

Depletion Interactions: A New Control Parameter for the Self-Assembly of Diblock Copolymer Micelles

Sayed Abbas and Timothy P. Lodge

Departments of Chemistry and Chemical Engineering & Materials Science, University of Minnesota, Minneapolis Minnesota 55455, USA

(Received 21 January 2007; published 28 September 2007)

Small angle neutron scattering was performed on disordered mixtures of nonadsorbing homopolymer (A) chains and diblock (A-B) copolymer micelles in an A selective solvent. Increasing the molecular weight or concentration of A led to an increase in the aggregation number, and a decrease in the effective hard-sphere diameter of the micelles. Furthermore an intermicellar attractive force developed, which was successfully modeled by the Asakura-Oosawa depletion potential. Via an alternative model we also extracted information about mesoscopic clusters of micelles formed due to this attractive force.

DOI: [10.1103/PhysRevLett.99.137802](https://doi.org/10.1103/PhysRevLett.99.137802)

PACS numbers: 61.25.Hq, 61.12.Ex, 83.80.Qr

The effects of depletion interactions induced by the addition of a nonadsorbing homopolymer have been extensively studied in colloidal systems [1–3] and star polymer solutions [4–6]. Direct experimental measurements of the effective pair potential between colloidal particles [7,8] along with theoretical calculations [9–11] show that a net attractive force develops between the particles when a homopolymer is added. The amplitude and range of the attractive force depends on the homopolymer concentration and molecular weight. As block copolymer micelles share many similarities with colloids and star polymers, it is of fundamental interest to explore whether depletion forces can also be induced in these systems. In contrast to colloidal or star polymer systems, however, block copolymer micelles offer two levels of hierarchical self-assembly: the micellization process itself, and the ordering of micelles onto a lattice. In this Letter, we show that addition of homopolymer affects both levels of self-assembly and thereby offers us a new tool to control the phase behavior of micelles. In an interesting precedent Won *et al.* showed that, when an adequate homopolymer was added to a dilute micellar solution, the system underwent phase separation [12]. However, the previous studies [13,14] on micellar systems did not document whether the addition of homopolymer affected the micelle self-assembly itself.

In this Letter we report small angle neutron scattering (SANS) experiments on dilute (1 vol%) and semidilute (10 vol%) solutions of poly(styrene-*b*-deuterated isoprene) (SdI) diblock copolymers in diethyl phthalate (DEP) with block molecular weights of 15 kDa and 14 kDa, respectively. Henceforth the diblock will be referred to as SdI(15-14) and the polystyrene homopolymers of molecular weights 48 kDa and 180 kDa as *S*(48) and *S*(180), respectively. The synthesis and characterization of these polymers has been described previously [15]. DEP is a selective solvent for *S* and, as a result, micelles with *S* in the corona and deuterated isoprene (dI) in the core are formed. Since

the neutron scattering length density of *S* ($\rho_S = 1.41 \times 10^{10} \text{ cm}^{-2}$) and DEP ($\rho_{\text{DEP}} = 1.53 \times 10^{10} \text{ cm}^{-2}$) are closely matched, the SANS intensity arose primarily from the dI cores ($\rho_{\text{dI}} = 6.85 \times 10^{10} \text{ cm}^{-2}$). Hence these “core contrast” conditions enabled us to study the effective intermicellar interactions in the presence of homopolymer. The SANS measurements were taken on the 30 m NG7 (ExxonMobil/University of Minnesota) beamline at NIST. Data were corrected for transmission, solvent scattering, background, empty cell, and detector sensitivity, and placed on an absolute scale using the direct beam method.

The SANS traces (intensity *I* versus scattering vector *q*) from 1% of SdI(15-14) alone, and mixed with either 2% (0.021 g/mL) of *S*(48) or *S*(180), were successfully fitted by a detailed form factor expression developed by Pedersen and coworkers [16], as shown in Fig. 1. The results from the fitting are shown in Table I. The aggregation number (*f*) and core radius (R_c) increase modestly with added homopolymer, and when the homopolymer molecular weight is increased. These trends are consistent with theoretical calculations by Halperin on a similar system [17]. We can rationalize these results by noting that the homopolymer can partly screen the excluded volume interactions in the corona. As a result, the free energy contribution from the corona diminishes and the interfacial free energy, which favors increasing the surface area of the core, drives up *f*. The screening of the excluded volume interactions and decrease in end-to-end length (R_{cor}) of the corona chains is evident from the reduction of effective sphere radius (R_s), which was calculated as $R_s = R_c + R_{\text{cor}}$. The large error bars of the Δf values are primarily due to the uncertainty in the contrast parameters. The scattering length densities of *S* homopolymer and DEP are not the same, and there is an inherent background noise in the sample which contributes to the large error bars. The density of the micelle core is approximately equal to the bulk density of PI, thereby indicating that all solvent is

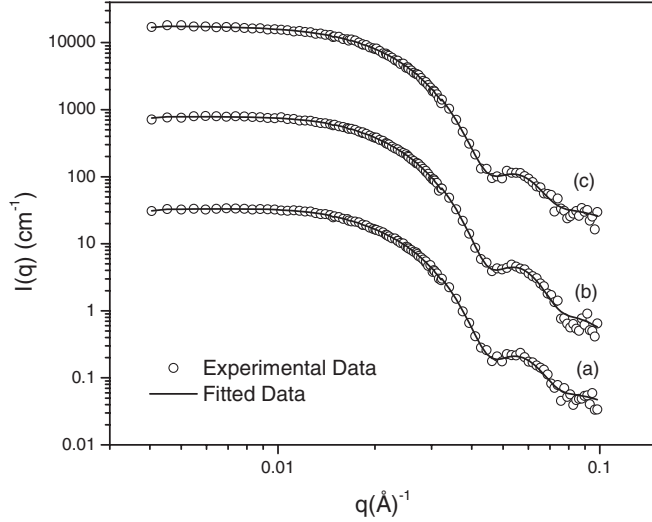


FIG. 1. Scattering from dilute solutions in DEP of (a) SdI(15-14) 1% (b) SdI(15-14) 1% + S(48) 2%, and (c) SdI(15-14) 1% + S(180) 2%. For clarity the experimental data in (b) and (c) have been shifted vertically by factors of 20 and 500.

excluded from the core of the micelles. If we calculate the Δf (by noting that $f \sim R_c^3$) from the increase in R_c , the results are identical to those obtained from direct fitting.

SANS measurements were performed on 10% solutions of SdI(15-14) in DEP, mixed with 2% (0.021 g/mL) and 4% (0.042 g/mL) of S(48) or S(180) homopolymer, as shown in Fig. 2. The Ornstein-Zernike (OZ) equation was solved iteratively utilizing the Percus-Yevick closure. The volume fraction of micelles (in the solution SdI 10% DEP) calculated by assuming the overall radius of micelles to be equal to 204 Å (estimated from form factor fitting and given in Table I) is $\approx 40\%$. However, direct comparisons with colloidal systems based on the volume fraction of micelles may be misleading because solvent is present in the corona of the micelles and hence the exact volume occupied by a micelle cannot be accurately calculated. At 10% diblock the micelle solution behaves like a disordered liquid, with a distinct structure factor peak. The Asakura-Oosawa (AO) depletion potential, as described by Eq. (1), was taken as the effective intermicellar pair potential [18]

$$U(r) = \begin{cases} +\infty & r \leq \sigma \\ -\Pi_0 V_0(r) & \sigma < r \leq \sigma + 2R_g \\ 0 & r > \sigma + 2R_g \end{cases} \quad (1)$$

Here R_g is the radius of gyration of the homopolymer and

TABLE I. Results from form factor fit.

Sample	R_c (Å)	f	R_s (Å)
SdI 1% DEP	104 ± 0.2	189 ± 7	204 ± 6
SdI 1% + S(48) 2% DEP	105 ± 0.2	196 ± 8	188 ± 6
SdI 1% + S(180) 2% DEP	106 ± 0.3	201 ± 17	174 ± 10

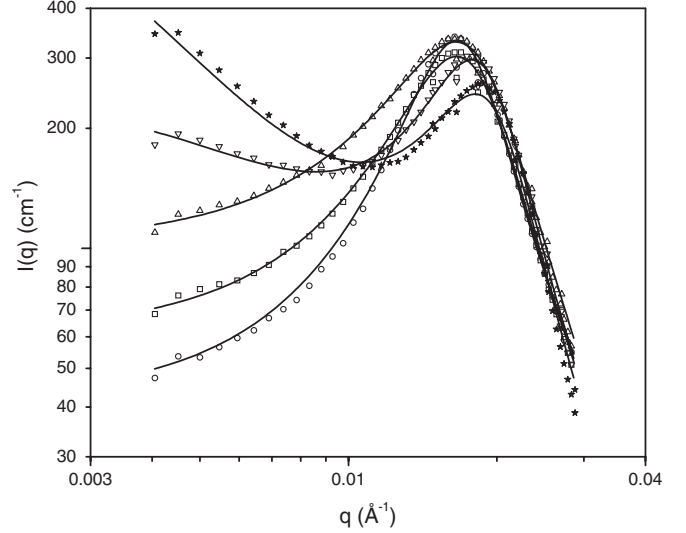


FIG. 2. SANS from semidilute DEP solutions containing (○) SdI(15-14) 10%, (□) SdI(15-14) 10% + S(48) 2%, (△) SdI(15-14) 10% + S(48) 4%, (▽) SdI(15-14) 10% + S(180) 2%, and (*) SdI(15-14) 10% + S(180) 4%. The fits are shown by solid lines.

σ is the hard-sphere diameter of the micelle. Π_0 is the osmotic pressure of the homopolymer chains in the solution. The overlapping depletion volume ($V_0(r)$) is given by the expression

$$V_0(r) = v_p \left(\frac{\lambda}{\lambda - 1} \right)^3 \left\{ 1 - 1.5 \left(\frac{r}{\sigma \lambda} \right) + 0.5 \left(\frac{r}{\sigma \lambda} \right)^3 \right\} \quad (2)$$

where v_p is the pervaded volume of an individual homopolymer chain and $\lambda = 1 + 2R_g/\sigma$. The form factor from dilute solution [$P(q)$], and the structure factor ($S(q)$) obtained by solving the OZ equation were then used to fit the net scattered intensity via the decoupling approximation [19]: $I(q) = nP(q)S(q)$, where n is the number density of micelles. The fitting parameters include σ , λ , η (the reduced micelle number density, defined as $\eta = \frac{\pi}{6} n \sigma^3$) and \hat{P} defined as $\hat{P} = \Pi_0 v_p / k_B T$. The results of the fitting are shown in Fig. 2 and are tabulated in Table II. In the high $2R_g/\sigma$ limit, it is known that the AO model does not give a satisfactory description of depletion interactions [20]. Furthermore, micelles act like soft spheres, whereas the AO model has always been applied to describe the phase behavior of hard spheres. Nevertheless we use the AO

TABLE II. Results from Asakura-Oosawa model fit.

Sample	η	σ (Å)	λ	\hat{P}	$+\Delta f$ (%)
SdI 10% DEP	0.273	357	NA	NA	0
SdI 10% + S(48) 2% DEP	0.234	346	1.384	0.03	5.7 ± 0.1
SdI 10% + S(48) 4% DEP	0.211	346	1.392	0.098	17 ± 0.1
SdI 10% + S(180) 2% DEP	0.215	338	1.732	0.322	7.5 ± 0.1
SdI 10% + S(180) 4% DEP	0.157	331	1.706	0.458	38 ± 0.7

model as a first approximation and, as the results show, the model satisfactorily fits the data provided. λ and Π_0 (subsumed in \hat{P}) are kept as fitting parameters. λ was kept as a fitting parameter because R_g of pure homopolymer chains will not necessarily be the same as when in the presence of micelles. The estimated bulk R_g values for $S(48)$ and $S(180)$ are 59 Å and 113 Å, respectively, and the fitted values are 66 Å and 123 Å, respectively. The fitted values are higher because the chains are in a good solvent.

The scattered intensity at low q increases markedly as more homopolymer is added, and the position of the primary peak shifts slightly to higher q values for the $S(180)$ solutions. These results indicate that attractive interactions between micelles are increasing, and the coronal chains are shrinking, as more homopolymer is added. The effects are more pronounced with the higher molecular weight $S(180)$. We also observe that for micelle solutions with $S(180)$, the intensity increases particularly sharply at low q , suggesting the presence of large mesoscopic structures in the solution. The σ values are lower than $2 \times R_s$, which can be attributed to compression of the corona chains due to the higher number density of micelles. The amplitude of the depletion potential (\hat{P}) increases with concentration and molecular weight of homopolymer, as expected. The reduced number density (η) of micelles also decreases, which supports the previous result that the aggregation number increases with the addition of homopolymer. By noting that $\eta/\sigma^3 \sim 1/f$, Δf was calculated by taking the sample SdI 10% DEP as the reference. The uncertainty in the Δf calculations was less than 1%, primarily because in semidilute solutions the signal to noise ratio is much better and uncertainty in contrast does not play a large role. However, for the solution SdI(15-14) 10% + $S(180)$ 4% DEP, η is suspiciously low, and the quality of the fit in Fig. 2 is less satisfactory. This raises the question as to whether the micelles in this regime can be described by assuming the solution is a homogeneous disordered liquid.

Recently, confocal microscopy showed that when homopolymer was added to a colloidal solution mesoscopic clusters of particles were formed [21,22]. We hypothesize that, by analogy, the sharp increase in $I(q)$ at low q for the $S(180)$ solutions indicates the formation of micellar clusters. We propose a very simple model where the net scattered intensity is approximated as a sum of the scattering from the clusters and from the solution of nonclustered “free” micelles:

$$I_{\text{net}} = I_{\text{free}} + I_{\text{cluster}}. \quad (3)$$

We further assume that the number density of the clusters is not high enough to consider a scattering contribution from intercluster correlations [23]. The structure factor of I_{free} was calculated by assuming the micelles interact via a hard-sphere potential. The expression for the structure factor of clusters is given by [24]:

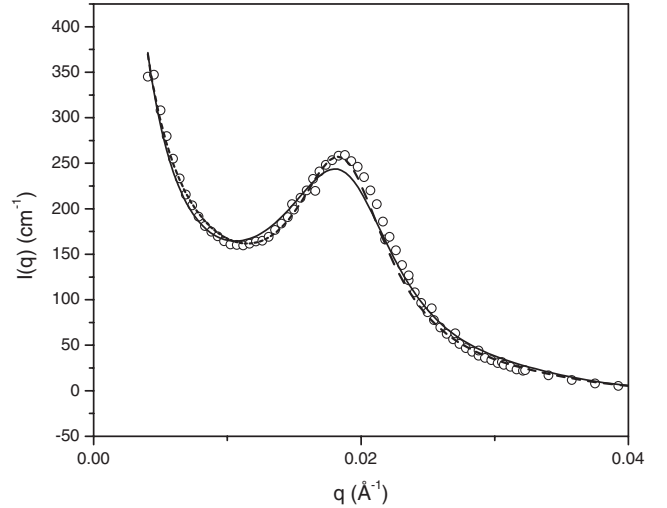


FIG. 3. Scattering (\circ) from the sample SdI 10% DEP + $S(180)$ 4%. The data has been fitted by the depletion model (solid line) and the cluster model (dashed line). The cluster model fits the experimental data better than the depletion model.

$$S(q) = 1 + A \left[\frac{\xi}{r_0} \right]^D \frac{\Gamma(D+1)}{(1+q^2\xi^2)^{(D-1)/2}} \times \frac{\sin[(D-1)\arctan(q\xi)]}{(D-1)q\xi} \quad (4)$$

where A is an amplitude parameter, D is the fractal dimension of the cluster, ξ is an exponential decay length to describe finite clusters, r_0 is the radius of the particle in the cluster, and Γ is the gamma function. Only the $S(180)$ solutions have pronounced low q scattering and hence they were fitted to this model. Figure 3 shows that the quality of fit for the sample SdI 10% + $S(180)$ 4% DEP has improved significantly by using this cluster model. The results are summarized in Table III.

The parameter ξ represents the correlation length of the clusters, whereas the shape of the cluster is revealed by D . The average aggregate size R_{clus} can be obtained from ξ as $R_{\text{clus}} = \xi[(D+1)(D+2)/2]^{1/2}$ [24]. The low values of R_{clus} and D for the sample SdI 10% + $S(180)$ 2% DEP suggest that the clusters are composed of tens of micelles and are extended objects. For the sample SdI 10% + $S(180)$ 4% DEP, both R_{clus} and D have increased, thus indicating that the clusters grow in size as more homopolymer is added to the solution. By comparing the value of r_0 with that of σ values reported in Tables I and II, we conclude that significant overlap of coronal chains occurs within the aggregates. The $S(180)$ solutions did not macro-

TABLE III. Results from cluster model fit

Sample	A	ξ (Å)	R_o (Å)	R_{clus} (Å)	D
SdI 10%DEP + $S(180)$ K 2%	2.303	610	149	1083	1.06
SdI 10%DEP + $S(180)$ K 4%	2.092	879	137	1822	1.474

phase separate or form a gel over time and thus we can infer that the clusters formed are equilibrium clusters. Such clusters can be viewed as pretransitional fluctuations in the system; eventually, when more homopolymer is added, the clusters continue to grow until the system macrophase separates.

These SANS experiments show that depletion interactions influence the properties of the micelles (e.g., f and R_g) and therefore we expect that depletion interactions will also influence the phase behavior of ordered micellar microstructures. Preliminary experiments performed on ordered microstructures show that addition of homopolymer polystyrene disorders the face-centered cubic (fcc) phase (at room temperature and with increasing homopolymer concentration) and lowers the order-disorder transition temperature (at constant homopolymer concentration). Furthermore the thermotropic order-order transition temperature from fcc to body centered cubic (bcc) phase [25] progressively increases and eventually the bcc phase window disappears. More details of these results will be published elsewhere.

In this Letter we demonstrate the effect of depletion interactions on block copolymer micelles by performing SANS experiments on dilute and semidilute micelle solutions. In all systems (colloids or star polymers) studied before, the size or aggregation of the nanoparticles are fixed by default, whereas block copolymers offer the added freedom of intraparticle self-assembly. Our results show that depletion forces affect both intermicellar and intramicellar packing, thus making this phenomena simultaneously fascinating and complex. Furthermore, the phenomena of depletion forces influencing micellization can be harnessed as an additional tool to control the phase behavior of diblock copolymer micelles.

This work was supported by the National Science Foundation through the University of Minnesota MRSEC (No. DMR-0212302). The research was also supported by National Institute of Standards, U.S Department of Commerce through the neutron research facilities. Use of

the Advanced Photon Source was supported by the U.S. Department of Energy, Basic Energy Sciences, Office of Science, under Contract No. W-31-109-Eng-38. Experiments were conducted at DND-CAT, which is supported by DuPont, Dow, NSF (No. DMR-9304725) and the Illinois Department of Commerce and Grant No. IBHE HECA NWU 96.

-
- [1] R. Tuinier, J. Rieger, and C.G. de Kruif, *Adv. Colloid Interface Sci.* **103**, 1 (2003).
 - [2] X. Ye *et al.*, *Phys. Rev. Lett.* **76**, 4640 (1996).
 - [3] X. Ye *et al.*, *Phys. Rev. E* **54**, 6500 (1996).
 - [4] E. Stiakakis *et al.*, *Phys. Rev. Lett.* **89**, 208302 (2002).
 - [5] E. Stiakakis, D. Vlassopoulos, and J. Roovers, *Langmuir* **19**, 6645 (2003).
 - [6] E. Stiakakis *et al.*, *Europhys. Lett.* **72**, 664 (2005).
 - [7] R. Verma *et al.*, *Phys. Rev. Lett.* **81**, 4004 (1998).
 - [8] R. Verma *et al.*, *Macromolecules* **33**, 177 (2000).
 - [9] C.N. Likos, *Phys. Rep.* **348**, 267 (2001).
 - [10] A.A. Louis, *Phil. Trans. R. Soc. A* **359**, 939 (2001).
 - [11] A. Striolo *et al.*, *Mol. Simul.* **30**, 437 (2004).
 - [12] Y.-Y. Won *et al.*, *J. Phys. Chem. B* **105**, 8302 (2001).
 - [13] H. Watanabe and T. Kotaka, *J. Rheol.* **27**, 223 (1983).
 - [14] M. Malmsten and B. Lindman, *Macromolecules* **26**, 1282 (1993).
 - [15] J. Bang *et al.*, *J. Chem. Phys.* **121**, 11489 (2004).
 - [16] J.S. Pedersen, *J. Chem. Phys.* **114**, 2839 (2001).
 - [17] A. Halperin, *Macromolecules* **22**, 3806 (1989).
 - [18] A. Vrij, *Pure Appl. Chem.* **48**, 471 (1976).
 - [19] M. Kotlarchyk and S.-H. Chen, *J. Chem. Phys.* **79**, 2461 (1983).
 - [20] A.M. Kulkarni *et al.*, *J. Phys. Condens. Matter* **12**, A301 (2000).
 - [21] A. Stradner *et al.*, *Nature (London)* **432**, 492 (2004).
 - [22] P.J. Lu *et al.*, *Phys. Rev. Lett.* **96**, 028306 (2006).
 - [23] M.D. Haw, W.C.K. Poon, and P.N. Pusey, *Phys. Rev. E* **56**, 1918 (1997).
 - [24] S.V.G. Menon *et al.*, *Phys. Rev. E* **53**, 6569 (1996).
 - [25] T.P. Lodge *et al.*, *Phys. Rev. Lett.* **92**, 145501 (2004).