

Added salt has little effect on surface tension at polymer concentrations greater than 10^{-3} g/mL. At lower polymer concentrations, some reduction in surface tension is caused by the addition of NaCl. The effect of the salt is probably to enhance the adsorption of the polymer onto the surface. In the absence of salt, the chains prefer to stay suspended in the aqueous medium.[24,25]

Discussion and Conclusions

We have presented results of light scattering and neutron scattering experiments on aqueous solutions of NaPSS/PtBS diblock copolymers. At the polymer concentrations investigated in this work (2.5×10^{-5} to 2×10^{-3} g/mL), the polymers form micelles composed of collapsed PtBS cores with NaPSS coronas. In pure water, the micelles behave as hard spheres, and the NaPSS chains are almost fully extended. As NaCl is added to the solution, the micelles become smaller due to electrostatic screening effects. The dependence of micellar size on salt concentration is weaker than predicted by theory,[14,39–41] but is similar to the behavior observed for brushes of NaPSS/PtBS adsorbed on mica.[25] In fact, an even weaker dependence of R_H on S was noted previously[43] for solutions of star-branched KPSS in KCl at varying ionic strengths. The greater decrease in size with increasing S for the current micellar materials reflects both electrostatic screening effects and decreased extent of aggregation, i.e., reduced molecular weight.

In a recent paper, Marko and Rabin[11] suggested that association is very unlikely for charged/neutral diblocks in a solvent that is selective for the charged block, unless the length of the neutral block is long relative to that of the charged block. Our experiments clearly do not agree with this theory since for our MT-2 sample the charged block is about 15 times as long as the neutral block. The driving force for micelle formation is certainly due to the strongly hydrophobic character of the PtBS block, but interactions between the NaPSS chains may also play a role. The NaPSS backbone is inherently hydrophobic and is only soluble because it is charged. This means that the association of chains, particularly if they are neutralized by a condensed sea of counterions, could lead to a lower energy state due to favorable backbone–backbone interactions. Ross and Pincus[44] have invoked such arguments in predicting collapsed metastable states for grafted polyelectrolyte brushes, and experimental data indicate the possible existence of such an effect in NaPSS/PtBS brushes.[25] It therefore would be interesting to study micelles of neutral/charged diblocks, where the polyelectrolyte backbone is inherently more hydrophilic. This should be unfavorable for aggregation. In this regard, it should be noted that Astafieva and co-workers[15] recently measured CMCs for aqueous solutions of diblock polyelectrolytes of polystyrene/sodium polyacrylate, where the polystyrene segments were kept short relative to the charged segment (as in our work). They found that changing the insoluble block length from 6 to 110 changed the CMC from 1.6×10^{-5} to 5×10^{-8} M. The CMC was almost independent of the length of the polyelectrolyte block. These data are also in conflict with the Marko–Rabin theory[11] since, as in our work, chains with relatively short hydrophobic segments formed micelles. Moreover, it is also possible that the theory overestimates the loss of entropy of the counterions since no theory of single-chain polyelectrolytes correctly addresses this problem.

In a recent theory of neutral/ionic polymer micelles, Dan and Tirrell[14] predicted P to be independent of S. Our experiments (Figure 5) suggest that this is true only at low ionic strengths, with P decreasing with S at higher ionic strengths. Clearly, more experimental work is necessary to test these predictions.

A progressive reduction in the surface tension with increasing polymer concentration is observed above a threshold of about 10^{-3} g/mL (Figure 6). This threshold concentration approximately corresponds to the concentration at which micelles begin to overlap. It may be that interactions ("squeezing") between the micelles force them out of the micelles and provide an opportunity for them to migrate to the surface. It is also possible that different structures such as hemispherical micelles could absorb at the surface and reduce the interfacial tension. A promising subject for future work appears to be interfacial properties of these kinds of polymers, e.g., monolayers at the air or oil/water interface or free bilayers such as soap films. More speculative, but also tempting is to study how the association structures are modified when a short-chain surfactant is added.

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