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Solution Properties of a Diblock Copolymer in a Selective Solvent of Marginal Quality. 2. Characterization of Micelles and Surface Tension

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ABSTRACT: Solutions of polystyrene-*block*-poly(butyl methacrylate) [P(S-*b*-BMA]—a narrowly distributed linear diblock copolymer consisting of 1200 monomeric units of styrene and 1200 units of butyl methacrylate—in 2-propanol (a nonsolvent for the S blocks and a Θ solvent (Θ = 23 °C) for the BMA blocks) were studied by carring out the following measurements: dynamic (DLS) and static light scattering (SLS), transmission elctron microscopy (TEM), small-angle X-ray scattering (SAXS), and surface tension. The results demonstrate that the polymer forms micelles as soon as a very low critical micelle concentration ($<4 \times 10^{-3}$ wt %) is exceeded. According to SLS these entities consist of approximately 75 unimers and exhibit an apparent radius of gyration of ca. 37 nm; this value is (in agreement with theoretical considerations) somewhat less than the sum of the radii of the S cores and of the BMA coronas, which are according to TEM 25 nm each. The hydrodynamic radius of the micelles observed in the DLS is 56 nm. It is concluded from SAXS (up to 15 wt %) of P(S-*b*-BMA) and from TEM that the core of the micelles does not change in size or shape; this finding is at variance with an increase of the aggregation number upon dilution concluded from SLS. The presence of micelles lowers the surface tension of the solvent measurably; the maximum reduction of ca. 1.5 mN/m is reached at a polymer concentration of 0.01 wt %, when the aggregates cover the entire surface.

Introduction

The first part of this work[1] has dealt with the phase diagram of the system 2-propanol/polystyrene-*block*-poly(butyl methacrylate) [2-POH/P(S-*b*-BMA)] and with the rheological behavior of the block copolymer solutions. Since 2-POH is a Θ solvent for the BMA blocks (Θ = 23 °C)[2,3] and a nonsolvent for the S blocks, this liquid differs from the normally studied *selective* solvents by the fact that its thermodynamic quality is only *marginal* instead of truly good.

To explain the behavior of solutions of P(S-*b*-BMA) in 2-POH, the hypothesis was made[1] that micelles are formed—similar to the situation with *selective* solvents—to protect the S blocks from unfavorable contacts with 2-POH. The observation that the solutions are non-Newtonian above a certain critical concentration was explained by the onset of entanglements between the BMA branches of the micellar coronas. Under these conditions the viscosity *increases* with temperature. This result can be rationalized in terms of an expansion of the outer layers of the micelles resulting from the improvement in the thermodynamic quality of the solvent.

In the present work, the micelles of P(S-*b*-BMA) formed in 2-POH are studied by dynamic and static light scattering (DLS and SLS), transmission electron microscopy (TEM), and small-angle X-ray scattering (SAXS); furthermore, the surface properties of these micellar solutions are investigated by surface tension (ST) measurements. To the knowledge of the authors, the micelle formation of block copolymers in solvents of *marginal* thermodynamic quality has not yet been investigated, in contrast to that in *selective* solvents. In the following the information referring to the latter case is briefly recapitulated.

Theoretical models applying to selective solvents have already been described in the literature.[4-6] There is also experimental evidence for micelle formation which is based on SAXS,[7-9] small-angle neutron scattering,[10] and electron microscopy.[11,12] As the concentration exceeds the entanglement concentration, a three-dimensional regular array of micelles can be observed[9,13-16] and spherical domains may turn to cylindrical or lamellar structures. Meier[6] has calculated the free energy of different domain morphologies as a function of concentration. When the molecular weights of the two blocks are identical, spherical domains have the lower energy under 20 wt %, whereas lamellar structures should predominate under equilibrium conditions in highly concentrated solutions.

The existence of true solutions (no chain association) was postulated for sufficiently low polymer concentrations; "unimolecular micelles" should form in such a way that the block for which the solvent is good wraps the other block for which it is bad, thus protecting it from interaction with the solvent.[15]

The determination of the critical micellar concentration (cmc) of block copolymer solutions is not trivial[17-19] because it generally lies in a very dilute regime, where the traditional techniques are no longer sensitive enough. When one compares solutins of block copolymers in a selective solvent with aqueous solutions of detergents, the latter have considerably larger cmc's than the former, due to their higher dissociation constants.

Experimental Section

Materials. The linear block copolymer polystyrene-*block*-poly(butyl methacrylate) [P(S-*b*-BMA)], purchased from Polymer Standard Service (Mainz, FRG), was fractionated by a method described elsewhere.[1,20] It consists (according to the characterization given by the supplier) of 1200 monomeric units of S and 1250 units of BMA. According to gel permeation chromatography,[1] M_w = 280 kg/mol and M_w/M_n = 1.17. 2-Propanol p.a. was purchased from Merck (Darmstadt, FRG).

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Light Scattering. Dynamic light scattering (DLS) measurements were performed on an ALV 3000 commercial digital correlator equipped with a 400 mW krypton ion laser (λ = 647 nm).

Autocorrelation functions, $g_1(t)$, were measured for the micellar solutions of P(S-*b*-BMA) in 2-POH at 23.0 °C for concentrations ranging from 0.004 to 0.6 wt % in an angle range from 40 to 150°. The results can be well represented by the following single exponential function, which is typical for monodisperse spheres:[21]

$$g_q(t) = \exp(-2Dq^2t) \qquad (1)$$

t is the time delay, D is the diffusion coeffient, and q is the length of the scattering vector.

The diffusion coefficients (D) and the hydrodynamic radii of the particles (R_h) are interrelated by the Stokes–Einstein relation

$$R_h = kT/6\pi\eta D \qquad (2)$$

where k is Boltzmann's constant and η is the viscosity of the solvent.

Static light scattering (SLS) measurements were performed at 23.0 °C for solutions of 0.06 and 0.6 wt % P(S-*b*-BMA), respectively, in 2-POH on a spectrometer consisting of an ALV-SP81 goniometer and a krypton ion laser (Spectra Physics, Model 2025) operating at 647.1 nm, in the usual manner.

Transmission Electron Microscopy (TEM). A Zeiss EM 902 transmission electron microscope was used to study the micelles of P(S-*b*-BMA) in 2-POH. The samples were prepared in two different ways depending on the concentration regime of interest:

(i) For a 0.0086 wt % solution of P(S-*b*-BMA) in 2-POH droplets were deposited on copper grids covered with a thin Parlodion film and the solvent was evaporated. After that, the micelles were stained with RuO_4, following the method proposed by Trent and co-workers.[22,23] It was verified that RuO_4 interacts more intensively with styrene than with methacrylates in a period up to 2 h.

(ii) For a 1 wt % copolymer solution in 2-POH droplets were deposited on a copper grid covered by a thin film of Triafol with holes. The sample was immediately frozen in liquid propane and transferred in liquid nitrogen to the cryo system of a Zeiss EM 902 microscope.

SAXS. Measurements were performed with solutions of 4.0, 8.5, and 15 wt % polymer at 30 °C by means of a Kratky camera with a slit of 40 μm, an optical path of 50 cm, and a Cu Kα source (λ = 1.54 Å, 60 kV, 30 mA) at angles ranging from 0.022 to 2.2°. The data were treated in the usual manner.[7]

Surface Tension. Surface tensions were obtained on a digital tensiometer (Krüss K10T, Hamburg, Germany) by the static Wilhelmy plate method. Pure 2-POH and solutions of P(S-*b*-BMA) in this solvent (0.0040–0.012 wt % polymer) were measured at 25, 30, 35, and 40.0 °C, respectively.

Results and Discussion

Light Scattering. Dynamic light scattering yields a constant diffusion coefficient, D, of 1.68 × 10^{-8} cm^2 s^{-1}, corresponding to a hydrodynamic radius, R_h, of 56.2 ± 0.6 nm within the concentration range from 0.6 down to 0.004 wt % (the equipment sensitivity does not allow measurements at still higher dilution). A typical result is shown in Figure 1.

The above finding implies that the cmc is less than 4 × 10^{-3} wt %. For comparison, Winnik and co-workers[19] report a cmc of ca. 6 × 10^{-4} wt % for aqueous solutions of di- and triblock copolymers consisting of S and ethylene oxide, i.e., for a system where the solvent is *selective* for one block. The present results are consistent with thermodynamic considerations of Joanny and Leibler[4] according to which the cmc should be proportional to $e^{-\gamma_{c/s}}$, where $\gamma_{c/s}$ is the interfacial tension between the core polymer and the solvent. Since 2-POH is a powerful precipitant for PS, one has to expect large $\gamma_{c/s}$ values, i.e., a very low cmc.

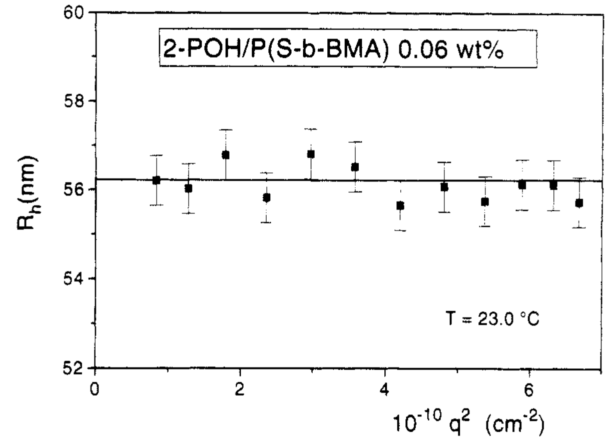

Figure 1. Typical dependence of the hydrodynamic radius R_h calculated from DLS measurements on the scattering vector q demonstrated for 0.06 wt % P(S-*b*-BMA) in 2-POH at 23.0 °C (Θ temperature of the system 2-POH/PBMA).

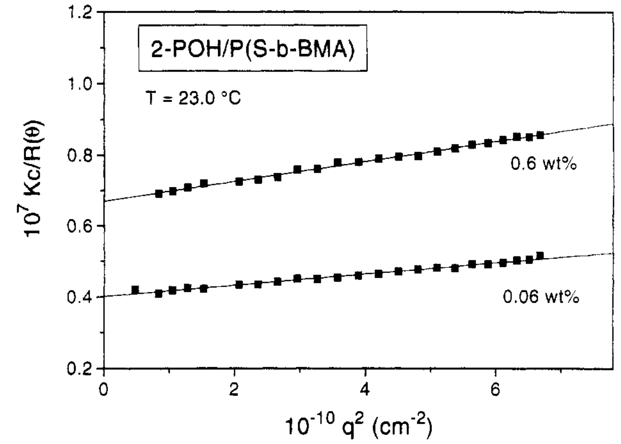

Figure 2. Evaluation of static light scattering data obtained for two solutions (0.6 and 0.06 wt %) of P(S-*b*-BMA) in 2-POH at 23.0 °C. $R(\Theta)$ is the Rayleigh ratio of the solution minus that of the solvent, θ and q are the scattering angle and scattering vector, respectively, c is the polymer concentration (mass per volume), and the value of the constant K is 8.14 × 10^{-5} cm^2 g^{-2} mol in the present case.

From the fact that the size distribution of the micelles is practically monodisperse it is inferred that these entities are formed in a closed association (single step) process.[24]

Static light scattering (SLS) measurements were performed for solutions of 0.06 and 0.6 wt % P(S-*b*-BMA) in 2-POH. The refractive index increment required for the evaluation of the data was calculated assuming additivity of the values for the two blocks in terms of their weight fractions. For the system 2-POH/PBMA the refractive index increment $(dn/dc)^{23 °C}_{546nm}$ was taken from the literature.[25] The corresponding information for 2-POH/PS cannot be obtained by measurements since the polymer is insoluble in this solvent. It was therefore read from the straight line one obtains when (dn/dc) for solutions of PS in different solvents is plotted as a function of their refractive index. For the evaluation of the light scattering data shown in Figure 2 it was assumed that $(dn/dc)^{23 °C}_{647nm}$ calculated in the above manner for the copolymer is very close to $(dn/dc)^{23 °C}_{546nm}$ due to the small dispersion in this range of wavelengths for both homopolymers.[26]

The apparent molar masses M^{mic}_{app} of the micelles obtained from the extrapolation of the data to the scattering vector zero are 2.5×10^6 g/mol for 0.6 wt % of the copolymer and 15×10^6 g/mol for 0.06 wt %. According to these preliminary[27] results, the second osmotic virial coefficient for the micelles would be on the order of 6×10^{-4} cm^3 g^{-2} mol. This unexpectedly large concentration dependence of $Kc/R(\theta=0)$ leads to a pronounced increase of the aggregation number ($N_{agg} = M_{app}^{mic}/M$) upon dilution from 10 via 60 to 280 in the limit of zero polymer concentration.

From the slopes of the dependence shown in Figure 2 one can calculate R_g^{app}, an apparent radius of gyration of the micelles, on the basis of the relation

$$\langle R_g^{app\ 2} \rangle = 3M_{app}^{mic}\, d[Kc/R(\theta)]/dq^2 \qquad (3)$$

Since the scattering power of the styrene core of the micelles is about 4 times larger than that of the n-butyl methacrylate of the shell, it can be anticipated that R_g^{app} will be too small as compared with reality. It is also interesting to note that the R_g^{app} values calculated according to eq 3 lie in the interval 37 ± 3 nm irrespective of polymer concentration.

The combination of static light scattering information and intrinsic viscosity data[1] allows one to evaluate the micellar molecular weight, M_{mic}, using the following relation:

$$M_{mic} = 10\pi(R_g^{app})^3 N_A/(3[\eta]_{mic}) \qquad (4)$$

in which $[\eta]_{mic}$ is the intrinsic viscosity of the micelles and N_A is Avogadro's number.

From eq 4 and $[\eta]_{mic} = 14 \pm 1$ mL/g at 25 °C (ref 1) one can estimate an aggregation number N_{agg} of 75. This value lies within the range (50–150) reported by Frank,[28] Mandema,[29] and Price[11] for block copolymer solutions in a *selective* solvent.

Transmission Electron Microscopy (TEM). Method i was applied to dilute solutions (0.0086 wt %) to study isolated micelles. To differentiate core and corona, the S blocks were selectively stained with RuO_4 (cf. Experimental Section); the results are shown in Figure 3. In this micrograph the cores represent the darkest parts, and their radius is ca. 25 nm; the dimension of the brightest parts—corresponding to the coronas of the BMA blocks—are also ca. 25 nm. Therefore, the TEM measurements yield a micelle radius, R_{mic}, of about 50 nm, which is in reasonably good agreement with $R_g^{app} = 37 \pm 3$ nm in view of the above-mentioned effect of the different refractive index increments of the core and the shell.

Method ii of sample preparation (cf. Experimental Section) was used to study solutions of higher polymer concentration. The micrograph given in Figure 4 refers to a 1 wt % solution and was obtained without staining. Since the cores of the micelles are denser than their coronas, the spherical structures with a radius of 28 ± 2 nm correspond to the cores. The picture suggests a very low polydispersity of the micelles.

Small-Angle X-ray Scattering (SAXS). All results discussed so far (DLS, SLS, and TEM) refer to concentrations above the cmc and below the micelle entanglement concentration, which was evaluated from intrinsic viscosity[1] to be 5 wt % at 25 °C. The SAXS measurements at 30 °C were performed with 4.0, 8.5, and 15.0 wt % solutions of P(S-b-BMA) in 2-POH, i.e., just below and above the entanglement concentration. The results are shown in Figure 5a.

From the scattering angle corresponding to the first-order peak, the distance between the periodic domains can be estimated to be 87 nm for the highest concentration. The shift of the maximum in $I(q)$ to lower scattering vectors q upon dilution shown in Figure 5a indicates that the distance between micelle cores increases.

Modeling the SAXS data with the Percus–Yevick hard-sphere liquid theory yields the contribution of the interparticle interference to the scattering intensity and

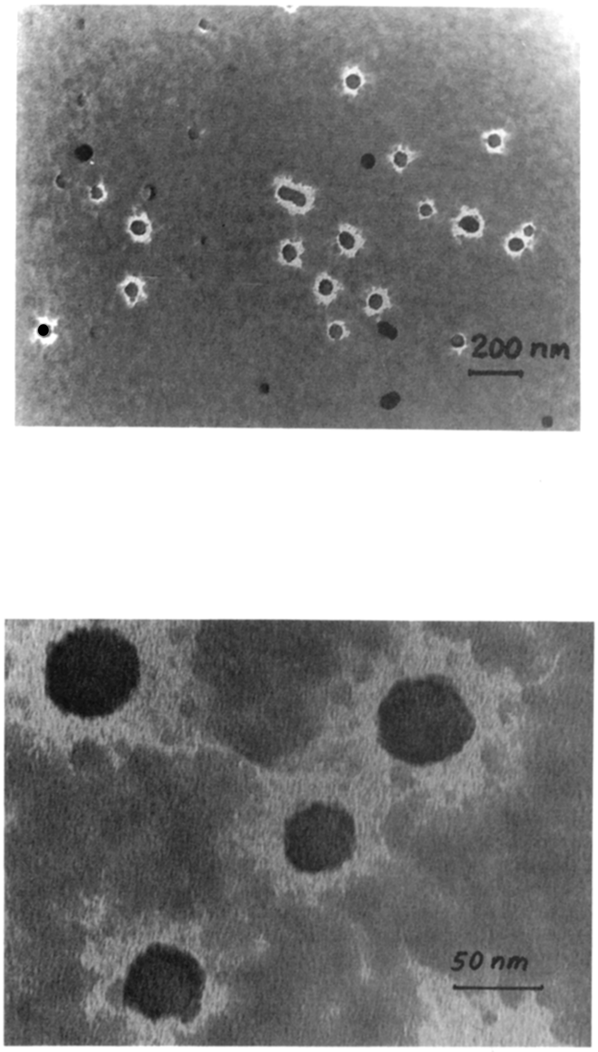

Figure 3. Transmission micrographs showing micelles of P(S-b-BMA) formed at a concentration of 0.0086 wt % in 2-POH. Due to staining with RuO_4 the cores appear dark, in contrast to the bright coronas.

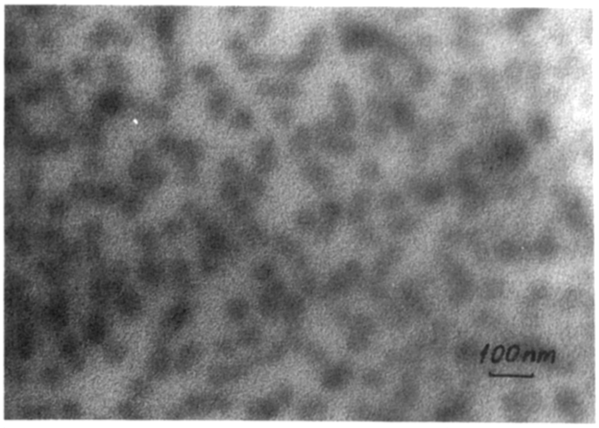

Figure 4. Transmission micrograph showing (not stained) micelles of P(S-b-BMA) formed at a concentration of 1 wt % in 2-POH. The cores appear dark because of the higher electron density of S as compared with BMA.

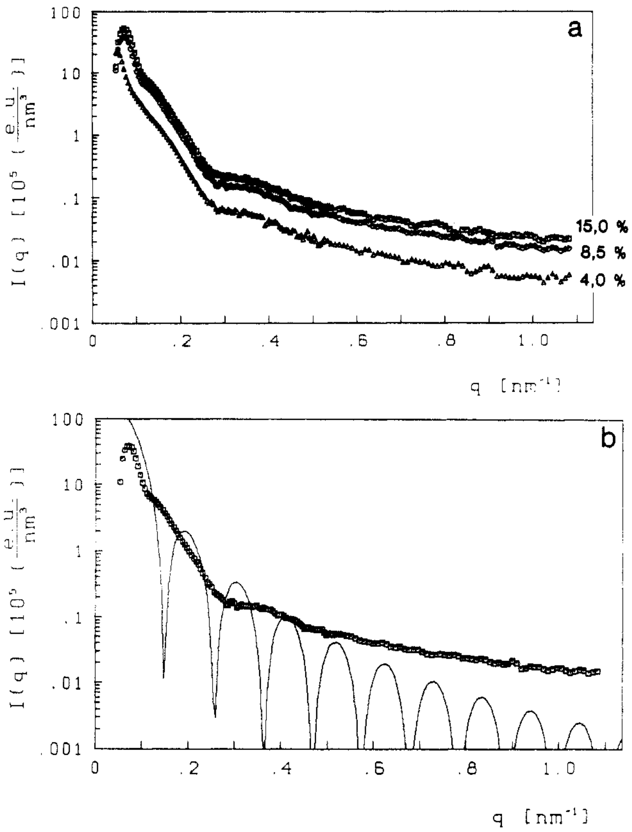

Figure 5. (a) Results of small-angle X-ray scattering measurements with solutions of P(S-*b*-BMA) in 2-POH at the indicated concentrations (wt %). I is the scattering intensity and q is the scattering vector. (b) Evaluation of the data for the two highest concentrations (yielding within experimental accuracy the same curve) according to the hard-sphere liquid theory.[30]

consequently the radii of the scattering centers of the micelles.[30] The result of this evaluation, shown in Figure 5b for the two higher concentrations, leads to ca. 30 nm; this value should refer to the core radius of the micelles of high electron density since the scattering contributions of the shell can be considered to be negligible. The above figure of 30 nm is in good agreement with the 28 ± 2 nm found in TEM measurements for the micelle cores.

The present findings are in accord with the prediction of Meier[6] for copolymers with two blocks of the same size in a *selective* solvent according to which spherical domains are the morphology with the lowest free energy in solutions up to at least 20 wt %. Spherical domains have also been reported by Shibayama and co-workers[7] for solutions of polystyrene-*block*-polybutadiene copolymer in *selective* solvents up to 60 wt % copolymer.

Surface Tension. The surface tension measurements show that up to 0.006 wt % of P(S-*b*-BMA) γ is essentially identical with that of the pure 2-POH. From 0.0066 to 0.01 wt % there is a decrease of about 1.5 mN/m; thereafter γ remains practically constant as shown in Figure 6.

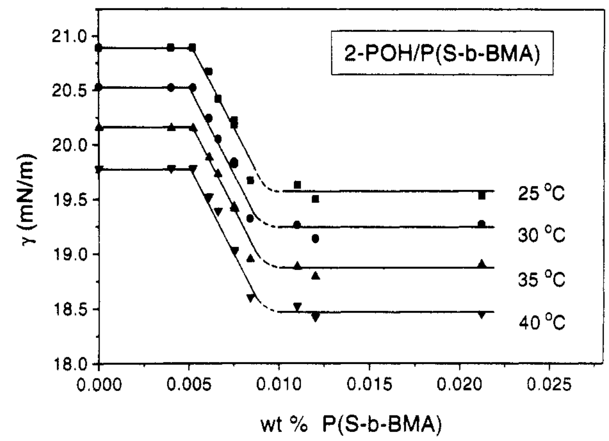

Figure 6. Concentration dependence of the surface tension γ of solutions of P(S-*b*-BMA) in 2-POH at the indicated temperatures; there is no indication of the critical micelle concentration (<0.004 wt %) in this diagram.

From Figure 6 it is obvious that the cmc (situated well within the region of constant γ on the side of low concentrations) cannot be seen in these measurements. A reduction of about 1.5 mN/m in surface tension by the presence of the solute appears small when compared to the effect of sodium dodecyl sulfate on the surface tension of water, but it is reasonable for a system composed of a block copolymer and a hydrocarbon or an alcohol. The present findings suggest that micelles of P(S-*b*-BMA) can lower the surface tension of 2-POH (20.8 mN/m at 25 °C) via an accumulation of the butyl and/or methyl groups of BMA on the air side (down to 19.6 mN/m at the same temperature). It is interesting to compare this reduced value to the liquid/vapor surface tension of hexane (18.4 mN/m at 25 °C). A reduction of γ similar to the present one was observed by Owen[31] for the system benzene/poly(styrene-*b*-dimethylsiloxane).

By means of the Gibbs adsorption isotherm[32] (using concentrations c instead of activities)

$$A = -RT/(\mathrm{d}\gamma/\mathrm{d}\ln c) \tag{5}$$

it is possible to estimate A, the area per micelle adsorbed to the surface of the solution. At 25 °C one obtains $A \approx 426.6$ nm^2; this value corresponds to a radius of ca. 11.6 nm. Since the radius of gyration of the micelles estimated from the light scattering measurements ($R_g^{app} = 37$ nm) is about 3 times larger at the same temperature, this could mean that the micelles at the surface (which are in equilibrium with the micelles situated in the interior of the phase) are deformed. In view of the fact that a change from spheres to prolate ellipsoids increases the area of enthalpically highly favorable intermicellar contacts, this explanation appears reasonable.

Conclusions

The present findings and the information reported in the previous paper[1] allow the following statements. The cmc of P(S-*b*-BMA) in 2-POH is less than 4×10^{-3} wt %. According to SLS the apparent radius of gyration of the micelles (core and shell) amounts to ca. 37 nm, in reasonable agreement (keeping in mind that the former quantity inevitably is too small) with the radii of the cores (ca. 25 nm) and of the coronas (ca. 25 nm) obtained from TEM and SAXS. From the R_g^{app} of SLS and $[\eta]_{mic}$ one calculates an aggregation number on the order of 75. The hydrodynamic radius of the micelles, as determined by DLS, is ca. 56 nm. From the fact that the core radii measured at different polymer concentrations with different techniques remain almost constant, one is inclined to conclude that the micelles practically do not change their size with composition; this, however, would be at variance with the SLS results which indicate concentration influences on the aggregation number. Surface tension measurements demonstrate that the micelles accumulate at the surface and reduce γ; this is interpreted in terms of a preferential exposure of the aliphatic parts of their coronas to the air. When the micelles cover the surface totally, they require a considerably smaller cross-section than anticipated from their dimension inside the solution; this is probably due to their energetically driven deformation.

The present investigation—mainly performed at high dilution of the block copolymer—demonstrates that the size and the structure of the micelles formed in *marginal* solvents do not differ qualitatively from those observed in *selective* solvents. As far as the surface activity of the polymer is concerned, the experimental information is too scarce to enable a comparison. This finding contrasts with the large differences between marginal and selective solvent detected in the field of the rheology of moderately concentrated solutions.[1]

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