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Structure of diblock copolymers in supercritical carbon dioxide and critical micellization pressure

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This paper reports a small angle neutron scattering investigation of micelle formation by fluorocarbon-hydrocarbon block copolymers in supercritical CO_2(sc-CO_2) at 65 °C. A sharp unimer-micelle transition is obtained due to the tuning of the solvating ability of sc-CO_2 by profiling pressure, so that the block copolymer, in a semidilute solution, finds sc-CO_2 a good solvent at high pressure and a poor solvent at low pressure. At high pressure the copolymer is in a monomeric state with a random coil structure. However, on lowering the pressure, aggregates are formed with a structure similar to aqueous micelles with the *hydrocarbon* segments forming the core and the *fluorocarbon* segments forming the corona of the micelle. This unimer-aggregate transition is driven by the gradual elimination of CO_2 molecules solvating the hydrocarbon segments of the polymer. Comparison of these results with related data on the same polymer at different temperatures indicates that the transition is critically related to the density of the solvent. This suggests the definition of a critical micellization density, to our knowledge a new concept in colloid chemistry.

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INTRODUCTION

The importance of supercritical carbon dioxide (sc-CO_2) as a ''clean'' replacement solvent for many industrial processes is now well documented [1]. Paradoxically, the main problem with sc-CO_2 is that only two classes of polymeric materials are known to be readily soluble in it: amorphous fluoropolymers and silicones. For this reason significant research effort has been directed toward the synthesis of diblock copolymer ''surfactants'' which are able to solubilize materials that would be otherwise insoluble [2]. In this regard a branch of surfactant science for sc-CO_2 is now emerging analogous to that describing solubilization in aqueous and oil media.

Supercritical fluids (SCF's) and diblock copolymers, however, have their own unique properties, with the consequence that the behavior of polymer solutions in sc-CO_2 is far more complex than the aqueous counterpart. For example, the solvating ability of a SCF can be easily tuned by profiling temperature and/or pressure, so a block copolymer in a semidilute solution may find sc-CO_2 a *good* solvent at high enough pressure. By decreasing the pressure (and therefore the density), sc-CO_2 may become, for the same polymer, first a *marginal* solvent, and then, at low enough pressures, a *poor* solvent [3]. If one of the two blocks is highly CO_2-*philic* and the other less so, at high pressure the entire polymer should be soluble and therefore should behave as a random coil [4]. By decreasing the pressure, the copolymer should then show a tendency to aggregate, thus forming structures similar to aqueous micelles with the CO_2-*phobic* segments forming the core. The situation may be even more complex if the polymer is polydisperse. In this case, even if the whole polymer is dissolved, the high molecular weight fraction of the polymer will be less soluble and may be closer to phase separation when the pressure is lowered. This effect, which can sometimes be used in selective fractionation of polymers, may give rise to critical fluctuations in the scattering [5] albeit of smaller extent than when the bulk of the polymer separates at lower pressure. Small angle neutron scattering (SANS) will detect all of these effects. In conclusion, it is expected that as the pressure is lowered the polymer will aggregate and a unimer-aggregate equilibrium exists below a certain pressure determined by the polymer structure. Equilibrium and dynamic properties of solutes in CO_2 are closely linked to the SCF density ρ_{CO_2}, and this critical micelle pressure is therefore expected to be affected by the temperature, which also determines ρ_{CO_2}. To a first-

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approximation this effect is expected to be related to a critical micellization density, as suggested previously [2(a)] based on measurements on a polystyrene-fluorinated octyl acrylate (PFOA) block copolymer in sc-CO_2, as a function of temperature and pressure. Similar effects have been detected by SANS measurements on a related copolymer [6], although no analysis of the data has been reported yet. More recently a careful study of the same copolymer reported an investigation by laser light scattering [7] (LS) of pressure induced aggregation processes in sc-CO_2 at 65 °C in the pressure range 140–500 bar. By making assumption on the composition of the aggregates, LS gives the aggregation number and size of the micelle, but cannot reveal the details of the internal structure on length scales of ~10 nm. However, such information is available from SANS, as demonstrated in this paper.

EXPERIMENT

A PVAc-PFOA block copolymer composed of a CO_2-phobic polyvinylacetate (PVAc, 10.3 kDa, polydispersity index 1.6) and a CO_2-philic fluorinated octyl acrylate (PFOA, 43.1 kDa, polidispersity index 2) of average effective molecular weight 90.4 kDa has been studied by time of flight SANS in sc-CO_2 as a function of pressure at constant temperature. Solutions of the polymer (~12 ml) were contained in a high pressure optical cell [8] fitted with sapphire windows with a pathlength of 1 cm. The pressure was transmitted by a hydraulic fluid (*n*-hexane) isolated from the sample by a freely moving piston within the cell. The temperature of the sample was maintained to ±0.2 °C by a Lauda bath which circulated a thermostatted fluid through the cell body. SANS measurements were made at 65 °C in the pressure range 240–480 bar, for which a micelle-unimer transition was expected [7]. The polymer concentration was a nominal 6% wt./vol. on filling the cell but this increases to approximately 7% due to compression of the SCF as the pressure is raised.

SANS measurements were performed on the LOQ spectrometer [9] using the ISIS pulsed neutron source of the EPSRC Rutherford Appleton Laboratory, UK. The magnitude of the momentum transfer vector Q is given by

$$Q=\frac{4\pi}{\lambda}\sin\left(\frac{\theta}{2}\right)$$

where λ is the incident wavelength (2.2–10.0 Å), determined by time of flight, and θ is the scattering angle. The intensity of neutrons was recorded on a position-sensitive 64×64 pixel two-dimensional detector at a fixed sample-to-detector position (4.3 m), providing an effective Q range of $0.01\rightarrow0.22\ \text{Å}^{-1}$ in a single measurement. The data were corrected for transmission and incoherent background scattering, and normalized to absolute scattering probabilities (cm^{-1}) using standard procedures. Further details of technical and experimental aspects together with data reduction procedures are given elsewhere [10].

DATA ANALYSIS

The coherent elastic differential scattering cross section of a collection of random coil chains partially aggregated, under conditions of validity of the decoupling approximation [11] is given by

$$\begin{aligned}[d\Sigma(Q)/d\Omega]_{\text{tot}}&=[d\Sigma(Q)/d\Omega]_{\text{RC}}+[d\Sigma(Q)/d\Omega]_{\text{agg}}\\&=2N_p[(QR_g)^2+\exp[(-QR_g)^2]-1]/\\&\quad(QR_g)^4+N_{\text{agg}}P(Q)[S(Q)^{\text{PY}}+S(Q)^{\text{ECF}}]\\&\quad+\Delta(Q),\end{aligned}\qquad(1)$$

where $[d\Sigma(Q)/d\Omega]_{\text{RC}}$ and $[d\Sigma(Q)/d\Omega]_{\text{agg}}$ are the contributions of random coil chains and of aggregated chains, respectively; R_g is the gyration radius of the random coil, $P(Q)$ [12] and $S(Q)^{\text{PY}}$ are the form factor and the repulsive structure factor [13] of the aggregates, respectively, and $S(Q)^{\text{ECF}}$ is the contribution due to the exponentially correlated fluctuations [5] which will be discussed later. $\Delta(Q)$ is the difference between the squared average and the averaged square of the scattering amplitude. For the spherical micelles observed in this work, it is roughly independent of Q, and a function of the same parameters used to calculate aggregate form factor [11]. Thus the inclusion of this term does not introduce an additional fitting parameter.

To fit $P(Q)$ we tested several structural models, and found that best fits were obtained by a ''core + shell'' polydisperse spheres model as used previously [2(a)]. For the structure function $S(Q)^{\text{PY}}$ we have used a hard spheres model in the Percus-Yevick approximation [13]. To account for exponentially correlated fluctuations in some samples, we have also included a Lorentzian contribution [5] $S(Q)^{\text{ECF}}$. We do not distinguish between fluctuations due to the proximity of phase lines or to the effect of pressure on the high molecular weight fraction of a polydisperse polymer sample, as both give a Lorentzian contribution in Q, which can be modeled within the Ornstein-Zernicke formalism [11].

Figure 1 shows the effect of pressure on the SANS obtained for the polymer solution at 65 °C. The appearance of a peak at $Q\sim0.026\ \text{Å}^{-1}$ and an enormous increase in intensity with decreasing pressure are clear indications of formation of aggregates. As the pressure is decreased below 280 bar, the solutions exhibit increasing opalescence, indicating that the polymer has a tendency to precipitate. At the same time the shape of the scattering curve indicates the retention of aggregate structure. Good fits to the SANS data in this region can be obtained with the polydisperse core plus shell spherical model for the aggregated polymer [Fig. 2(a)].

Preliminary fits gave values of both the core radius and scattering-length density, which were higher than would be expected from condensation of the polyvinylacetate section of the copolymer alone. In particular, the core scattering length density was closer to that of the dispersion medium than expected, which indicates that solvent molecules occupy a fraction of the core. As we shall show below, there is clear evidence that by increasing the pressure, CO_2 progressively invades the core. We have therefore calculated the number of CO_2 molecules (per chain unit) that would be necessary to produce the increase of volume and scattering-length density of the core. This provides a measure of core solvation (CS), and has been normalized to the corresponding value at the lowest pressure at which the polymer is still dispersed in CO_2 (parameter CS in Table I). Dimensions and

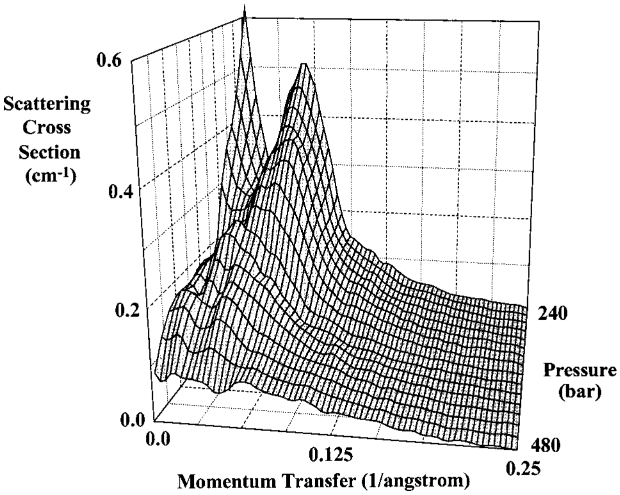

FIG. 1. Pressure dependence of the SANS pattern as obtained from a 6% wt./vol. CO_2 solution of 10.3 kDa PVAc-b–43.1 kDa PFOA at 65 °C. The random coil morphology turns into a micellar one, as soon as the solvent density is lowered across a critical micellization density (CMD).

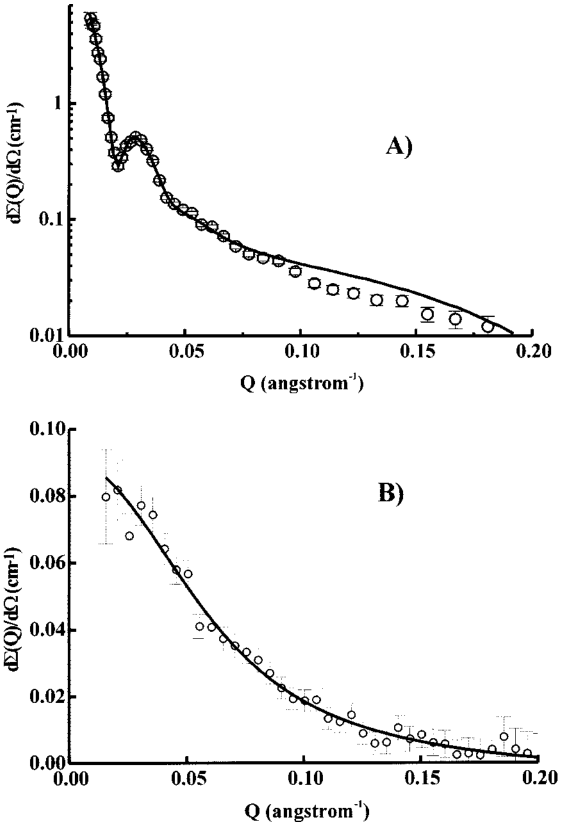

FIG. 2. Example of the fitting of experimental SANS data from a CO_2 solution of 10.3 kDa PVAc-b–43.1 kDa PFOA at 65 °C by means of the models described in the text: (a) In a “low density” state at 242 bar the system presents micellar morphology. (b) At 483 bar the SANS pattern is well represented by a random coil model. In this “high density” state CO_2 is a good solvent for the block copolymer.

scattering-length density change slightly in a wide range of pressures (less than 10% in the pressure range in which aggregates are dominant structures). As the CO_2 pressure is further increased, core swelling and increased stiffness of the core-shell interface [14] are indicated by systematic changes in the core radius and polydispersity index Z. This result provides support for a progressive solvent penetration inside the aggregate with increasing pressure as would be expected since CO_2 becomes a better solvent for the polymer.

At higher pressures the change of the scattering curves indicates a complete change in the shape of the scattering and the SANS measured at the highest CO_2 pressures (>400 bar) are consistent with the scattering of random coils [Fig. 2(b)]. The transition from a mixture of random coils and aggregates to pure random coils is reasonably sharp, falling somewhere between 370 bar ($\rho_{CO_2}=0.855\,\mathrm{g\,cm^{-3}}$) and 420 bar ($\rho_{CO_2}=0.882\,\mathrm{g\,cm^{-3}}$), and involves all the polymer present. The concentration of unimers remains approximately constant at 1.8% up to 345 bar, then increases sharply, indicating that the aggregates are quickly breaking down. Attempts to fit the data at 415 bar with the core-shell model described above failed. At the highest pressure a model of isolated random coils [12] fits the scattering curve very well. Results of the fit are shown in Table I. CS, the core swelling parameter, is displayed together with the aggregation number (Agg.) and the Schultz polydispersity parameter Z. The values of R_g are not fitting parameters for the solutions showing aggregates, but are actually obtained from the dimensions of the aggregates, and are displayed to show the dramatic change which accompanies the aggregate-unimer transition. The slight increase of Z (from 240 to 310 bar) indicates a stiffening of the core-shell interface [14] due to the penetration of CO_2 deep inside the aggregate, while the sharp decrease at 345 bar is a clear indication of aggregate rupture. Similar information is obtained from the aggregation numbers, which remain reasonably constant for pressures below 320 bar, but decrease sharply, approaching the transition region. In a series of preliminary runs the transition was found to be both reproducible and reversible.

It can be noted that in a wide range of pressures the aggregation number and the aggregate polydispersity index are only slightly affected by the CO_2 pressure. However, when the pressure is further increased the micelle is invaded by the solvent, and suddenly the aggregate breaks down when the pressure exceeds 310 bar. In other words, above a certain pressure the system does not aggregate, while the opposite is true above a certain pressure to which a “critical density”

TABLE I. Fit using a model of isolated random coils. Numbers in parentheses correspond to the uncertainty in the last digit shown.

P (bar)	R_g (Å)	CS	Agg.[a]	Z[b]
242	105	1.0(1)	19(1)	24(2)
260	109	1.0(2)	19(2)	28(8)
275	106	1.0(1)	19(1)	27(3)
310	108	1.1(1)	18(1)	30(2)
345	105	1.4(2)	12(1)	19(4)
379	Transition region, $\rho_{CO2}-0.87$ g/cm^3			
415	Transition region			
483	30.7(6)	$I(0)=0.095(5)$ cm^{-1}		

[a] Refers to the effective molecular weight.

[b] Shultz polydispersity parameter.

corresponds. The effect is quite similar to the one found in aqueous media with pluronics by changing the temperature. Although we have not fully analyzed the results at 40 °C [6,15], we found that the unimer-aggregate transition there occurs in a different range of pressures, but corresponding to the same range of densities.

These characteristics—the sharpness of the transition and the fact that the aggregation number and the polydispersity hardly depend on pressure—are a clear indication that we are dealing with a transition due to the change in density. For this reason, we have named this effect critical micellization density.

CONCLUSION

The SANS study of the unimer-aggregate transition of the diblock copolymer 10.3 kDa PVAc-43.1 kDa PFOA in sc-CO_2 shows that above a certain solvent density the polymer chains do not aggregate, and their scattering is given by the random coil equation. Below this density most of the chains undergo an association process, forming ''core-shell'' micellar aggregates which change slightly by further decreasing the density. The range of densities in which this transition happens does not seem to depend on the temperature. By changing the temperature the pressure range in which the transition happens changes, but the density range remains constant. This allows us to define a concept, critical micellization density, which seems to be a general characteristic of compressible fluids.

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