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Critical micellization density: A small-angle-scattering structural study of the monomer-aggregate transition of block copolymers in supercritical CO_2

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In this paper we report a small-angle neutron-scattering investigation of micelle formation by the fluorocarbon-hydrocarbon block copolymer, polyvinyl acetate-*b*-poly (1,1,2,2-tetrahydroperfluoro-octyl acrylate) in supercritical CO_2 ($scCO_2$) at 313 K. At high pressure the copolymer is in a monomeric state with a random coil structure, while at low pressure the polymer forms spherical aggregates stable in a wide range of thermodynamic conditions. By profiling pressure, a sharp monomer-micelle transition is obtained due to the tuning of the solvating ability of $scCO_2$. We confirm the previous finding that this aggregate-monomer transition is driven by the gradual penetration of CO_2 molecules toward the core of the aggregate and is critically related to the density of the solvent, thus giving additional support to the concept of a critical micellization density reported earlier on a similar polymer.

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INTRODUCTION

Small-angle neutron scattering (SANS) has been used recently to gain quantitative information on the structure of aggregates of amphiphilic fluoropolymers in supercritical CO_2 ($scCO_2$) [1–4] in a variety of thermodynamic conditions.

Supercritical fluids (SCF's) have a number of features which offer potential advantages, including a high compressibility which facilitates large changes in solvent density, and hence solvation, with pressure. For this reason, in the past 15 years there has been a growing interest in SCF's as new solvent media for separation, reaction, and crystallization [5,6]. The change of solvation of solutes in SCF's has been exploited to control solubilities through both temperature and pressure variation. Recently [2–4], we have reported SANS studies of copolymers polyvinyl acetate-*b*-polyfluoro-octyl acrylate (PVAc-*b*-PFOA) in $scCO_2$. These copolymers are made with a portion containing a fluorocarbon polymer with a high affinity towards $scCO_2$ and a hydrocarbon polymer portion not quite as affine. In these polymers, PVAc acts as a ''CO_2-phobic'' block, while PFOA acts as a ''CO_2-philic'' block. (In what follows, we shall classify these polymers using their number average molecular weights, $\langle M_n\rangle_{\mathrm{VAc}}$-*b*-$\langle M_n\rangle_{\mathrm{FOA}}$). The amphipatic nature of these compounds facilitates the formation of aggregates in which the contact between the hydrocarbon portion of the molecules and the solvent is minimized, while, at the same time, the solvophilic interaction is maximized. Therefore, we may expect that, at low pressure, where CO_2 is not a good solvent for one of the blocks, structures similar to micelles may form. On the other hand, as the existence of these aggregates is due to the different solvating ability of $scCO_2$ for the two blocks, by increasing the pressure, and thus by making $scCO_2$ a better solvent for both blocks, one may reach a condition when the aggregate collapses, freeing the single random coil chains. The concentration and the nature of the polymer, the temperature, as well as the pressure are all parameters affecting the monomer-aggregate transition. However, most likely temperature and pressure are not acting as independent variables, but rather affect the transition by modulating the solvent density, primarily responsible for the transition itself. The situation is actually more complex, as the polymer is in general polydisperse, and the solvating ability of $scCO_2$ depends also on the molecular weight of the various fractions of the polymer. So, at a certain pressure it may happen that, while CO_2 is a good solvent for the majority of the polymer, at the same time it is a poor solvent for the high molecular weight fraction of the dispersion. Under these conditions, the high molecular weight fraction may undergo concentration fluctuations which are correlated exponentially in space and affect the Gibbs free energy of the solution. This might affect the pressure transition, although marginally, as the transition happens when CO_2 becomes a good solvent for the whole polymer. In short, the two most important parameters controlling the monomer-aggregate transition should be the concentration and the density; we have therefore introduced the concept of critical micellization density (cmd), i.e., the density of the solvent at which a sharp, reversible monomer-aggregate transition occurs [2–4]. The cmd is expected to depend also on the nature of the blocks (especially the solvo-phobic block) making up the polymer and to be a general characteristic of supercritical fluids [4], not only of $scCO_2$.

In principle, aggregates of different shapes can be obtained in these solutions, depending on the concentration and the nature of the CO_2-phobic chain and of the CO_2-philic portion. So far, however, there has been evidence only of core-shell spherical aggregates even at high concentrations. Moreover, the core may solubilize an appreciable amount of high molecular weight apolar materials which otherwise have low solubility in scCO$_2$ to form dispersions similar to oil-in-water microemulsions. This feature may be exploited in recently developed precision cleaning and garment cleaning applications of scCO$_2$ [7]. The fact that the core can solubilize materials which find scCO$_2$ a poor solvent has strong implications when the scattering data of polydisperse polymeric materials of the kind investigated here are analyzed. This arises since the least soluble components of the polymer, particularly the high molecular weight hydrocarbons, may be located in the core at low pressures when solvation by scCO$_2$ is poor.

EXPERIMENT

We have investigated the small-angle scattering behavior of a block copolymer in scCO$_2$ containing a ''CO$_2$-philic'' moiety (60.4 K Dalton PTAN) and a ''CO$_2$-phobic'' moiety (10.3 K Dalton PVAc), equal to the one previously investigated [3,4]. The ''CO$_2$-philic'' moiety, although larger, is similar to PFOA, for which we had previously obtained very accurate SANS measurements and derived values of a critical micellization density (cmd) for several concentrations at different temperatures [3,4]. The values of cmd obtained depend slightly on the molecular weight of the blocks [2], concentration, and temperature [3,4], indicating that the critical variable is the solvent density. In fact, our studies have shown that for this kind of polymer, the cmd is in the range of 0.87–0.92 g/cm^3. In particular, based on our studies [2–4], given the same ''CO$_2$-phobic'' moiety, at 40 °C we expect a value of 0.92 g/cm^3 for the polymer under investigation.

A 6% (w/V) solution at 40 °C was investigated as a function of pressure. Solutions of the polymer were contained in a high-pressure optical cell [1,2] fitted with sapphire windows with path length 1 cm. The temperature of the sample was maintained to +/−0.2 °C by means of a heating ribbon. SANS measurements were made at 40 °C in the pressure range of 170–360 bar.

SANS measurements were performed on the ORNL 30 m camera [8] using 4.78-Å neutrons. The magnitude of the momentum transfer vector Q is given by $Q=4\pi\lambda^{-1}\sin(\theta)$, where λ is the incident wavelength and 2θ is the scattering angle. The intensity of neutrons was recorded on a position-sensitive 64×64 pixel 2D detector at a fixed sample-to-detector position providing an effective Q range from 0.006 to 0.06 Å^{-1}. The data were corrected for transmission, incoherent background scattering, and normalized to absolute scattering cross sections per unit volume (cm^{-1}) using standard procedures [9]. Further details of technical and experimental aspects together with data reduction procedures are given elsewhere [1–4,8].

DATA ANALYSIS

The coherent elastic differential scattering cross section $d\Sigma(Q)/d\Omega$ of a collection of random coil chains partially aggregated to form N_{agg} aggregates can be calculated as a weighted average of contributions of N_p random coils and of the N_{agg} aggregated chains, $[d\Sigma(Q)/d\Omega]_{\mathrm{RC}}$ and $[d\Sigma(Q)/d\Omega]_{\mathrm{agg}}$, respectively. Under conditions of validity of the decoupling approximation, $d\Sigma(Q)/d\Omega$ is given [2] by

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

where R_g is the radius of gyration of the random coil, $P(Q)$ and $S(Q)^{\mathrm{PY}}$ are the form factor and the structure factor of the aggregate, respectively, and $S(Q)^{\mathrm{ECF}}$ is the contribution due to the exponentially correlated fluctuations [2,10].

To compute $P(Q)$ we tried several models and best fits were obtained with a ''core+shell'' polydisperse spheres model, while for the structure function we have used the hard-spheres model in the Percus-Yevick approximation [11] modified [2] for exponentially correlated fluctuations $[S(Q)^{\mathrm{PY}}+S(Q)^{\mathrm{ECF}}]$. In fact, statistical thermodynamics of polymer solutions in the semidilute poor solvent regime [12,13] suggests that the free-energy density F can be simply expressed as a virial expansion in terms of binary and ternary cluster integrals [14]. From a structural point of view, a polymer in the semidilute regime shows density fluctuations correlated exponentially in space with a correlation-length simple function of the cluster integrals [15], and shows up in the scattering cross section of the solution as a Lorentzian contribution [10] quite similar to the Ornstein-Zernicke contributions described in a different context [16]. As before [2], we obtained large core radii and core scattering length density not dissimilar from the scattering length density of the pure solvent. In addition, a better fit was obtained when a small fraction of the polymer was supposed to be present as a monomer even at the lowest pressures. The lowest pressure presented here was at least 10 bar higher than the precipitation pressure which was obtained visually before starting the data collection.

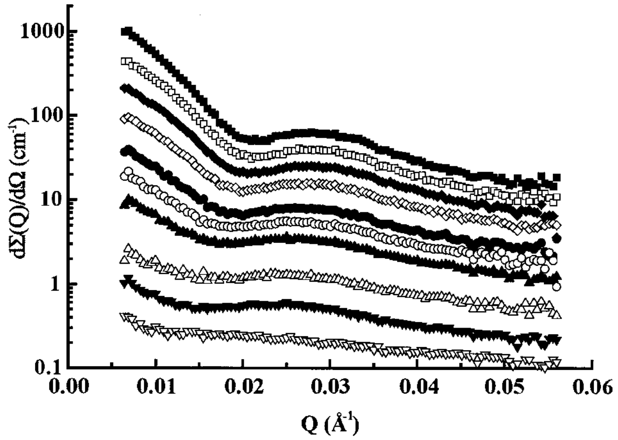

FIG. 1. Pressure dependence of the SANS pattern as obtained from selected runs of a 6% w/V CO$_2$ solution of 10.3 K PVAc-b-60.4 K PT-AN at 313 K. Pressure decreases from bottom to top.

RESULTS AND DISCUSSION

Figure 1 shows the effect of the CO$_2$ pressure on the scattering function of the 6% (w/V) solution at 40 °C. It can be noticed that, by decreasing the pressure, the intensity in-

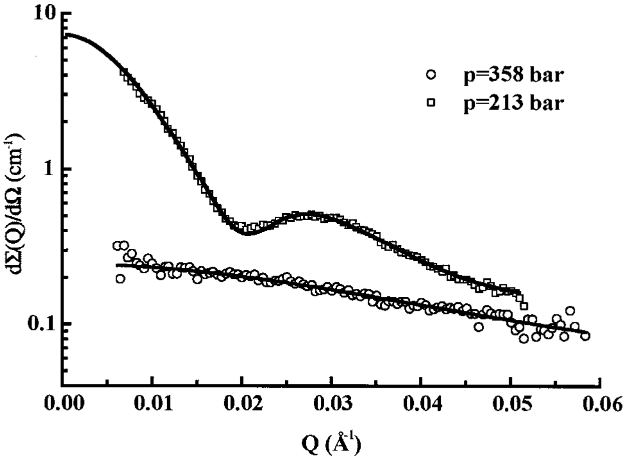

FIG. 2. Example of the fitting of experimental SANS data from a 6% w/V CO_2 solution of 10.3 K PVAc-b-60.4 K PT-AN at 313 K by means of the models described in the text: in a ''low-density'' state, the system presents micellar morphology. At 358 bar the SANS pattern is well-represented by a random coil model. In this ''high-density'' state, CO_2 is a good solvent for both blocks of the copolymer.

creases and a peak in the scattering intensity appears. This is a clear indication that the system undergoes a monomer-aggregate transition. When we modeled the aggregates as polydisperse ''core+shell'' spherical particles, excellent fits to the scattering intensities were obtained, provided a fraction α of the polymer was always present as a random coil, the remaining fraction (1-α) forming spherical aggregates; solvent penetration in the core was allowed by defining the fit parameter CS, which gives information on the core swelling due to the solvent penetration. In practice, at a given pressure, CS is given by the number of CO_2 molecules penetrating the core normalized to its value at the lowest pressure at which the polymer is still dispersed in CO_2. By increasing the pressure, CS also increases and its change parallels the increase of stiffness of the core-shell interface, measured by the polydispersity parameter Z [17]. At high enough pressures, the aggregates start to break down and eventually the scattering curves become consistent with the scattering from random coils. The transition from a mixture of random coils and aggregates to pure random coils is reasonably sharp and falls, at 40 °C, in a pressure range between 280 ($\rho_{CO_2}=0.91\,\mathrm{g/cm^3}$) and 320 bar ($\rho_{CO_2}=0.92\,\mathrm{g/cm^3}$). This value is in excellent agreement with the value expected on the basis [1–4] of our previous studies discussed earlier.

Figure 2 shows typical fits for the high-density (random coil) and for the low-density regime (aggregates). The concentration of monomers in equilibrium with aggregates remains low ($\alpha=0.025$) and approximately constant far from the transition pressure, then increases quickly upon approaching the transition, indicating that the aggregates are breaking down. Results of the fits are collected in Table I. CS, the core swelling parameter, is displayed together with the aggregation number (Agg.) and the Schultz polydispersity parameter Z. Dilute solutions (>2%) of the same polymer have been studied earlier at 45 °C by means of static and dynamic light scattering [18]. However, although the transition was found in the same range of densities reported here, no comparison with the present data is possible because of the different concentration range and also because the authors evaluated aggregation numbers by assuming ''dry micelles'' and therefore neglecting the solvent penetration. In our case, the value of R_g for the monomers, obtained by fitting the data to the random coil scattering equation [19], is 43.5 Å. As indicated previously, a slight increase of Z upon increasing the pressure indicates stiffening of the core/shell interface [17], due to the penetration of CO_2 deep inside the aggregate. Figure 3 shows a fit of the experimental fraction of a polymer aggregated to a Boltzmann sigmoidal curve,

$$Y(x)=A_2+(A_1-A_2)/[1+\exp(x-x_0)/dx],$$

where A_1 and A_2 are the upper and the lower values of (1-α), respectively, x_0 is the center of the transition, and dx is the width.

TABLE I. Results of the fits for the high- and low-density regimes.

P[a]	$(1-\alpha)$[b]	ρ[c]	CS[d]	Agg.[e]	Z[f]
172	0.925	0.821	1.00	29.5(1)	17.0(1)
179	0.925	0.830	1.0(1)	29.3(3)	17.0(1)
186	0.925	0.838	1.1(1)	29.2(5)	17.4(1)
199	0.900	0.849	1.1(1)	28.0(3)	19.5(3)
213	0.900	0.858	1.1(1)	24.8(5)	18.4(5)
227	0.875	0.868	1.1(2)	21.7(2)	18.0(2)
241	0.875	0.879	1.1(3)	19.4(2)	17.0(2)
255	0.850	0.889	1.1(1)	18.6(2)	17.0(2)
268	0.750	0.900	1.6(2)	14.8(3)	17.0(2)
282	0.65	0.909	1.8(2)	12.0(2)	10.0(2)
295		transition zone, $\rho_0-0.91\,\mathrm{g/cm^3}$			
310		transition zone, $\rho_0-0.92\,\mathrm{g/cm^3}$			
358		0.917	Random coil, $R_g=43.5$ Å		

[a] Pressure in bar.

[b] Concentration of aggregated polymer expressed as percent of the total polymer concentration (6% w/V).

[c] Density of CO_2 (g/cm^3).

[d] Core swelling ratio number based on the number average molecular weight of the polymer. Errors in parentheses.

[e] Aggregation numbers. Errors in parentheses.

[f] Schultz polydispersity parameter. Errors in parentheses.

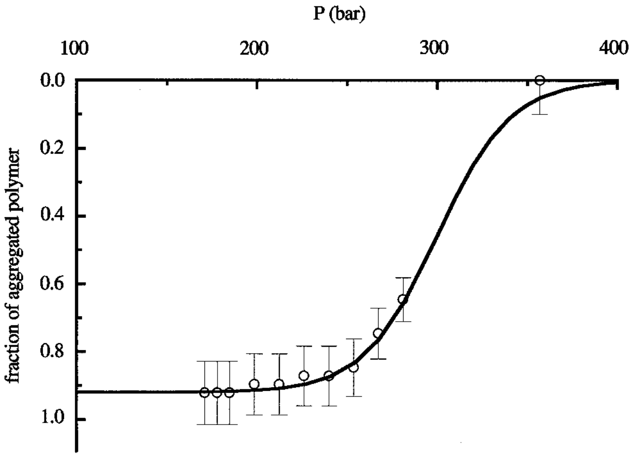

FIG. 3. Concentration of the aggregated polymer as a function of the pressure.

The sharpness of the transition and the fact that the aggregation number and the polydispersity, away from the transition region, hardly depend on pressure and temperature (as well as concentration and composition of the polymer) is a clear indication that we are dealing with a transition basically due to the change in density of the solvent.

CONCLUSION

The small-angle scattering investigation of solutions of a block-copolymer in scCO$_2$ has given details on the mechanism controlling the aggregate-monomer transition triggered by increasing the pressure above a critical value. When the pressure exceeds this value, the core of the aggregates becomes more ‘‘solvent penetrable’’ so that by increasing the pressure, more and more solvent can penetrate the aggregate, reaching the core, making the core-shell surface stiffer and eventually leading to the breakdown of the structure. This makes possible the aggregate-monomer transition, happening in a relatively narrow range of pressures. The characteristics of this transition seem to indicate that we are dealing with a phenomenon due to the change in density. It is therefore natural to propose the existence of a critical micellization density (cmd) to describe the condition at which a reversible micelle-monomer transition occurs in solutions of block-copolymers in scCO$_2$. Further experiments are in progress to examine in detail the extent by which the cmd depends on polymer structure and temperature.

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