Star-Like Micelles with Star-Like Interactions: A quantitative Evaluation of Structure Factors and Phase Diagram

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PEP-PEO block copolymer micelles offer the possibility to investigate phase behaviour and interactions of star polymers (ultra-soft colloids). A star-like architecture is achieved by an extremely asymmetric block ratio (1:20). Micellar functionality $f$ can be smoothly varied by changing solvent composition (interfacial tension). Structure factors obtained by SANS can be quantitatively described in terms of an effective potential developed for star polymers. The experimental phase diagram reproduces to a high level of accuracy the predicted liquid/solid transition. Whereas for intermediate $f$ a bcc phase is observed, for high $f$ the formation of a fcc phase is preempted by glass formation.

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Star polymers, i.e. $f$ polymer chains tethered to a central microscopic core, can be regarded as ultra-soft colloids bridging the properties of linear polymer chains and hard sphere colloids 1. The hybrid character is reflected in their effective interaction potential introduced by Likos et al. 2,

$$
\beta V(r) = \frac{5}{18} f^{3/2} \left[ -\ln \left( \frac{r}{\sigma} \right) + \frac{1}{1 + \sqrt{f/2}} \right], \quad r \leq \sigma
$$

$$
= \frac{5}{18} f^{3/2} \frac{\sigma/r}{1 + \sqrt{f/2}} \exp \left[ -\sqrt{f}(r - \sigma) \right], \quad r \geq \sigma
$$

(1)

with $\beta = 1/k_B T$, $r$ the distance between star centers and $\sigma$ the corona diameter. Eq. (1) has given good results in modelling small angle neutron scattering (SANS) data of star polymer solutions 2, 3. The corresponding theoretical phase diagram 4 shows unique features, such as different crystalline phases depending sensitively on volume fraction $\phi$ and $f$. Recently the phase diagram has been revisited to include the glass transition as a result of dynamical arrest of the system 2, corroborating several experimental studies 3, 4, 5.

Unfortunately, the high interest in star polymers is not reflected in their availability. Synthesis requires considerable preparative efforts, therefore it is of particular interest to substitute star polymers by an easy to establish model system. Ideally, this analogue should not only show the typical molecular architecture of star polymers, but also interact via the effective potential given in Eq. (1).

A few attempts to connect micellar systems to star polymers have been done, however, approaching the star-like regime 4, 6 defined by the block ratio $N_a/N_b \gg 1$ (with $a/b$ the soluble/insoluble block) is not trivial. Gast et al. investigated poly(styrene)-poly(isoprene) (PS-PI) block copolymers 7. They found experimental evidence for fcc and bcc phase formation, with crystalline geometry determined by block composition ($0.8 \leq N_a/N_b \leq 4$). Recently PS-PI 11 and PEO-PBO 12 micelles showed a temperature induced fcc-bcc transition. This transition could be related to changes in $f$ and compared to the phase diagram of star polymers indicating some similarities in the interactions although the block ratio was rather small, $N_a/N_b \approx 2$ 11. Micelles formed by hydrophobically modified PEO with $N_a/N_b \approx 150$ have been investigated 13, but interactions were characterized by mapping onto an equivalent hard sphere system. Therefore, a systematic study to correlate the star-like architecture of the individual micelle with star-like interactions has never been performed.

In this Letter we show that structure factors of poly(ethylene-alt-propylene)-poly(ethylene oxide) (PEP-PEO) micelles (which fulfill all prerequisites of the star-like regime 14, 17, 16) provide the basis to investigate such a correlation. SANS measurements at core contrast allow a direct determination of experimental structure factors $S(Q)$ which can be described starting from Eq. (1) with parameters $\phi$, $f$, and $\sigma$ directly given by experimental values. In addition, we can reproduce to a high level of accuracy the liquid-solid transition of the theoretical phase diagram. This was done over a wide range of $f$ and spanning the range from dilute to concentrated solutions, providing a comprehensive characterization of block copolymer micelles in terms of the microscopic, effective potential originally developed for star polymers.

The micellization behavior of PEP-PEO in aqueous solution is governed by the high interfacial tension, $\gamma = 46\; mN/m$, between PEP and water and shows the following features 14, 17: i.) PEP-PEO forms micelles with the hydrophilic PEO constituting the core and the hydrophobic PEO constituting the corona. ii.) Micelles are even formed in a very asymmetric block composition with high PEO content ($N_a/N_b \approx 20$). iii.) All micellar
cores are completely segregated, i.e. not swollen by solvent. iv.) The micelles are kinetically frozen: Although chemically not linked, exchange of block copolymers between different micelles could not be observed, even not at elevated temperatures [18]. This means that no free chains, i.e. no depletion effects [19] are present in contrary to ref. [11]. v.) Adjusting γ by addition of a PEO selective cosolvent like N,N-dimethylformamide (DMF), allows to smoothly vary f even in the star-like regime (where f ∼ γ 6/5 was confirmed by experiments [15]).

The asymmetric PEP-PEO block copolymer under study was synthesized by anionic polymerization [17]. To exploit h/d-contrast variation in our SANS experiments, the individual blocks have been selectively protonated/deuterated, see Tab. I. Using water/DMF mixtures we prepared samples with six different f going from dilute to the very concentrated regime. Since the micelles are kinetically frozen, all samples were directly prepared in the corresponding solvent mixture and annealed for at least 1 week, for experimental details see [17]. SANS data were corrected following standard procedures and normalized to absolute units to allow a quantitative theoretical interpretation.

The macroscopic scattering cross section, (dΣ/dΩ)(Q), measured by SANS can be expressed as a product of single particle contributions, the particle form factor P(Q), and the structure factor S(Q), which contains all information about particle interactions:

\[
\left(\frac{d\Sigma}{d\Omega}\right)(Q) = N_z \ P(Q) \ S(Q)
\]  

Here \(N_z\) is the number density of particles. Experimental S(Q) can be extracted from SANS data by dividing out the experimental P(Q) measured in dilute solution. However, this procedure is only valid, if particle size and shape, i.e. P(Q), are unaffected by concentration. This is in general not the case for deformable particles like micelles, but we can overcome this problem by proper application of contrast variation techniques. Performing all SANS experiments in core contrast, i.e. adjusting the scattering length density \(\rho_0\) of the solvent by use of h/d-isotopic mixtures to that of PEO, reduces the contrast factor between corona and solvent to zero, see Tab. I. Only the compact PEP core, which is completely unaffected by increasing concentration, is “visible” in the SANS experiment.

Micellar characteristics, i.e. functionality f, core radius \(R_c\) and overall micellar radius \(R_m\) have been determined as described in [15, 16]. \(R_m\) in Tab. I is calculated according to \(R_m^6 = \sqrt{5/11}R_m\) valid for star polymers, \(R_{g,core}\) according to \(R_{g,core} = \sqrt{3/5}R_c\) valid for solid spheres.

In this Letter we will focus on the results obtained from concentrated solutions, where particle interactions are dominant. Fig. 1 shows the comparison between S(Q) obtained for micelles with \(f = 63\) (■) compared to 64-arm (nominal) PB star (○), both samples have the same ratio \(\phi/\phi^* \approx 1\). Solid line: Theoretical S(Q) calculated by applying the RY-closure for the OZ-equation starting from Eq. I see text.

| Table I: Characterization of PEP-PEO block copolymer |  |
|-----------------------------------------------------|---|
| \(M_n\) | \(M_W/M_n^z\) | \(D_p\) | \(x_b\) | \(\rho\times10^3\text{cm}^{-2}\) |
| PEP (block) | 1100 | 1.06 | 15 | 1.0 | -0.31 |
| PEO (block) | 20700 | 1.04 | 436 | 0.11 | 6.32 |
| \(x_{DMF}\) | \(\rho_0\times10^3\text{cm}^{-2}\) | \(f\) | \(R_{g,core}\) | \(R_b\) | \(R_g\) |
| 0.0 | 6.33 | 136 | 31 | 194 | 192 |
| 0.1 | 6.32 | 94 | 29.5 | 179 | 161 |
| 0.2 | 6.34 | 82 | 29 | 164 | 154 |
| 0.3 | 6.33 | 73 | 27 | 150 | 140 |
| 0.4 | 6.31 | 67 | 27 | 140 | 136 |
| 0.5 | 6.31 | 63 | 26 | 135 | 127 |

\(^a\)overall polydispersity by SEC
\(^b\)From form factor analysis
\(^c\)From \(\sigma\) values obtained from fits
FIG. 2: Experimental intensities I(Q) for f = 63 at different φ in the fluid phase, φ < φ*: (●) φ = 0.017, (□) φ = 0.034, (▲) φ = 0.051, (○) φ = 0.067 and fits (solid lines). For clarity I(Q) are divided by factors: (○) 1, (▲) 1.5, (□) 2, (●) 3. Inset: volume fraction dependence of σ for f = 63, showing the expected scaling behavior σ ∼ φ′ for φ > φ∗.

FIG. 3: Experimental phase diagram (symbols) of star-like micelles vs. theoretical phase diagram (lines) of star polymers. (○) liquid, (■) bcc crystal and (▲) gels. Dashed line represent equilibrium phase diagram from Ref. 2. The solid line is the RY-ideal MCT glass line from Ref. 2. Inset: 2-dimensional SANS detector picture of f = 63, φ = 0.16 evidencing Bragg reflections.

On the basis of the good agreement between theory and experiment we then applied this analysis procedure to all f and φ studied. The excellent quality of the fits for \( Q \geq 10^{-2} \text{Å}^{-1} \) is shown in Fig. 2 for samples of different φ but same functionality f = 63. For φ ≤ φ∗ we found a nearly constant corona diameter giving a mean value \( \bar{\sigma} = 226 \pm 4 \), which corresponds to the low concentration, unperturbed corona diameter. \( \bar{\sigma} \) was then used to transform the given experimental number density \( N_z \) to the packing fraction \( \eta = N_z / \sigma^3 \). \( R_g \) values calculated from \( \bar{\sigma} \) are compared to results from form factor analysis in Tab. I.

Above φ* we had to use a different approach for recalculating \( \eta \). According to the Daoud-Cotton theory \( \eta \) the stars are expected to shrink as \( \propto \phi^{1/8} \), and indeed, the fit values for \( \sigma(\phi > \phi^*) \) show exactly this scaling behaviour as shown in the inset of Fig. 2. Therefore we decided to use the individual \( \sigma(\phi) \) for recalculating \( \eta \). Calculating \( \eta \) this way for all f, we could then compare experimental and theoretical phase diagrams, as shown in Fig. 3. The transition from the liquid to the crystalline state (body centered cubic, bcc) predicted by theory is perfectly reproduced in experiments for f = 63 and f = 67. The experimental critical packing fraction for crystallization is found to be \( \eta = 0.21 \). Direct evidence for crystal formation comes from the presence of Bragg peaks in the 2-dimensional SANS pattern as shown in the inset of Fig. 3 for f = 63 and \( \phi = 0.16 \). Moreover crossing \( \phi^* \) the first peak of \( S(Q) \) assumes a value bigger than 2.8, which is the minimum value for a freezing transition according to the Hansen-Verlet criterion (see Fig 3). The peak is further growing with increasing \( \phi \). Additionally for \( \phi > \phi^* \) a third small peak is forming, and the position ratio between the three peaks is \( 1: \sqrt{2} : \sqrt{3} \) corresponding to a simple cubic (sc) or bcc lattice. The A15 lattice can be directly excluded, since its additional third reflection at \( \sqrt{5}/2 \) is expected to occur in a region.
The lattice constants where the form factor is close to unity. A comparison of
ratios characteristic for bcc crystal (bold arrows). Expected
peak positions for fcc (dashed arrows) and A15 crystals. Solid lines: Guide to the eye.

where the form factor is close to unity. A comparison of
the lattice constants \( a_{\text{sc}} = 270 \text{Å} \) and \( a_{\text{bcc}} = 381 \text{Å} \) with
\( 2R_m = 377 \text{Å} \) at \( \Phi^* \) excludes the sc lattice, identifying the
crystal as a bcc lattice. With increasing \( \eta \) no evidence
for the predicted transition to a fcc phase is found in our
data. However, we also note that for regular star polymers
a bcc-fcc transition was never observed, probably
due to the small free energy difference, \( \approx kT \), between
the two crystalline phases [26].

With increasing \( f \) the experimentally observed liquid-solid transition is in nearly perfect agreement with the
phase boundary predicted by theory, but instead of ob-
serving a fcc phase we observe disordered solid-like structures
for all \( f \geq 73 \). Location of the solidus line comes
from a double evidence: First from tube inversion, which
means that we tested the non-flowing behavior of the
sample inverting sample holders in a bath at constant
temperature. In addition, preliminary rheology exper-
iments confirm a non-zero storage modulus. Structure
factor peaks for \( \phi > \phi^* \) are definitely smaller than 2.8,
excluding formation of a crystal, as shown in Fig. 4.
Therefore we identify this disordered phase as a crystal.
The suppression of the expected equilibrium fcc phase
and the early onset of glass formation at packing frac-
tions smaller than expected from theory, might arise from an "effective" polydispersity induced by the clusters dis-
cussed above [27]. At lower \( f \), where MCT glass line and
crystal line are well separated, this effect does not play
such an important role and we do observe the crystal
there.

In conclusion, we have shown that star-like PEP-PEO
micelles show the same interactions as star polymers, giv-
ing a significant experimental support to the picture of
star polymers as ultra-soft colloids. We have been able
to quantitatively describe experimental structure factors
\( S(Q) \) starting from a microscopic effective potential pre-
dicted for star polymers. The softness of the interaction
potential between star-like micelles can be precisely var-
ied by adjusting the interfacial tension \( \gamma \) between PEP
and the used solvent. In addition, we performed a de-
tailed investigation of the phase diagram as a function
of functionality \( f \) and packing fraction. In particular
we determined the critical packing fraction for liquid-
bcc crystal transition, finding excellent agreement with
theory. The simple synthesis of PEP-PEO block copoly-
mers compared to star polymers in combination with the
shown analogy in terms of effective interactions establish
these micelles an excellent alternative for investigating
the phase behaviour of ultra-soft colloids.

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