Temperature Dependence of the Structure and Interaction of Starlike PEG-Based Block Copolymer Micelles

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In the literature, there have been reported a large number of studies of the structure and interactions of block copolymer micelles by scattering techniques.[1,2] The micelles consist of a compact core of the lyophobic block and a swollen corona of the lyophilic block. The corona may be narrow relative to the core size, and the micelles are similar to sterically stabilized colloid particles.[3] The corona may also be much wider than the core, and the particles are similar to multiarmed polymer stars.[4−6] However, it is only recently that it has become possible to do a full qualitative analysis at relatively high resolution of scattering data from such systems.[5−7] A recently published approach is based on Monte Carlo simulations.[7−9] For a micellar model with a compact core and semiflexible chains interacting with a hard-sphere potential, scattering functions were generated and it was shown that they can be described by (partly) empirical expressions. It was shown that the interchain interaction effects manifest themselves in the form factor that describes the scattering from the micelles.[9] The effects of interchain interactions can be investigated in basically two different ways: (i) The grafting density of chains is varied for a constant core size. (ii) The effective intra- and interchain interaction potential is varied by changing the solvent quality. There are obvious difficulties related to (i), whereas (ii) is more readily obtained by choosing an appropriate model system. In the present paper, the influence of solvent quality is investigated.

In polymer systems the interaction effects vanish (“to lowest order”) when approaching the Θ temperature. Polystyrene in cyclohexane, which has a Θ temperature around 35 °C, is one of the most frequently studied Θ-point systems in the literature.[10] However, this polymer system has only minor technological interest. We have instead turned our attention to PEG-containing block copolymers in water which have particular technological interest as the homopolymers as well as PEG-containing block copolymers are important components for controlling the physical properties of, for example, pharmaceutical and cosmetic products. For PEG the solvent quality of water changes dramatically with temperature. It becomes poorer as the temperature is raised, and it has a Θ temperature of about 100 °C.[11,12] As examples of the influence of the temperature dependence of the solvent quality of water for PEG, one can mention the change in micelle structure and rheological properties of block copolymer micelles of PEG and poly(propylene oxide) at high temperature.[13−15]

In many block copolymer systems, the PEG is combined with a block, which also has a temperature-dependent behavior in water. This often leads to problems in distinguishing which effects stem from the core block and which stem from the PEG. We have for the present study looked for a polymer with an aggregation state of the micelles, which is fairly independent of temperature. We chose the diblock copolymer Brij700, $C_{18}E_{100}$. This Brij molecule has relative to most surfactants a large hydrophobic octadecyl chain, and the aggregation state of the micelles formed in water can be expected to be fairly independent of the temperature. Polymers of this type are often termed “hydrophobically modified” polymers due to the large asymmetry of the two blocks. For such polymers the corona is much wider than the core, and the micelles are starlike.

In the present Communication we study the structure and interactions of the starlike micelles in dilute solution by small-angle X-ray scattering (SAXS) in a particular large temperature range. We used the most advanced model available for deriving detailed information on the temperature dependence of both structure and intermicellar interaction effects. We use molecular constraints in the model in order to reduce the number of parameters for describing the structure. The contrast for the C18 and the PEG chains is given by the electron density difference between solvent and the blocks, and the contrast is in particular for the PEG chains quite low, and for both blocks, it is temperature dependent. We have therefore performed measurements of the apparent specific density of the two blocks in water over the full temperature range studied by SAXS.

The sample was prepared by weight by dissolving Brij700 (Sigma-Aldrich) in D_2O (purity higher than 99.9%) at a concentration of 2 wt %. The sample was left overnight, and clear homogeneous solutions formed. We chose a concentration of 2 wt % to avoid a large influence of interparticle interactions. D_2O was used in order to allow direct comparison with later small-angle neutron scattering (SANS) experiments, for which the contrast is optimal in D_2O. The SAXS measurements were performed on the SAXS instrument at the University of Aarhus, which is optimized for solution scattering.[16] The scattering length density of the C_{18} and E_{100} blocks for SAXS were determined from density measurements[17] performed at 5−90 °C with a DMA5000 densitymeter on solutions of Brij700 and Brij78 ($C_{18}E_{20}$). We note that some polydispersity of the PEG blocks is expected; however, this has only minor influence on the results of the present work.

With SAXS a temperature range between 10 and 90 °C in steps of 10 deg was investigated. A subset of the data is shown in Figure 1. The plot confirms that the structure factor effects are modest at this concentration and that the data behave similarly with a progressive evolution as the temperature is increased.

The data were analyzed on absolute scale and fitted by means of least-squares methods using a model based on Monte Carlo simulations, where the micelles have a spherical homogeneous core (C_{18} chains) surrounded by a corona of self-avoiding, semiflexible interacting chains (PEO chains).[7−9] The scattering cross section of the model is[7,18]

$$I(q) = n_{\mathrm{part}}[P_{\mathrm{mic}}(q) + A_{\mathrm{mic}}^{2}(q)\{S(q) - 1\}] \qquad (1)$$

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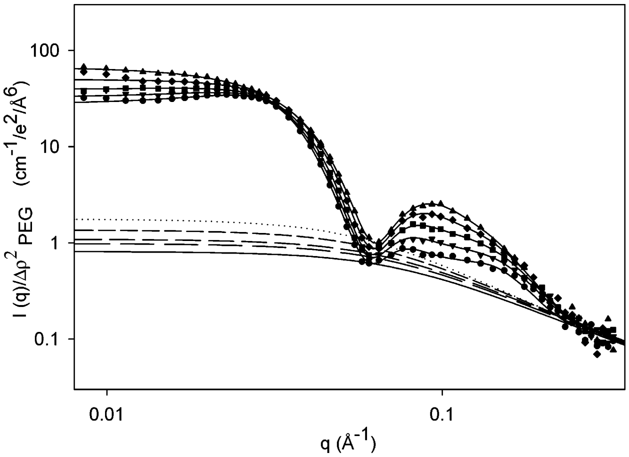

Figure 1. SAXS data from a 2% Brij700 solution together with model fits using the model described in the text. Only data for 10 °C (circles), 30 °C (inverse triangles), 50 °C (squares), 70 °C (diamonds), and 90 °C (triangles) are shown. The lines below represent the fitted effective single chain form factor *P′(q)* at 10 °C (solid), 30 °C (long dash), 50 °C (medium dash), 70 °C (short dash), and 90 °C (dotted). All data have been divided by the square of the excess electron density of the PEO chains in order to reduce the influence in the plot of the change in contrast with temperature.

where q is the modulus of the scattering vector, n_{part} is the number density of particles, $S(q)$ is the hard-sphere structure factor,[19] and

$$P_{\mathrm{mic}}(q) = A_{\mathrm{core}}(q)^2 + 2A_{\mathrm{core}}(q)\, A_{\mathrm{corona}}(q) + P_{\mathrm{corona}}(q)$$
$$\text{and} \qquad A_{\mathrm{mic}}(q) = A_{\mathrm{core}}(q) + A_{\mathrm{corona}}(q) \qquad (2)$$

where $A_{\mathrm{core}}(q)$ is the core scattering amplitude given as the Fourier transform of the radial scattering length density distribution of the core (a box function with a smooth interface).

$$P_{\mathrm{corona}}(q) = \Delta\rho^2\{n[n - P'(q{=}0)]A_{\mathrm{corona}}(q)^2 + nP'(q)\} \quad (3)$$

is the total corona scattering with $A_{\mathrm{corona}}(q)$ being the Fourier transform of the ensemble-average radial corona profile. $\Delta\rho$ is a contrast factor, n is the number of chains in the corona, and $P'(q)$ is the effective single chain form factor, which can be described by a random phase approximation (RPA) expression.[20−23]

$$P'(q) = \frac{P(q)}{1 + \nu P(q)} \qquad (4)$$

where $P(q)$ is the single chain form factor and ν is a parameter depending on the reduced surface coverage which is the two-dimensional equivalent of c/c^*, where c^* is the overlap concentration in a semidilute solution. For $P(q)$ we used the form factor of semiflexible chains.[24]

The radial profile of the corona is modeled using a set of three partial cubic *b* spline functions[6] in order to allow a certain degree of free-form determination of the profile. One has $\rho(r) = \sum_{i=1}^{3} a_i B_i(r)$, where a_i are coefficients to be determined in the fit and $B_i(r)$ are the cubic *b* splines.

The model was fitted to the data. At high q the data have a significant contribution from the effective single chain scattering $P'(q)$. This contribution is also shown in the figure. In the fits, the contour length ($L = 450$ Å) and Kuhn length ($b = 10$ Å[25]) were kept fixed. The $P'(q)$ curves are tangential to the data points in the first subsidiary zero of the $A_{\mathrm{mic}}(q)^2$ term, where the $P'(q)$ term is the only term contributing. Beyond the first subsidiary minimum, there is still a significant contribution from the $A_{\mathrm{mic}}(q)^2$ term, and it changes due to the changes in the radial PEG profile (Figure 2) when the temperature is varied.

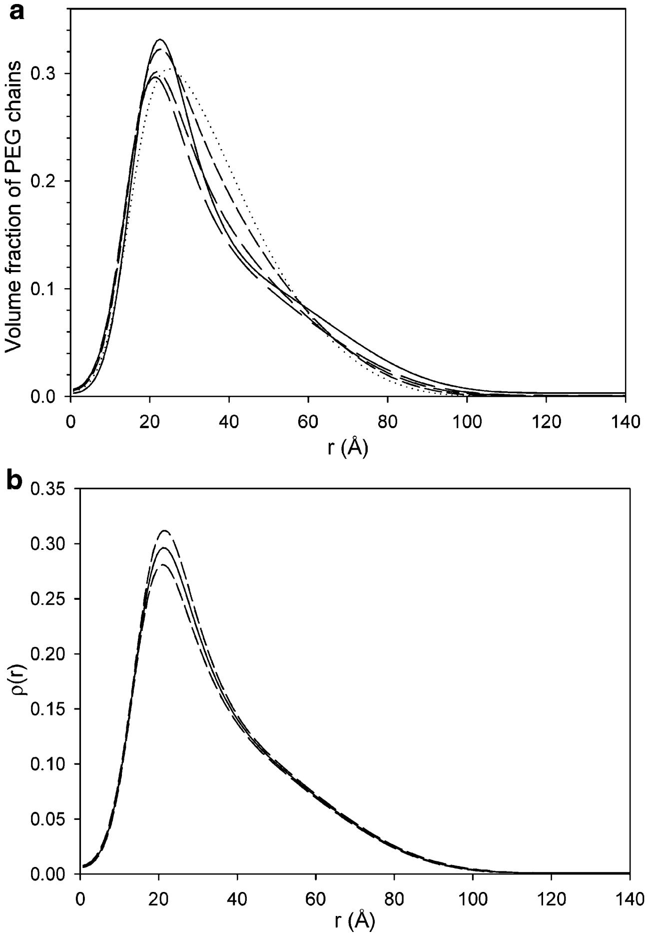

Figure 2. (a) Radial volume profile of PEO chains in the Brij micelles with 2 wt % concentration at 10 °C (solid), 30 °C (long dash), 50 °C (medium dash), 70 °C (short dash), and 90 °C (dotted). (b) The profile at 30 °C with error bands.

The quality of the model fits in the full q range is excellent, and from them, we obtain various parameters describing the system. Even though some polydispersity of the micelles is expected, the data could be fitted satisfactorily without, which demonstrates that the polydispersity is relatively low. The radial volume fraction profile of the PEG chains is shown in Figure 2a, and Figure 2b shows the profile at 30 °C with estimated error bands. The variations with temperature are significantly larger than the errors. The C18-containing core (not shown) has a radius of about 17 Å and is fairly independent of the temperature, in agreement with a constant aggregation number. The PEG profile has a maximum in the local concentration of about 35 vol %. It decays smoothly to zero at around 110 Å with some temperature dependence, which is due to the variation in the PEG interaction; the profiles are somewhat more compact and decays more rapidly at high temperatures, where the polymer interactions are weaker.

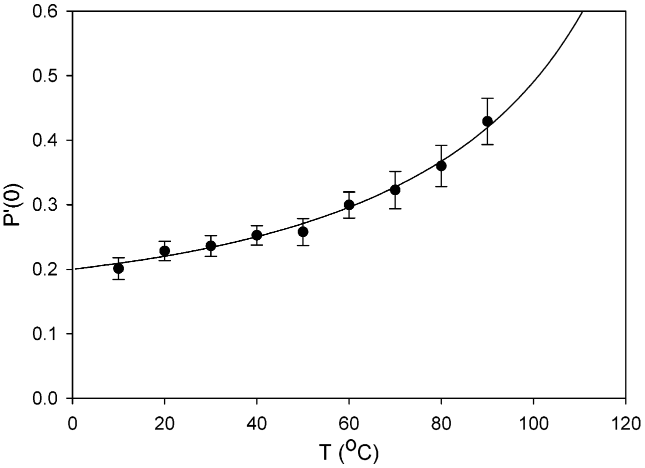

Figure 3. Forward value of the effective single chain form factor of the Brij micelles. The curve is a fit with the model described in the text.

The effective forward scattering of the chains, $P'(0)$, which is given by

$$P'(0) = \frac{1}{1+\nu} \tag{5}$$

is one of the parameters determined in the fits (Figure 3). Although the errors increase as the temperature is raised, there is a clear increase in $P'(0)$ with temperature. This is in agreement with the weakening of the polymer interactions with increasing temperature.

For a low but finite surface coverage one expects that $\nu \rightarrow 0$ (or $P'(0) \rightarrow 1$) for $T \rightarrow T_\theta$, in agreement with the low-concentration behavior in bulk semidilute solutions. However, at higher concentrations, one expects a residual contribution at T_θ. In other words, the second virial coefficient A_2 vanishes at the T_θ; however, the higher coefficients do not, and they are important at higher concentrations. One sees clearly in Figure 3 that for the corona $P'(0)$ does not approach unity as $T \rightarrow T_\theta \approx 100$ °C due to the relatively high volume fraction within the corona. To investigate this point further, we employ the recently derived expression from the Flory−Huggins RPA theory.[23,26] It can be shown that

$$\nu = \eta \frac{V_{\mathrm{PEG}}}{V_{\mathrm{H_2O}}}\left[\frac{1}{1-\eta} - 2\chi\right] \tag{6}$$

where η is the polymer volume fraction, V_{PEG} is the volume of a PEG block, $V_{\mathrm{H_2O}}$ is the volume of a water molecule, and χ is the Flory−Huggins interactions parameter. One sees as expected that $\nu \rightarrow 0$ for $\chi \rightarrow {}^1/_2$ when η is small but finite. When the expression is applied to the corona data, η is an average value of the corona. We will now show that we can estimate a reasonable value for η so that the data are in agreement with $T_\theta \approx 100$ °C. We will assume the simplest possible temperature dependence of χ, namely $\chi = {}^1/_2 + \alpha(T - T_\theta)$. Expression 5 with 6 and the expression for χ are fitted to the data, and the temperature dependence of V_{PEG} and $V_{\mathrm{H_2O}}$ derived from the density measurements is taken into account. One obtains $\eta = 0.070 \pm 0.002$ and $\alpha = 0.00124 \pm 0.00009$ 1/°C for $T_\theta = 100$ °C with an excellent fit to the data (Figure 3). χ varies linearly from 0.388 at 10 °C to $^1/_2$ at 100 °C. The average volume fraction of 7% seems reasonable for the corona, as there is a large weighting of the large distance regions in the radial profile, which has a large volume and a low polymer concentration. The consistency of the approach can be checked by calculating an average forward scattering from the profiles and comparing it to the values determined by the direct modeling of the SAXS data. In the calculation, $P'(0)$ from (6, 7) is weighted by the volume ($\rho(r)r^2$), taking $\eta = \rho(r)$ and using the dependence of χ on temperature just determined. This gives values of $P'(0)$ in the range 0.22−0.27, in reasonable agreement with those determined from the modeling of the SAXS data, although the temperature dependence is weaker.

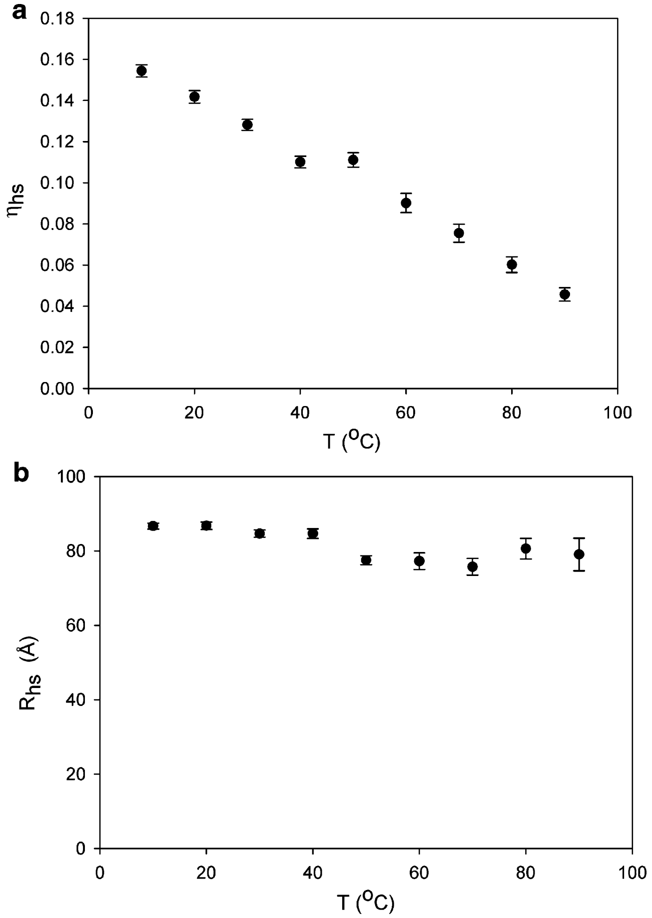

Figure 4. Parameters from the effective structure factor as a function of temperature: (a) hard-sphere volume fraction η_{HS}; (b) hard-sphere volume radius R_{HS}.

The effect of temperature is also significant for the parameters related to the intermicellar structure factor. The hard-sphere volume fraction η_{HS} of the micelles (Figure 4a) is around 15% at 10 °C and about 4% at 90 °C. Despite the low polymer concentration of 2 wt %, the highly swollen character of the PEG corona leads to quite high volume fractions. For dilute solutions, η_{HS} should approach zero for $T \rightarrow T_\theta$; however, the quite high volume fraction of the swollen particles prohibits this. A linear extrapolation of η_{HS} from the data at 80 and 90 °C suggests that η_{HS} reaches zero only at 110 ± 2 °C. The effective hard-sphere interaction radius R_{HS} (Figure 4b) decreases from about 87 Å at 10 °C to about 80 Å at 90 °C, in agreement with the changes in the PEG profile (Figure 2) as the PEG interactions becomes weaker. Note that the errors on R_{HS} increase at high temperature as the influence of the structure factor becomes weaker.

The detailed modeling has provided extensive quantitative information on the structure and profile of the core and corona, the chain interactions, and the structure factor effects as a function of temperature. We find it remarkable that the temperature dependence of the interchain interactions can be determined. It was shown that it is in agreement with the bulk Θ temperature of PEG using the Flory−Huggins RPA theory with a realistic average polymer concentration in the corona. The temperature dependence of the corona shape and the parameters related to the intermicellar interactions effects are both in agreement with the presence of Θ point at 100 °C.

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