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Study of the Association of a Diblock Copolymer and Absorption of an Insoluble Homopolymer in CO_2

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Introduction. Amphiphilic block copolymers have received widespread attention over the past 30 years. This attention can be attributed to the now well-known fact that block copolymers self-assemble to form micelles in solution when placed in a selective solvent.[1−3] A selective solvent is a solvent that is a good or Θ solvent for one block and a poor or nonsolvent for the other block. Extending this concept to carbon dioxide (CO_2) systems, the formation of micelles occurs in a CO_2 medium, where the micellar core is CO_2-phobic, and the CO_2-philic shell extends into the solvent.

When compressed into its liquid or supercritical fluid state, CO_2 is a good solvent for many small molecules; however, most polymeric materials have a very low solubility in CO_2. Only two classes of polymers are significantly soluble in CO_2 at practical operating conditions. These are amorphous fluoropolymers and polysiloxanes.[4] However, fluoropolymers and siloxanes represent only a very small fraction of industrially important polymers; therefore, amphiphilic molecules are needed to broaden the efficacy of liquid and supercritical CO_2 to include the synthesis of other polymers using heterogeneous polymerization methods.[5−7] The extensive synthetic use of these amphiphiles necessitates the study of their solution properties.

In the past 10 years, small-angle neutron (SANS), X-ray (SAXS), and light scattering methods have been used to provide information on the conformational and physical properties of polymeric micelles formed from amphiphilic block copolymers in CO_2.[8−12] Previous literature results have even shown the absorption of a polystyrene oligomer into a poly(styrene)-*b*-poly(fluorooctyl acrylate) diblock copolymer micelle core in CO_2.[12] Building on those results, it seemed reasonable that, in the right solvent conditions, diblock copolymer micelles would also be able absorb low molecular weight homopolymers. In this communication, we report light scattering and SANS results for micelles formed from a 35 kg/mol poly(*tert*-butyl methacrylate)-*b*-35 kg/mol poly(fluorooctyl methacrylate) (35−35 PBF) sample in CO_2. We also demonstrate the absorption of a CO_2-insoluble poly(*tert*-butyl methacrylate) homopolymer by the micelle. This is the first report that combines LS and SANS to described the physical properties of polymeric micelles in CO_2.

Experimental Section. a. Materials and Synthesis. The P*t*BMA-*b*-PFOMA diblock copolymer was prepared through anionic polymerization by sequential addition of *t*BMA and FOMA using a 1,1-diphenylhexyllithium and lithium chloride initiating system. A more detailed synthetic scheme has been described elsewhere.[13] The molecular weight of the PFOMA block was determined by ^1H NMR in hexafluorobenzene (benzene-d_6, lock solvent) based on the molecular weight of the P*t*BMA prepolymer determined by GPC based on polystyrene standards. The polydispersity of the prepolymer was narrow (1.03) based on GPC analysis.

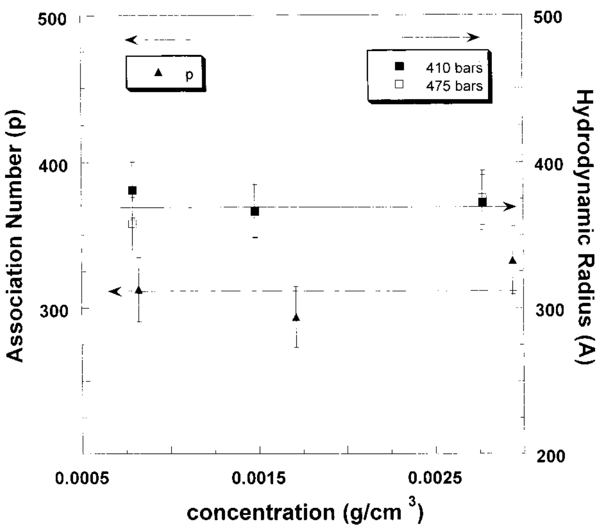

Figure 1. Association number and hydrodynamic radius plotted as a function of concentration for the 35 kg/mol PtBMA-*b*-35 kg/mol PFOMA diblock copolymers. The association number was measured at $p = 475$ bar.

b. High-Pressure Scattering Measurements. The design and construction of the high-pressure light scattering and refractive index measurement cells have been discussed in detail elsewhere.[14,15] The sample was placed in the high-pressure cell and then pressured with carbon dioxide to the experimental pressure using an ISCO pump. The sample was then stirred for 15−30 min and then allowed to sit for another 15−120 min before the beginning of the experiment, depending on the time it takes for dust to settle and the sample to equilibrate. The cell was then placed in the sampling position and the scattering measurement performed. Static and dynamic light scattering experiments were performed using an argon ion laser and computer-controlled motor-driven variable angle detection system from Brookhaven Instruments. SANS experiments were performed at Institut Laue Langevin in Grenoble, France, on instruments D11.

Results and Discussion. a. Light Scattering Measurements. The micellar properties of the 35−35 PBF copolymer were extensively studied by light scattering. The absolute mass of the sample was determined by measuring the differential concentration refractive index (dn/dc) of the polymer in CO_2. The measured dn/dc value is 0.15 ± 0.02 cm^3/g. Both the association number and size were concentration- and pressure-independent in the pressure range from 250 to 500 bar and concentration range $c = 0.0007$ to 0.005 g/cm^3. The association number and hydrodynamic radius were 315 ± 16 and 370 ± 18 Å, respectively. See Figure 1.

b. Small-Angle Neutron Scattering Results. Small-angle neutron scattering was performed on the 35−35

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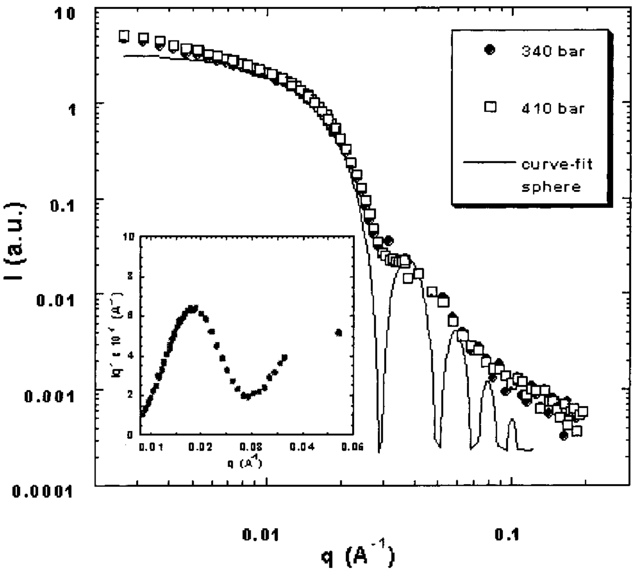

Figure 2. SANS curve for the 35 kg/mol PtBMA-*b*-35 kg/mol PFOMA diblock copolymers at two difference pressures, 340 and 410 bar, and at $c = 0.005$ g/cm^3. The inset shows the Porod analysis with the position of the first minimum being located at 0.0296 Å^{-1} corresponding to 151 Å.

PBF sample in CO$_2$. The difference in the scattering length density between the PFOMA diblock and CO$_2$, 5.1×10^{-11} cm^{-2}, was small in comparison with the difference of the scattering length density between PtBMA and CO$_2$, 3.21×10^{-10} cm^{-2}. In essence, the scattering from the micelles was mainly due to the cores, and the shells were nearly contrast matched with CO$_2$. The difference in the scattering length density of the PtBMA with CO$_2$ was large enough to study the diblocks over a range of concentrations, from 0.001 up to 0.025 g/cm^3.

Figure 2 shows the scattering data for sample 35−35 at $c = 0.005$ g/cm^3 for two different pressures, 340 and 410 bar. Because the intensity scattered from the micelle is mostly due to the core, only the form factor for a monodisperse sphere is needed to fit the scattering curves. The size of the core measured from the Porod analysis is 151 ± 2 Å. See inset in Figure 2. The effect of pressure on the micelle cores is negligible in the range of concentrations (0.001−0.005 g/cm^3) and pressures studied, as evidenced by the practically indistinguishable curves at the two different pressures.

By combining the light scattering and the SANS results, we are able to calculate the density of the core of the micelle. By defining the density as

$$\rho = \frac{3M_{\mathrm{D}}p}{4\pi R_{\mathrm{core}}^{3}N_{\mathrm{A}}} \tag{1}$$

where p is the association number, M_{D} is the mass of the polymer in the core block, and N_{A} is Avogadro's number, we estimate that the density for the micelle core of the 35−35 PBF is of the order of 1, demonstrating that the core is dense and contains little if any solvent molecules.

c. Absorption of Homopolymer. An 11K PtBMA homopolymer was dissolved in CO$_2$ solution with the 35−35 PBF sample at 410 bar; the concentration of the homopolymer was 0.001 g/cm^3, while that of the diblock was 0.005 g/cm^3. At this concentration, solubility measurements confirm that an 11K PtBMA homopolymer is insoluble below 500 bar. Optically, the diblock/homopolymer solution appeared transparent; there was no visual detection of homopolymer at the bottom of the cell. In Figure 3 the scattering curves for sample 35−35 at $c = 0.005$ g/cm^3 and sample 35−35 at the same concentration with added homopolymer, both at 410 bar, are shown. The unmistakable increase in the size of the core is evident with the shift of the peak to smaller q. The increase in the amplitude of curve in the Guinier region is most probably due to scattering from the unabsorbed homopolymer. Using a sphere form factor to fit the data, the size of the core with the added homopolymer is 169 ± 2 Å, in comparison the size of the core without homopolymer, 151 ± 2 Å. This is a 10% increase in the size of the core and a 30% increase in the volume.

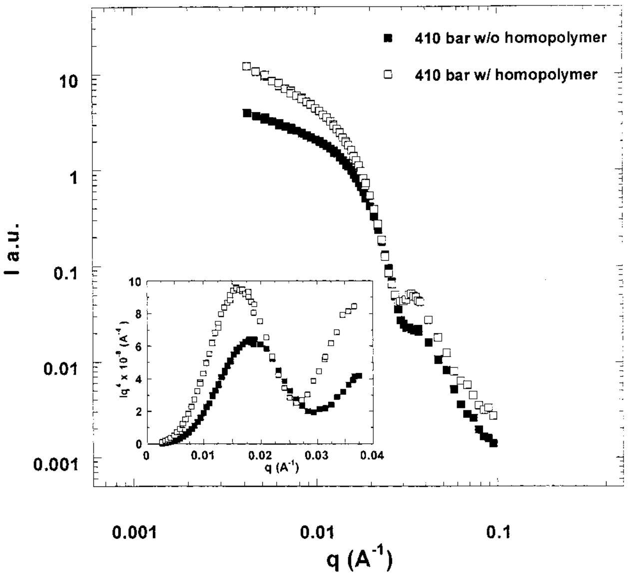

Figure 3. SANS curve for the 35 kg/mol PtBMA-*b*-35 kg/mol PFOMA diblock with and with added 11 kg/mol PtBMA homopolymer at 410 bar. The concentration of the diblock copolymer is $c = 0.005$ g/cm^3 and $c = 0.001$ g/cm^3 for the homopolymer. The inset shows the Porod analysis for scattering curves. The shift to smaller q for the sample with the added homopolymer clearly indicates an increase in the size of the core.

On the basis of the change in the size of the core with the addition of homopolymer, it is possible to calculate the number of 11K PtBMA chains inside the core of the micelle. The volume of the core R_{core}^{3} can be expressed as

$$R_{\mathrm{core}}^{3} \approx M_{\mathrm{D}}p_{1} \tag{2}$$

where M_{D} is the molecular weight of the PtBMA block of the copolymer (35K) and p_1 is the association number of the micelle without added homopolymer. Likewise, the volume of the core with added homopolymer R_{hcore}^{3} is

$$R_{\mathrm{hcore}}^{3} \approx M_{\mathrm{D}}p_{2} + M_{\mathrm{H}}f \tag{3}$$

where M_{H} is the molecular weight of homopolymer (11K), p_2 is the association number of the micelle with added homopolymer, and f is the number of homopolymer chains in the core of the micelle.

Light scattering experiments[16] have shown that the concentration of dissolved 11K P*t*BMA in CO_2 is undetectable, and therefore we can assume that the presence of homopolymer has a negligible effect on the CO_2 solvent quality. Then it can be assumed that the concentration in the core of the micelle and the association number ($p = p_1 = p_2$) are constant. The ratio of the volume of the core with homopolymer to the volume without homopolymer is then

$$\frac{R_{\mathrm{hcore}}^3}{R_{\mathrm{core}}^3} = \frac{M_{\mathrm{H}} f}{M_{\mathrm{D}} p} + 1 \tag{4}$$

Taking the experimentally determined values for R_{core} and R_{hcore} and the mass of the diblock and homopolymer, the ratio f/p is 1.3 ± 0.1. This means that for every diblock copolymer chain in the micelle there are 1.3 homopolymer chains in the core.

With further investigation, when the total number of homopolymer chains in cell volume is estimated with respect to the total number of diblock chains in the cell volume, the above results are within reason. Say the total number of chains in any solution is proportional to the concentration of the chains divided by the molecular weight; then for this system, the number of homopolymer chains N_{H} to the number of diblock copolymer chains N_{D} is simply

$$\frac{N_{\mathrm{H}}}{N_{\mathrm{D}}} = \frac{C_{\mathrm{H}}/M_{\mathrm{H}}}{C_{\mathrm{D}}/M_{\mathrm{D}}} \tag{5}$$

where C_{H} and C_{D} are the concentrations of the homopolymer and diblock copolymer. The ratio N_{H} to N_{D} is approximately 1.3. This ratio demonstrates that most, if not all, of the homopolymer chains added to the scattering cell are in the core of the micelle.

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