

## Ionic and Zwitterionic Model Macromolecular Surfactants

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Micellization of ionically end-capped and diblock copolymers in a selective polar solvent was investigated using small-angle neutron scattering. In the monofunctional case, either the soluble block (sample Q) or the insoluble block (sample S) is end-functionalized with an ionic group. In the bifunctional case, both chain ends are ionically end-capped with groups of opposite charges, thus leading to a macrozwitterionic block copolymer (sample Z). Results for these model macromolecular surfactants were compared to that of an uncharged block copolymer of identical mass and block sizes (sample H). Large qualitative differences on the scattering curves were observed as a function of the position of the charge on the chain. The aggregation numbers were obtained by fitting data with the form factor of a spherical micelle, showing differences up to a factor of 2. For sample Q, an experimental structure factor was obtained and fitted by that of a monodisperse hard sphere. A structure for the micelles (chain conformation) is proposed, introducing the concept of a bound counterion in case of sample Z.

Diblock copolymer chains when dissolved in a selective solvent can be considered as the macromolecular counterparts of low molecular weight surfactants.<sup>1–3</sup> In such a solvent, the nonsoluble A block adopts a collapsed conformation, minimizing contact with the solvent, while the B-soluble block is well-swollen by the solvent. Depending on the length of the blocks and polymer volume fraction,<sup>4</sup> phases of different geometries are found such as spherical micelles, cylindrical micelles, lamellae, etc. Low molecular weight surfactants, which also assemble in similar phases depending on the geometry of the surfactant molecule and on the surfactant concentration, generally possess an ionic headgroup. When placed in a sufficiently polar solvent (usually water), the headgroup dissociates releasing a counterion. The ionization of the headgroup is the mechanism responsible for the partial solubility of the surfactant molecule. Hydrophobic interactions between tails and solvent provide the tendency of the system to self-assemble. In low molecular weight surfactants, the structure and the dynamics of the observed phases is, therefore, a consequence of the competition between electrostatic and hydrophobic interactions.

An analogy between diblock copolymer chains in a selective solvent and ionic surfactants cannot be complete when electrostatic interactions are not considered in the former system. This motivated us to investigate diblock copolymers in a polar selective solvent condition using a polymer that contains ionizable groups only at the chain ends. The well-defined functionalization of the diblock copolymer chain ends with ionizable end-groups provides *model systems* in which the self-assembly can be studied as a consequence of the competition between hydrophobic and electrostatic interactions. For a given block molecular weight, the position of the charge on the chain can, in principle, strongly influence the self-assembly. Different

behavior should therefore be observed whether the charge is placed, for instance, at the end of the soluble block or at the end of the nonsoluble one.

Self-assembly can be strongly altered when surfactant molecules of opposite charges are mixed together. In such systems, the two surfactant molecules tend to stick together forming a kind of complex and very large assemblies can be found even for very low concentrations. It is therefore interesting to consider also the case of a macrozwitterionic diblock copolymer, i.e., a copolymer containing ionizable groups with *opposite charges* at the extremities of each block.

In the present Letter, we report results on the micellization of ionically end-capped polystyrene-*block*-polyisoprene (PS-*b*-PI) copolymers in deuterated dimethylacetamide (DMAc), a selective polar solvent for PS,<sup>5</sup> using small-angle neutron scattering (SANS). Micellization of the charged species is compared to that of the neutral block copolymer (sample H). Monofunctional samples either contain a sulfonate group at the PI end (sample S) or a quaternary ammonium group at the PS end (sample Q). The bifunctional macrozwitterionic block copolymer (sample Z) contains both groups at the respective chain ends. All four species have been synthesized from one single polymerization batch and, therefore, show identical molecular characteristics. All samples exhibit narrow molecular weight distribution ( $M_w/M_n \cong 1.09$ ) and a degree of chain end functionalization >95%.<sup>6</sup> The molecular weight is 12k for each block. For the synthesis, the reader is referred to ref 7. After synthesis, all polymers were also precipitated in methanol. In the case of the zwitterionic sample, part of the counterions were therefore lost since sample Z contains counterions of both signs. The counterion content remaining in sample Z after precipitation was measured by means of neutron activation analysis, and it was shown to be only 25% of the original content.<sup>8</sup>

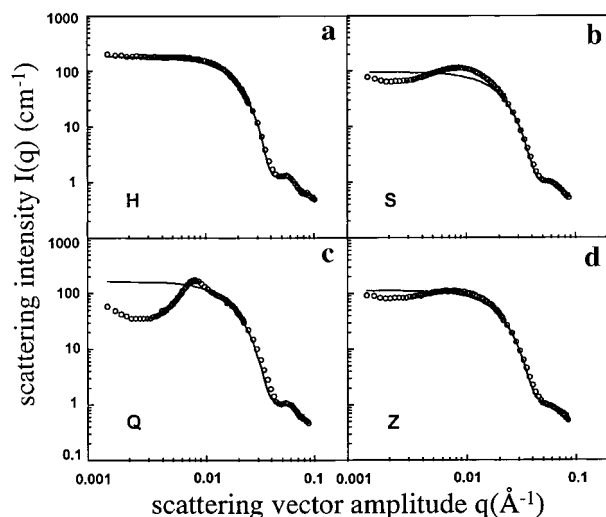
At low concentrations, symmetric PS-*b*-PI forms spherical micelles in DMAc.<sup>9</sup> As in the case of low-molecular weight surfactants, thermodynamic equilibrium can be easily achieved

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**Figure 1.** 1: Scattering intensity as a function of scattering vector amplitude of all four species, (a) H, (b) S, (c) Q, and (d) Z, investigated in the present study. The polymer volume fraction is 0.01 for all curves. The full line is the result of the fitting of the form factor  $P(q)$  of a spherical micelle. As explained in the text, only high  $q$  data were used for the fitting.

since the PI core is liquid at ambient temperature, in contrast to most block copolymer (bc) micellar systems described in the literature where bc micelles present glassy cores.<sup>10</sup> At the same time, the high dielectric constant of DMAc ( $\epsilon \sim 39$ ) ensures a high degree of dissociation of the ionic end groups. Micellization of differently charged systems was studied in solutions of 10 g/dm<sup>3</sup>. DMAc was purchased from Promochem chemicals and used without further purification. SANS experiments have been performed at spectrometer D11 at Institute Laue-Langevin (Grenoble, France), and the spectrometer configurations used were  $\lambda = 7$  Å and sample detector distances of 40, 10, and 3 m. Standard procedures of data treatment have been applied to raw data. As shown below, strong effects on the scattering spectra are observed as a function of the position of the charge even though no partial labeling of the chains was used.

In Figure 1, the absolute scattered intensity at small angles is plotted as a function of the scattered vector in a log–log scale for solutions of H, S, Q, and Z block copolymers. Consider the scattering from sample H, Figure 1a. At this polymer volume fraction ( $\phi \cong 0.01$ ), one observes a typical scattering function of a spherical micelle: at very small angles, an Ornstein–Zernicke function describes data well, while at the other extremity of the vector transfer window, the scattering function exhibits a strong oscillation owing to the scattering of the PI micelle core and PS corona. No correlation maximum due to the interaction between neighboring micelles is observed at intermediate scattered vectors. When an ionic group is added to either the PI (Figure 1b) or PS chain end (Figure 1c), the scattering spectra significantly change with respect to sample H. At the same polymer concentration, both spectra present an oscillation at high  $q$  values. This is a strong indication that micellization still occurs for both samples irrespective of the position of the charge. The oscillations are shifted to higher  $q$ 's with respect to that of sample H, with the shift being larger for sample S than for sample Q. The most apparent difference is the existence of a correlation maximum for both samples S and Q, indicating a stronger interaction between neighboring micelles than found for H. The S spectrum exhibits a broad correlation maximum at  $q \sim 0.011$  Å<sup>-1</sup>, while that of sample Q, centered at  $q \sim 0.009$  Å<sup>-1</sup>, is rather sharp. The intermicellar interactions in sample Q are apparently much stronger than in

S. The above results indicate a strong dependence of micellization and interaction between micelles on the position of the ionic group on the bc chain. Whereas a charge at the corona chain ends strongly increases the interaction between micelles, a charge at the core chain ends significantly decreases the aggregation number.

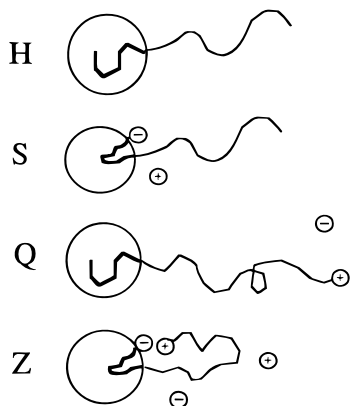
When charges are present at both chain ends, one could argue that both effects described above, that is, a decrease in aggregation number and an increase in the interaction between micelles, should be observed. The scattering from the macrozwitterionic sample Z at the same polymer volume fraction is depicted in Figure 1d. The scattering function is similar to that of sample S. The position of the oscillation at high  $q$  values is practically the same as that observed for sample S, while the correlation maximum at intermediate  $q$  is slightly softer. From this we conclude that the effect of a charge at the core chain is retained while the effect due to the charge at the corona is not. This absence of strong interactions between neighboring micelles can be attributed to the existence of screening effects present in sample Z. We will come back to this point later in the discussion.

More quantitative information can be obtained from the above spectra if one considers the form factor,  $P(q)$ , of a spherical micelle. It was recently shown<sup>11</sup> that the scattering from a micelle with corona chains under good solvent conditions can be well-described by the  $P(q)$  of the equation below using certain assumptions.<sup>11</sup>

$$P(q) = p^2 \rho_s^2 F_s(q, R) + p \rho_c^2 F_c(q, L) + p(p-1) \rho_c^2 S_{cc}(q) + 2p^2 \rho_s \rho_c S_{sc}(q) \quad (1)$$

where  $F_s(q, R)$  is the self-correlation of the micelle core of radius  $R$ ,  $F_c(q, L)$  is the self-correlation of the chains in the corona with  $L$  the contour length of the shell chain,  $S_{sc}(q)$  is the cross-correlation term between the spherical core and the corona chains, and  $S_{cc}(q)$  is the cross-correlation between different chains in the corona. Here,  $p$  is the aggregation number and  $\rho_s$  and  $\rho_c$  are the excess scattering lengths of the core and the outer chains, respectively. We assume below that the micellar core is dry:  $(4/3)pR^3 = pNa^3$  with  $N$  the polymerization degree of the nonsoluble chain and  $a^3$  the monomer volume ( $N = 176$ ,  $a = 5.1$  Å). The total scattered intensity,  $I(q)$ , is given by  $I(q) = S(q)P(q)$ , where  $S(q)$  is the structure factor. Since  $S(q) \rightarrow 1$  for high  $q$ 's, one can, as a first approximation, fit data with eq 1 in this vector transfer range. The resulting fits are shown in Figure 1, where polydispersity was used in order to compensate for smearing.<sup>12</sup> The quality of the fits is reasonably good in the high  $q$  range, permitting one to extract the aggregation numbers. Proceeding in the same fashion for all data sets and imposing the supplementary constraint of  $S(q) \rightarrow 1$  for high  $q$ 's, we find, using a gyration radius for the shell chain of 21 Å, core radii of 83, 78, 65, and 65 Å for samples H, Q, S, and Z corresponding to aggregation numbers of 108, 90, 52, and 52, respectively.

The presence of the electric charges at the PI core partially solubilizes the PI chain and therefore reduces the aggregation number of sample S by a factor of 2 with respect to that of the neutral polymer. In a recent study we have shown that this reduction can be quantitatively accounted for by a micellization model that assumes localization of the charges at the core surface.<sup>13</sup> This charge distribution is favored by two mechanisms: (i) the high mobility of the chain ends in the liquid micelle core and (ii) the fact that the Flory parameter between the core polymer and solvent is finite. This always provides a



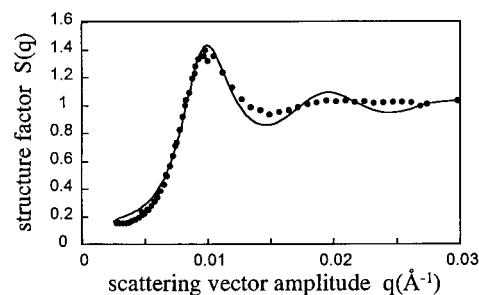
**Figure 2.** 2: Schematic representation proposed for the structure of spherical micelles formed by end-capped block copolymers.

residual amount of the polar solvent in the micelle core, thus strongly avoiding formation of ionic aggregates in the PI-core.<sup>14</sup> Therefore the PI-chain ends are preferentially located at the surface of the micellar core. One can imagine that at least part of them fold back as schematically depicted in Figure 2.

The core radius obtained for sample Q is intermediate between that of H and S. One can argue that, in sample Q, the chains in the corona are stretched owing to electrostatic repulsion between corona chain ends. This can pull the chains out of the micelle and concomitantly decrease its aggregation number with respect to the neutral micelle. The stretching of the corona chains in the Q sample is also represented schematically in Figure 2. The aggregation numbers obtained here are in good agreement with those determined from light-scattering measurements.<sup>15</sup>

The aggregation number of sample Z, as determined by the above fitting procedure, is the same as that for S. Therefore one can argue that the main feature governing aggregation number is the presence of an ionic group at the chain end of the nonsoluble block. Note that, in the intermediate scattering vector window, the soft maximum of Z sample resembles that of S rather than that of Q. With respect to sample Q, one can therefore conclude that (i) the interaction between micelles Z is screened by an increase of ionic strength or (ii) that the effect of the quaternary ammonium groups at the PS chain end is partially suppressed by an *intramolecular* screening. As recalled above, analysis of the counterion content in sample Z showed that 75% of the original counterions present in sample Z were lost during sample preparation. Therefore, the intramolecular screening (ii) is likely to occur via back-folding of the PS chain ends toward the corona. This effect is represented schematically in Figure 2. In this case, the charges at the outer shell can be viewed as *bound counterions* that cannot leave the micelle.

An experimental structure factor can be obtained by dividing the scattering data by the fitted form factor in the whole vector transfer range. This procedure has been described for sample S in ref 9. Here, we will concentrate on sample Q. The result for the experimental structure factor,  $S_{\text{exp}}(q)$ , of sample Q is plotted in Figure 3. The structure factor of hard spheres of radius 322 Å is also plotted and the agreement is almost



**Figure 3.** 3: Experimental structure factor  $S_{\text{exp}}(q)$  for sample Q obtained by dividing experimental data by the form factor fitted at high  $q$  values (see Figure 1c).

quantitative, suggesting that micelles Q interact as effective “electrostatic” spheres of radius 322 Å. This effective sphere radius is larger than the value of the physical micelle (78 Å + 21 Å). This suggests that the electrostatic screening length in the bulk solution is  $\sim 223$  Å. Note, however, that the presence of the electric charges on the extremity of the corona arms can contribute to stretch the chains of the corona, leading to an increase of the volume occupied by the physical Q micelle. The electrostatic screening length obtained above might therefore be slightly overestimated.

The above study on micellization of ionically end-capped block copolymers in a polar, selective solvent leads to the following qualitative picture: In the case of monofunctional samples the aggregation number and the interaction between micelles strongly depend on whether the charge is located at the soluble or the nonsoluble block of the copolymer chain. In micelles formed by the bifunctional (macrozwitterionic) copolymer, the charge at the end of the nonsoluble chains governs the aggregation number while the absence of strong correlation between micelles suggests that the charge in the corona acts as a bound counterion, linked to the micelle by a polymer coil. The suggested charge structure and chain conformations of different micelles are roughly summarized in Figure 2.

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