Communications to the Editor

Scattering Form Factor of Block Copolymer Micelles

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When block copolymers are dissolved in a solvent which is a good solvent for only one of the blocks, micelles are formed.[1−4] Depending on the concentration, the temperature, and the relative length of the blocks, the shape of the micelles may be spherical, elliptical, or cylindrical.[1] The structure of the spherical micelles has been suggested to consist of a spherical core of the insoluble part surrounded by a shell of dissolved polymer chains. This shell is similar to the outer region of a multiarm star polymer or a brush consisting of end-grafted polymer chains. In this communication, we report an analytical expression for the form factor of a spherical micelle model consisting of a dense spherical core and polymer chains attached to the surface. To our knowledge, this is the first time that analytical expressions for the form factor have been calculated for such a model. We note that previous works based on scaling arguments have only given qualitative results[5] for the form factor.

In order to calculate the form factor, several different terms have to be determined: The self-correlation of the sphere, the self-correlation of the chains, the cross term between the sphere and chains, and the cross term between different chains. The normalized [$F_s(q=0,R) = 1$] self-correlation term for a sphere[6] with the radius R is given by $F_s(q,R) = \Phi(q,R)^2$, where $\Phi(q,R)$ is the amplitude of the form factor:

$$\Phi(q,R) = \frac{3[\sin(qR) - qR\cos(qR)]}{(qR)^3} \tag{1}$$

and q is the length of the scattering vector. For chains with Gaussian statistics, the self-correlation term is given by the Debye function:[7]

$$F_c(q,L,b) = \frac{2[\exp(-x) - 1 + x]}{x^2} \tag{2}$$

where $x = R_g^2q^2$ and R_g is the radius of gyration given by $R_g^2 = Lb/6$, with L the contour length and b the statistical segment (Kuhn) length of the chain.

The cross terms are calculated taking as a starting point the well-known Debye equation,[8] which gives the scattering function of particles consisting of subunits with spherical symmetry. Considering two separated infinitely thin shells, integrations over the radius of these shells and their separation have to be performed taking into account the correct weighting functions for, respectively, a solid sphere and the Gaussian chains.

The interference cross term between the sphere and a Gaussian chain starting at the surface of the sphere can be obtained after a few simple integrations. These include integrations over the Gaussian probability distribution and the contour of the chains. One thus obtains

$$S_{sc}(q) = \Phi(q,R)\psi(q,L,b)\frac{\sin(qR)}{qR} \tag{3}$$

The function $\psi(q,L,b)$ is the form factor amplitude of the chain:[9]

$$\psi(q,L,b) = \frac{1 - \exp(-x)}{x} \tag{4}$$

where $x = R_g^2q^2$ as before.

The interference term between the chains attached to the surface of the sphere can similarly be calculated as

$$S_{cc}(q) = \psi(q,L,b)^2\left[\frac{\sin(qR)}{qR}\right]^2 \tag{5}$$

after integrations over the two chains and over the distance distribution of the starting points of the two chains.

It is now possible to calculate the form factor of the micelle. If the aggregation number of the micelle is N_{agg} and the total excess scattering length of the blocks in the spherical core and in the chain are, respectively, ρ_s and ρ_c one obtains

$$F_{mic}(q) = N_{agg}^2\rho_s^2F_s(q,R) + N_{agg}\rho_c^2F_c(q,L,b) + N_{agg}(N_{agg} - 1)\rho_c^2S_{cc}(q) + 2N_{agg}^2\rho_s\rho_cS_{sc}(q) \tag{6}$$

The forward scattering is

$$F_{mic}(q=0) = N_{agg}^2(\rho_s + \rho_c)^2 \tag{7}$$

Note that these expressions reproduce the form factor of a Gaussian star polymer for $R \to 0$.[10]

In the derivation of the form factor the chains are free to penetrate into the core, which is obviously unphysical. In order to investigate this effect, we have carried out Monte Carlo simulation on micelles both with and without core penetration of the chains.[11] The Gaussian chains were generated as random walks in three dimensions starting at the surface of the sphere. In the case of nonpenetration of the core, the chains were first generated and simply rejected if they penetrated the core. Excluded volume interactions between the chains were neglected. Simulations were performed for a micelle with 60 attached chains with 15 random steps in each. The core radius is 10 times the unit step length of the random walks used for generating the chains. For each example 1000 independent samples were generated. For the penetrating chains there is very good agreement between the analytical and simulated results for the form factor.

Figure 1 shows the form factor for nonpenetrating chains for two contrasts $\rho_s/\rho_c = {}^7/_9$ and $-{}^7/_9$, respectively

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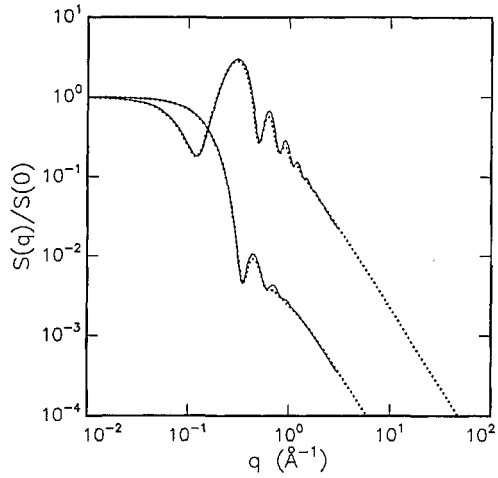

Figure 1. Calculated and simulated normalized scattering functions for two different contrasts. The full curves are the results from the Monte Carlo simulations for nonpenetrating chains. The dotted curves are for the analytical expression with the chains starting at $R' = R + R_g$.

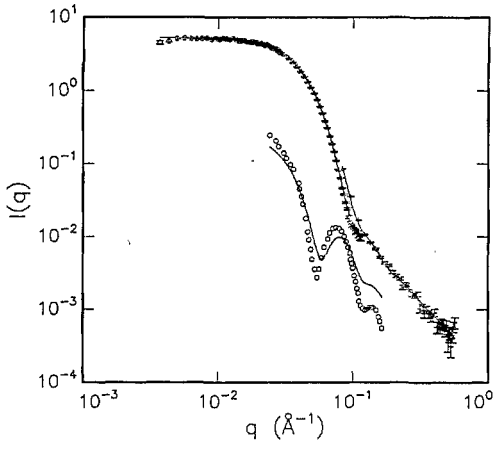

Figure 2. Small-angle neutron scattering data of 0.5% P85 ($EO_{25}PO_{40}EO_{25}$) in D_2O (upper data). The data were recorded using three different instrumental settings. The curve is the fit by the analytical model including polydispersity of the micelles. Note that the fitted curve is discontinuous where the data from different settings overlap due to the instrumental smearing. The lower data are SAXS results on similar micelles.[4] The curve is calculated for the results determined by fitting the SANS data.

(arbitrarily chosen). The scattering curves show a q^{-2} behavior at large q, which is characteristic of the Gaussian chains. For $\rho_s/\rho_c = {}^7/_9$ the scattering function is dominated by the scattering from the spherical core at low q, whereas for $\rho_s/\rho_c = -{}^7/_9$ the scattering functions show large-amplitude oscillations due to the abrupt change in the sign of the scattering length density at the surface of the sphere. Also show in Figure 1 is the form factor calculated by the analytical solution with the chains starting at $R' = R + R_g$.[12] The agreement is good and this shows that (for $R \gg R_g$[11]), the effect of nonpenetration can be mimicked by moving the starting points of the chains from the distance R to $R' \approx R + R_g$ from the center.

The analytical expression for the form factor has been used for analyzing scattering data. The first example (Figure 2) is micelles in a 0.5% solution of P85 [poly(ethylene oxide)−poly(propylene oxide)−poly(ethylene oxide)] in D_2O at $T = 50$ °C. The measurements were performed on the SANS instrument at Risø National Laboratory.[13] Note that at large q the q^{-2} scattering from the chains around the core is observed. For comparison, the small-angle X-ray scattering (SAXS) data recorded by Glatter *et al.*[4] are also shown. The two scattering curves are remarkably different.

The intermicellar effects were included in the analysis of the SANS data using a hard-sphere structure factor.[1,14,15] The theoretical scattering curve was smeared by the instrumental resolution function,[16] when the fit to the experimental scattering data was performed. The excess scattering length densities were calculated from the composition of the P85 triblock copolymer and the specific volumes, which can be derived from density measurements.[17] The contour length of the PEO chains were calculated to be 90 Å.[19,20] Polydispersity of the micelles was included using a Schultz distribution for the aggregation number.[18] In a first attempt the core was assumed to be constituted solely of the PPO parts of the chains. The distance from the surface of the core to the starting points of the Gaussian chains was a fitting parameter.

The model fits the scattering data reasonably well. The main deviations are in the region where there is a crossover in the scattering data to the q^{-2} behavior. In order to achieve perfect agreement in this region, it was necessary to include a low-density PEO shell around the core in accordance with the suggestion in ref 1. For this model the average aggregation number was $N_{agg} = 74$, which corresponds to a radius of the PPO core of $R = 40$ Å. The additional shell contains 23% of the PEO chains with a water content of 77%. The outer radius of this shell is 49 Å. The Kuhn length is determined to be $b = 10$ Å, which agrees well with previous estimates.[20] The starting point for the PEO chains is $0.25R_g$ away from the surface of the PEO core shell. The polydispersity of the aggregation number is $\sigma(N_{agg})/N_{agg} = 0.37$, where $\sigma(N_{agg})$ is the standard deviation of the Schultz distribution. The corresponding polydispersity of the radius of the core is $\sigma(R)/R \approx 0.13$. This relatively large polydispersity could explain why the shear-induced single-crystal bcc phase observed at higher concentration possesses only angular order and not positional order.[21]

The corresponding scattering intensity of the resulting model for X-rays was also calculated. The excess electron density of the PPO is slightly negative and significantly smaller than the (positive) electron density of the PEO. Thus the scattering is dominated by the PEO shell. The resulting intensity, after adjusting only an overall scale factor, is shown in Figure 2. The model intensity curve reproduces the pronounced oscillation close to $q = 0.1$ Å^{-1} in the measured data and a reasonable qualitative agreement is obtained.

The small-angle neutron scattering data of 2% polystyrene-*d*-polyisoprene (*d*-PS−PI) in decane-*d* are shown in Figure 3.[2] The PS is insoluble in decane and micelles are formed. The deuterated PS core has a scattering length density which is close to that of the solvent, and therefore the main part of the scattering intensity originates from the PI chains. One observes also for this example a q^{-2} behavior at large q. The SANS data from the shell of PI chains has a pronounced secondary maximum in the form factor at around $q = 0.03$ Å^{-1}, which is quite different from the SANS data for the P85 micelles but similar to the SAXS data for the P85 micelles, for which the scattering is dominated by the scattering from the chain shell.

The scattering length density were determined from the densities[22] using the known composition of the

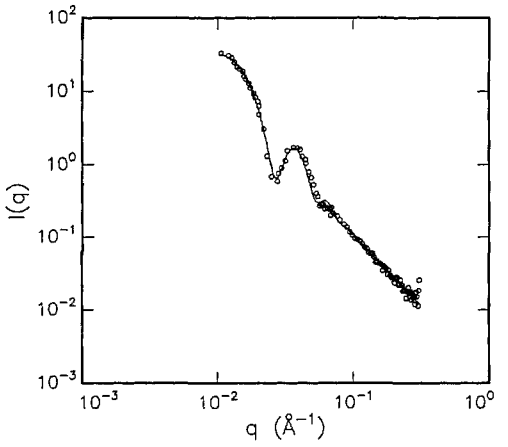

Figure 3. Small-angle neutron scattering data of 2% *d*-PS–PI in decane-*d*.[2] The curve is the fit by the analytical model including polydispersity of the micelles.

molecules. The contour length of the PI chains was calculated to be 139 Å.[20] The fit to the scattering data is shown in Figure 3. The model reproduces quite well the pronounced maximum at 0.03 Å^{-1} and the q^{-2} behavior at large q. The fit was obtained with the following parameters: $N_{agg} = 230$ ($R_{av} = 95$ Å), $\sigma(N_{agg})/N_{agg} = 0.30$, and $b = 19$ Å. The center of the Gaussian chains is moved $0.90R_g$ away from the surface of the core. The aggregation number and radius are in good agreement with the estimates in ref 2. The value for b is somewhat larger than previous estimates for PI.[20]

In this communication we have calculated simple expressions for the form factor of a spherical micelle with a dense core and Gaussian chains attached to the surface. The method used for the calculation is straightforward to apply to derive semianalytical expressions for the form factor of elliptical and cylindrical micelles. We note that the present expressions also apply to the case of polymers adsorbed on a spherical particle and include the fluctuation term discussed in refs 23 and 24.

We have demonstrated that the analytical expressions can be used for analyzing the experimental small-angle scattering data for P85 and PS–PI micelles. The new expression makes it possible to give a higher resolution interpretation of the data as the scattering data can be described by the model in the full range of measured scattering vectors. Further details on the calculations and simulations, including work on elliptical and cylindrical micelles, will be published in the future.[11]

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