

## Critical micellisation density: a SAS structural study of the unimer–aggregate transition of block-copolymers in supercritical CO<sub>2</sub>

Fabio Triolo<sup>ab</sup>, Alessandro Triolo<sup>cb</sup>, Roberto Triolo<sup>b\*</sup>, Doug E. Betts<sup>d</sup>, James B. McClain<sup>d</sup>, Joe M. De Simone<sup>d</sup>, David C. Steyler<sup>e</sup>, George D. Wignall<sup>f</sup>, Bruno Demé<sup>g</sup> and Richard K. Heenan<sup>h</sup>

<sup>a</sup>Mount Sinai School of Medicine, New York, NY, USA

<sup>b</sup>Department of Physical Chemistry, University of Palermo, Palermo, Italy

<sup>c</sup>Heriot-Watt University, Edinburgh, UK

<sup>d</sup>Department of Chemistry, University of North Carolina, Chapel Hill, NC, USA

<sup>e</sup>School of Chemical Sciences, University of East Anglia, Norwich, UK

<sup>f</sup>Oak Ridge National Laboratory, Oak Ridge, TN, USA

<sup>g</sup>Institut Laue-Langevin, Grenoble, FR

<sup>h</sup>Rutherford Appleton Laboratory, Chilton, UK

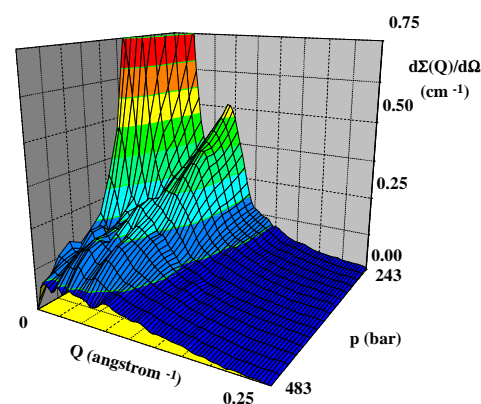
Email: triolo@unipa.it

In this paper we report a SANS investigation of micelle formation by fluorocarbon-hydrocarbon block copolymers in supercritical CO<sub>2</sub> (scCO<sub>2</sub>) at 313K. A sharp unimer-micelle transition is obtained due to the tuning of the solvating ability of scCO<sub>2</sub> by profiling pressure. At high pressure the copolymer is in a monomeric state with a random coil structure. By lowering the pressure aggregates are formed with the *hydrocarbon* segments forming the core and the *fluorocarbon* segments forming the corona of spherical aggregates. This aggregate-unimer transition is driven by the gradual penetration of CO<sub>2</sub> molecules toward the core of the aggregate and is critically related to the density of the solvent, thus suggesting the definition of a critical micellisation density (CMD).

### 1. Introduction

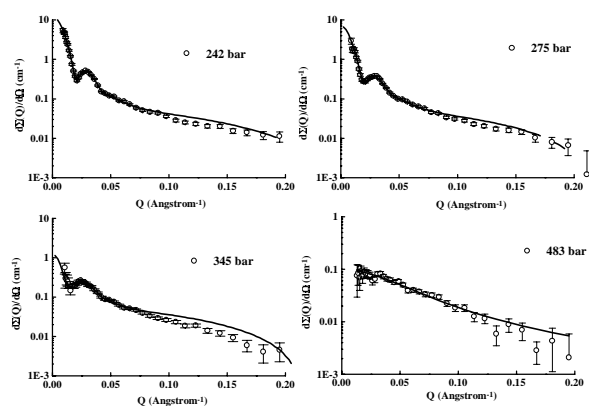
Small Angle Neutron Scattering (SANS) in the last decade has been used extensively to gain information on the structure of a variety of polymer systems including amphiphilic polymers in supercritical CO<sub>2</sub> (scCO<sub>2</sub>) (Wignall, 1999). Compared with liquid solvents, near- or super-critical fluids (SCF) have a number of features which offer potential advantages, including a high compressibility which facilitates large changes in solvent density with pressure. For this reason in the last 15 years there has been growing interest in SCFs as new solvent media for separation, reaction and crystallisation (DeSimone, 1992-94). Since solvation of solutes in a SCF increases dramatically with density, this feature can be exploited to control solubilities through both temperature and pressure variation. Recently (Triolo, F. et al., 1999,a) we have reported a SANS study of a copolymer Polyvinyl acetate-*b*-Perfluoro octyl acrylate (PVAc-*b*-PFOA) in scCO<sub>2</sub> composed of a “CO<sub>2</sub>-phobic” block (4.4K PVAc) and a “CO<sub>2</sub>-philic” fluorinated octyl acrylate block (43.1K PFOA) blocks. (We classified these polymers using their number average molecular weights as  $\langle M_n \rangle_{\text{vac}}\text{-}b\text{-}\langle M_n \rangle_{\text{FOA}}$ ). This copolymer is made with a portion containing a fluorocarbon polymer very soluble in scCO<sub>2</sub> and a hydrocarbon polymer portion not quite as soluble in CO<sub>2</sub>. Accordingly, these block-copolymers are sensitive to changes in

solvation and to show a variety of structures when the density of the solvent (scCO<sub>2</sub>) changes. On one hand the CO<sub>2</sub>-phobic interaction between the hydrocarbon portion of the molecule and the CO<sub>2</sub> molecules tends to prevent the dissolution of the polymer. On the other hand the energetically favorable CO<sub>2</sub>-philic interactions tend to stabilize the surfactant molecule in solution. The amphipatic nature of these compounds facilitates 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. The structures formed are similar to micelles formed in aqueous solvents by surfactants (Triolo & Caponetti, 1990), with aggregation numbers between 20 and 40 with the “CO<sub>2</sub>-phobic” PVAc blocks forming a central core of surprisingly high scattering length density and volume, surrounded by a shell of “CO<sub>2</sub>-philic” fluorocarbon blocks strongly solvated by the scCO<sub>2</sub>. However, the peculiar solvent properties of CO<sub>2</sub> may give body to phenomena not present in “normal” solvent like water. Interestingly, at temperature and pressure conditions where the density of CO<sub>2</sub> is sufficiently high, the micelles break down to give monomeric polymer with a random coil configuration. This was observed in the case of a block-copolymer PVAc-PFOA with a rather small PVAc moiety (Triolo, F. et al., 1999,a) but also in a similar polymer having a larger (10.3 K) PVAc moiety (Triolo, F. et al., 1999,b).



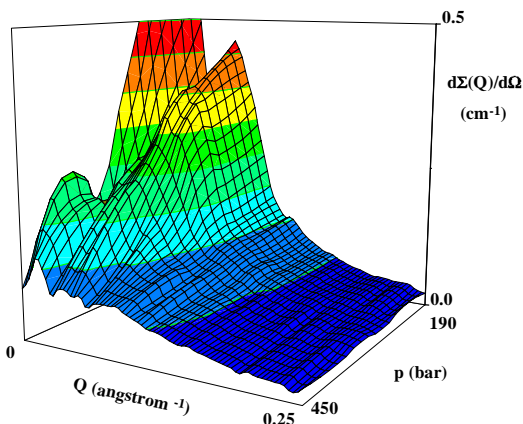
**Figure 1.** Pressure dependence of the SANS pattern as obtained from a 6 % w/v CO<sub>2</sub> solution of 10.3 K PVAc-*b*-43.1K PFOA at 338K. The random coil morphology turns into a micellar one, as soon as the solvent density is lowered across a Critical Micellisation Density (CMD).

Figure 1 shows the change of the scattering cross section with pressure at constant temperature (338K) and concentration (~6%) for the latter polymer. A few selected runs are shown in figure 2 together with the best fits to a core-shell model (low pressures) (Triolo, F. et al., 1999,b) and a random coil model (highest pressure). Interesting enough a transition from aggregated polymer to unimer is experimentally observed in a range of pressures which is higher for the polymer studied at 338K than for the polymer with smaller PVAc moiety (studied at 313K). However, in both cases, the range of densities is the same. We have therefore introduced the concept of critical micellization density (cmd), i.e. the density of the solvent at which a sharp, reversible unimer-aggregate transition occurs (Triolo, F. et al., 1999,a). The cmd is expected to depend also on the nature of the blocks making up the polymer and to be a general characteristic of supercritical fluids, not only of scCO<sub>2</sub> (Triolo, F. et al., 1999,c).



**Figure 2.** Example of the fitting of experimental SANS data from a CO<sub>2</sub> solution of 10.3 K PVAc-b-43.1K PFOA at 338K by means of the models described in the text: in a “low density” state (below 344 bar)the system presents micellar morphology. At 483 bar, the SANS pattern is well represented by a random coil model. In this “high density” state, CO<sub>2</sub> is a good solvent for the block copolymer.

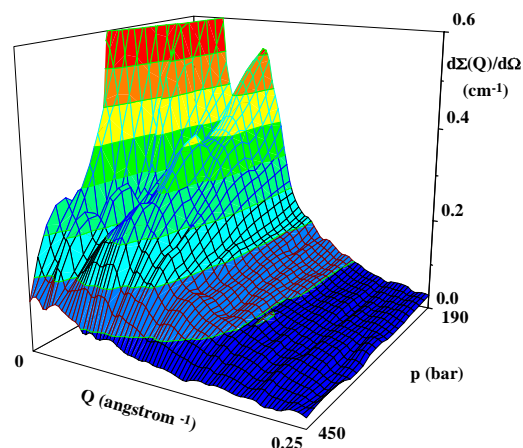
In principle aggregates of different shapes can be obtained in these solutions, depending on the concentration and the nature of the CO<sub>2</sub>-phobic chain and of CO<sub>2</sub>-philic portion. So far, however, there has been evidence only of core-shell spherical aggregates even at high concentrations (Triolo R., 1999). Moreover, the core may solubilize an appreciable amount of high molecular weight apolar materials which otherwise have low solubility in scCO<sub>2</sub> 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<sub>2</sub> (see for example <http://www.micell.com>). The fact that the core can solubilize materials which find scCO<sub>2</sub> a poor solvent, has strong implications when the scattering data of polydisperse polymeric materials of the kind investigated here are analysed. This arises since the least soluble components of the polymer, particularly the high molecular weight hydrocarbons, may locate in the core at low pressures when solvation by scCO<sub>2</sub> is poor.



**Figure 3.** Pressure dependence of the SANS pattern as obtained from a 6 % w/v CO<sub>2</sub> solution of 10.3 K PVAc-b-43.1K PFOA at 313K.

## 2. Experimental

We have investigated the small-angle scattering behavior of a block copolymer in scCO<sub>2</sub> containing a “CO<sub>2</sub>-philic” moiety (43.1K Dalton PFOA) and a “CO<sub>2</sub>-phobic” moiety (Poly vinyl acetate, 10.1K Dalton PVAc). Experiments were conducted over a range of polymer concentration (6%, 8% and 12% w/V) as a function of pressure. Solutions of the polymer (~12 ml) were contained in a high pressure optical cell (Eastoe, Robinson, Young & Steytler, 1990) fitted with sapphire windows with path length 1cm. 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 thermostated fluid through the cell body. SANS measurements were made at 40 °C in the pressure range 190 to 480 bar. The nominal polymer concentration increases approximately 15% due to compression of the SCF as the pressure is raised. SANS measurements were performed on the LOQ spectrometer (Heenan, Penfold & King, 1997) using the ISIS pulsed neutron source of the EPSRC Rutherford Appleton Laboratory UK. The magnitude of the momentum transfer vector Q is given by  $Q = 4\pi\lambda^{-1} \sin(\theta)$ , where  $\lambda$  is the incident wavelength (2.2 - 10.0 Å), determined by time-of-flight, and 2θ is the scattering angle. The intensity of neutrons was recorded on a position-sensitive 64 x 64 pixel 2-D detector at a fixed sample-to-detector position (4.3m) providing an effective Q-range from 0.01 → 0.22 Å<sup>-1</sup> in a single measurement. The data were corrected for transmission, incoherent background scattering and normalised to absolute scattering probabilities (cm<sup>-1</sup>) using standard procedures. Further details of technical and experimental aspects together with data reduction procedures are given elsewhere (Heenan, King, Osborn & Stanley, (1989).



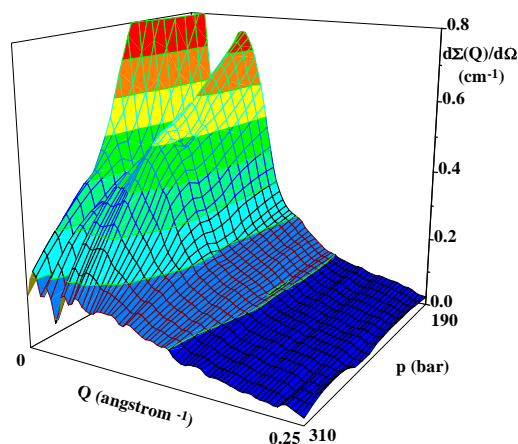
**Figure 4.** Pressure dependence of the SANS pattern as obtained from an 8% w/v CO<sub>2</sub> solution of 10.3 K PVAc-b-43.1K PFOA at 313K.

## 3. 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 is given by (Triolo F. et al., 1999,a)

$$[d\Sigma(Q)/d\Omega]_{tot} = [d\Sigma(Q)/d\Omega]_{RC} + [d\Sigma(Q)/d\Omega]_{agg} = 2 N_p [(Q R_g)^2 + \exp[(Q R_g)^2] - 1] / (Q R_g)^4 + N_{agg} P(Q) [S(Q)^{PY} + S(Q)^{ECF}] + \Delta(Q)$$

where  $[d\Sigma(Q)/d\Omega]_{RC}$  and  $[d\Sigma(Q)/d\Omega]_{agg}$  are the contributions of random coils chain and of aggregated chains, respectively;  $R_g$  is the radius of gyration of the random coil,  $P(Q)$  and  $S(Q)^{PY}$  are the form factor and the structure factor of the aggregate (Triolo & Caponetti, 1990), respectively, and  $S(Q)^{ECF}$  is the contribution due to the exponentially correlated fluctuations described in what follows (Shimizu, Kimura, Maruyama & Kurita, 1997). To compute  $P(Q)$  we tried several models and best fits were obtained with a "core+shell" polydisperse spheres model. For the structure function  $S(Q)^{PY}$  we have used hard spheres model in the Percus-Yevick approximation (Ashcroft & Leckner, 1966). In this experiment in a few solutions we included a Lorentzian contribution  $S(Q)^{ECF}$  (Shimizu, Kimura, Maruyama & Kurita, 1997). Statistical thermodynamics of polymer solutions in the semidilute poor solvent regime (Flory, 1953; de Gennes, 1979) suggests that the free energy density  $F$  can be simply expressed as a virial expansion in terms of binary and ternary cluster integrals (Okano, Takada, Kurita & Furusaka, 1994). From a structural point of view, a polymer in the semidilute regime shows density fluctuations correlated exponentially in space. The correlation length is a simple function of  $F$  and therefore of the cluster integrals (Okano et al, 1983-1994), and shows up in the scattering cross section of the solution as a Lorentzian contribution (Shimizu, Kimura, Maruyama & Kurita, 1997) quite similar to the Ornstein-Zernicke contributions described in different context (Triolo & Caponetti, 1990). In these preliminary fits 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 unimer 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.



**Figure 5.** Pressure dependence of the SANS pattern as obtained from a 12% w/v  $CO_2$  solution of 10.3 K PVAc-b-43.1K PFOA at 313K.

#### 4. Results and Discussion

Figures 3-5 show the effect of the  $CO_2$  pressure on the scattering function of the 6%, 8% and 12% (w/v) solution at 40 C. A tenfold increase in intensity and the appearance of a peak in the scattering intensity by decreasing the  $CO_2$  pressure is a clear indication of formation of aggregates. At the lower pressures (<200 bar) the solutions are from slightly to moderately opalescent. Good fits can be

obtained with the polydisperse "core+shell" spherical model for the aggregated polymer.

As indicated in the introduction, the polydisperse nature of the material studied in this paper increases the probability for the high molecular weight fraction of the polymer to locate itself inside the core of the micellar aggregates especially at low pressure when  $CO_2$  is a poor solvent. The consequence is that  $CO_2$  can penetrate deep into the micelle and also both the volume and the scattering length density of the core are quite large. In our model we allow for solvent penetration in the core (normalized to the value at the lowest pressure at which the polymer is still dispersed in  $CO_2$ ). The corresponding parameter in the model (CS) is an indication of the core swelling due to the solvent penetration; in fact, by increasing the pressure, the CS increase parallels the increase of stiffness of the core-shell interface, measured by the polydispersity parameter (Gradzielski, Langevin & Farago, 1996). The higher the pressure the "better solvent"  $CO_2$  becomes and eventually at high enough pressures the aggregates break down and the scattering curves become consistent with the scattering from random coils. The transition from mixture of random coils and aggregates to pure random coils is reasonably sharp and falls, at 40C, in a pressure range between 250 ( $\rho_{CO_2}=0.878 \text{ g/cm}^3$ ) and 350 bar ( $\rho_{CO_2}=0.914 \text{ g/cm}^3$ ). At 65C the transition takes place, for a 6% solution of the same polymer, at a slightly higher density (Triolo F. et al., 1999,b).

**Table I.**

Conc. <sup>1</sup>	P <sup>2</sup>	$R_g$ <sup>3</sup>	CS <sup>4</sup>	Agg. <sup>5</sup>	Z <sup>6</sup>
6 (0.3)	191		1.0	23(2)	13(2)
6 (0.3)	206		1.1	22(1)	15(1)
6 (0.3)	224		1.1	24(2)	19(3)
6 (0.5)	275		1.4	25(3)	20(4)
6	344	transition zone, $\rho_0 = 0.92 \text{ g/cm}^3$			
6	443	25.0	-	-	-
8 (0.2)	189		1.0	22(1)	15(1)
8 (0.2)	206		1.1	17(1)	13(1)
8 (0.2)	224		1.2	16(1)	13(1)
8 (0.4)	241		1.3	27(2)	17(1)
8 (0.5)	275		1.3	26(2)	17(2)
8	310	transition zone, $\rho_0 = 0.90 \text{ g/cm}^3$			
8	344	41.0	-	-	-
8	447	25.4	-	-	-
12 (0.3)	191		1.0	36(2)	21(2)
12 (0.3)	206		1.2	31(1)	21(1)
12 (0.4)	224		1.4	27(2)	20(2)
12 (0.5)	241		1.5	30(2)	18(1)
12	275	transition zone, $\rho_0 = 0.89 \text{ g/cm}^3$			
12	310	50.0			

<sup>1</sup> Nominal concentration (w%/V). In parenthesis the concentration of unimer expressed as percent of the polymer concentration.

<sup>2</sup> Pressure in bar

<sup>3</sup> Radius of gyration in Å

<sup>4</sup> Core Swelling ratio number based on the number average molecular weight of the polymer. Errors in parentheses.

<sup>5</sup> Schultz Polydispersity parameter. Error in parenthesis.

The concentration of unimers in equilibrium with aggregates remains approximately constant far from the transition pressure, then increases quickly upon approaching the transition, indicating that the aggregates are breaking down. The core-shell model described earlier fails to reproduce the data at pressures corresponding to the transition region, while a model of isolated random coils gave a good representation of the scattering curves at the highest pressures. Results of the fits 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  $R_g$  for the unimers are obtained by fitting the data to the random coil scattering equation (Debye, 1944). As indicated previously, a slight increase of Z upon increasing the pressure indicates stiffening of the core/shell interface (Gradzielski, Langevin & Farago, 1996), due to the penetration of CO<sub>2</sub> deep inside the aggregate.

The sharpness of the transition and the fact that the aggregation number and the polydispersity, away from the transition region, hardly depend on pressure is a clear indication that we are dealing with a transition due to the change in density.

### 5. Conclusion

The small-angle scattering investigation of solutions of a block-copolymer in scCO<sub>2</sub>, has given details on the mechanism controlling the aggregate-unimer transition triggered by increasing the pressure above a critical value. When the pressure exceeds this value the core of the aggregates become 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-unimer 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-unimer transition occurs in solutions of block-copolymers in scCO<sub>2</sub>. Further experiments are proposed to examine in detail the extent by which the cmd depends on polymer structure and temperature.

The authors thank ISIS for provision of beam time and help of ISIS staff during the experiments is gratefully acknowledged. GDW acknowledges support from the Divisions of Advanced Energy Projects and Materials Sciences, U. S. Department of Energy under contract No. DE-AC05-96OR22464 with Lockheed Martin Energy Research Corporation. AT, FT and RT acknowledge financial support from the Italian National Research Council and The Italian Department of Education and Research (MURST).

### References

- Ashcroft, N. W. & Leckner, J. (1966). *Phys. Rev.*, **145**, 83-90.  
 Cooper, A. I. et al. (1997). *Nature*, **389**, 368-371.  
 Debye, P. (1944). *J. Appl. Phys.*, **15**, 338-344.  
 DeSimone, J.M., Guan, Z. & Elsbernd, C.S. (1992). *Science*, **257**, 945-947.  
 DeSimone, J.M. et al. (1994). *Science*, **265**, 356-359.  
 DeSimone, J.M. et al. (1999). *Macromolecules*, submitted.  
 Eastoe, J., Robinson, B. H., Young, W. K. & Steytler, D. C. (1990). *J. Chem. Soc. Faraday*, **86**, 2883-2889.  
 Flory, P.J. (1953). *Principles of Polymer Chemistry*. Ithaca, NY: Cornell University Press.  
 Gennes P. -G de. (1979). *Scaling Concepts in Polymer Physics*. Ithaca, NY: Cornell University Press.  
 Gradzielski, M., Langevin, D. & Farago, B. (1996), *Phys. Rev. E*, **53**, 3900-3919.  
 Heenan, R. K., King S. M., Osborn, R. and Stanley, H. B. (1989) Rutherford Appleton Laboratory Report RAL-89-128.  
 Heenan, R. K., Penfold, J. & King S. M. (1997). *J. Appl. Cryst.*, **30**, 1140-1147.  
 McClain, J. B. et al. (1996). *Science*, **274**, 2049-2052.  
 Melnichenko, Y. B. et al. (1998). *Macromolecules*, **31**, 8436-8438.  
 Okano, K. et al. (1983). *Physica*, **B120**, 413-417.  
 Okano, K., Takada, M., Kurita, K. & Furusaka, M. (1994). *Polymer*, **35**, 2284-2289.  
 Rocha, S. R. P. da, Harrison, K. L. & Johnston, K. P. (1999). *Langmuir*, **15**, 419-428.  
 Shimizu, S., Kimura, M., Maruyama, T. & Kurita, K. (1997). *J. Appl. Cryst.*, **30**, 712-716.  
 Triolo, F. et al. (1999,a). *Langmuir*, in press.  
 Triolo, F. et al. (1999,b). *Phys. Rev. E*, in press.  
 Triolo, F. et al. (1999,c). *in preparation*  
 Triolo, R. & Caponetti, E. (1990). *Adv. Coll. Inter. Sci.*, **32**, 235-244.  
 Triolo, R. et al. (1999). *unpublished data*  
 Wignall, G.D. (1999). *J. Physics Condensed Matter*, in press.  
 Zhou, S. Q. & Chu, B. (1998). *Macromolecules*, **31**, 5300-5308.