Diffusion of Block Copolymers in Liquid CO_2: Evidence of Self-Assembly from Pulsed Field Gradient NMR

Judith B. Cain, Kewei Zhang, Douglas E. Betts,
Joseph M. DeSimone,* and Charles S. Johnson, Jr.*

Department of Chemistry, University of North Carolina
Chapel Hill, North Carolina 27599-3290

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In recent years liquid/supercritical CO_2 has become an increasingly important solvent system for polymerization reactions because of the environmentally driven need to phase out chlorofluorocarbons (CFCs), to avoid emission of volatile organic compounds, and to reduce aqueous waste streams. Since few polymeric materials are soluble in CO_2 under relatively mild conditions (exceptions being amorphous fluorocarbons and silicones), polymerization technologies depend on specially designed block copolymer surfactants. A particularly successful CO_2-philic block for such amphiphilic copolymers is poly(1,1-dihydroperfluorooctyl acrylate) or PFOA.[1] Polystyrene (PS) is CO_2-phobic and small angle neutron scattering (SANS) data show that the copolymer PS-*b*-PFOA forms micelles in CO_2. In contrast to this behavior, poly(vinyl acetate) (PVAc) is only slightly soluble in liquid CO_2 at higher pressures,[2] and the copolymer PVAc-*b*-PFOA is expected to form micelles only at lower densities.

The self-assembly of micelle-forming block copolymers in CO_2 has been confirmed by SANS.[3] This method provides information about the structure of micelles but requires computer modeling of the data and is limited to high concentrations. Light scattering has the advantage over SANS for the study of block copolymers in CO_2 that data can be collected at very low concentrations, thus permitting the determination of the critical micelle concentration and the critical micelle density.[4] Small-angle X-ray scattering (SAXS) has also been used[5] to characterize the formation of micelles by graft copolymers in CO_2. However, none of these methods can identify molecules or detect small solutes in the presence of polymers.

It is, therefore, desirable to have an independent method for investigating micelle formation and solubilization capabilities. NMR is a promising method because of its ability to identify molecules from their chemical shift spectra and, with the help of pulsed magnetic field gradients (PFGs), to determine size-dependent diffusion coefficients.[6] NMR has proved useful in the detection of phase separation for fluoropolymers in CO_2 and the determination of the volume fraction of CO_2 in the polymer-rich phase[7] as well as for the detection of specific solute−solvent interactions between fluorocarbons and CO_2.[8] Here we present a preliminary report of a study of self-assembly of the block copolymers PVAc-*b*-PFOA and PS-*b*-PFOA in liquid CO_2 by means of PFG-NMR.[9]

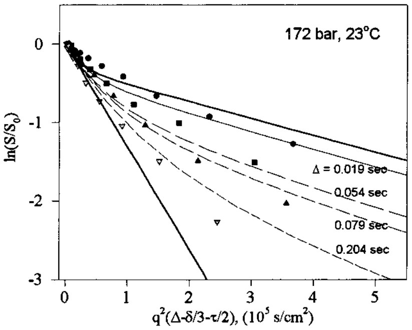

Figure 1. Plot of relative signal amplitude versus $q^2(\Delta - \delta/3 - \tau/2)$ for PS-*b*-PFOA for various diffusion times along with calculated curves for the same times.

The essential findings are the following. In the temperature/density regime where micelles do not form, a narrow distribution of diffusion coefficients is found for the copolymer. However, when self-assembly occurs, the PFG-NMR data become strongly dependent on the diffusion time and are consistent with a two-site exchange model involving fast and slow diffusive modes. At the shortest diffusion times (∼10 ms) two diffusion rates are resolved, while in the long diffusion time limit only an average diffusion rate can be measured. Thus, the signature for self-assembly in these systems is the exchange of polymers between relatively free and associated states on a time scale accessible to PFG-NMR.

The NMR spectrometer system, the gradient driver, and the experimental design have previously been described.[10,11] All data were acquired with the bipolar LED sequence in which the echo attenuation for a molecule having the diffusion coefficient D is given by[12]

$$S(q) = S(0)\exp\left[-Dq^2\left(\Delta - \frac{\delta}{3} - \frac{\tau}{2}\right)\right] \qquad (1)$$

where $S(0)$ is the echo amplitude in the limit of small but nonzero gradient pulses, the effective gradient pulse areas are $q = \gamma g \delta$ where γ is the gyromagnetic ratio, and g and δ are the gradient pulse amplitude and duration, respectively. The diffusion time is Δ, and τ is the delay between the gradient pulses and the following 180° rf pulses.

The experiments were performed with a Bruker AC-250 spectrometer equipped with a Nalorac 5-mm diffusion probe (0.101 $\mathrm{T\,m^{-1}\,A^{-1}}$) and a home-built computer-controlled gradient driver. A folded capillary-type pressure cell with inner and outer diameters of 150 μm and 360 μm, respectively, was used to contain the high-pressure CO_2 mixtures.[13] The capillary was folded so that it would fit into a standard 5-mm NMR tube and make 22 passes through the NMR active volume. This arrangement provided convenience and safety because of the small volume of compressed sample. Furthermore, the small diameter of the capillary is expected to suppress Rayleigh-Bernard convection in liquid and supercritical CO_2.[14] We verified this point by demonstrating that the apparent diffusion coefficient of FOA in CO_2 at 323 K and 241 bar is independent of capillary i.d. in the

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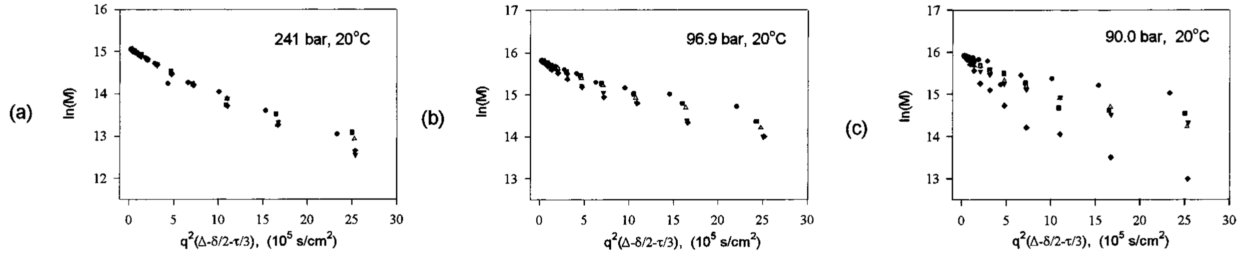

Figure 2. Plots of relative signal amplitude versus $q^2(\Delta - \delta/3 - \tau/2)$ for PVAc-*b*-PFOA for various diffusion times at: (a) 241 bar ($\rho = 0.965$ g/cm^3), (b) 96.9 bar ($\rho = 0.858$ g/cm^3), and (c) 90.0 bar ($\rho = 0.848$ g/cm^3), all at 20 °C.

range from 100 μm to 320 μm. Note that the root-mean-square displacement $(2D\Delta)^{1/2}$ perpendicular to the capillary axis is 15% of the capillary diameter in the worst case ($D_{av} = 1.3 \times 10^{-5}$ cm^2/s, $\Delta = 0.2$ s); however, this has no effect on diffusion measurements which depend on displacement in the z-direction.

The method of preparing the block copolymer solutions and filling the high pressure NMR cell has previously been reported.[7] PFG-NMR diffusion experiments were performed on an 8% (w/v) solution of PS-*b*-PFOA (4k/28k) in CO_2 at 296 K and 172 bar. CO_2 is a selective solvent for the PFOA block and does not dissolve the PS block. Such differences in solubilities often lead to the formation of multimolecular micelles in block copolymer systems. Micelle formation typically leads to a decrease in diffusion coefficients because of the resulting increase in the hydrodynamic radii and the obstruction effect. The primary effect discovered in this work was a severe curvature of $\ln(S/S_o)$ versus $\alpha = q^2(\Delta - \delta/3 - \tau/2)$ curves and their dependence on the diffusion time Δ. Figure 1 shows representative diffusion decay curves obtained with four diffusion times varying from 19 to 204 ms out a total set of seven diffusion times. We note that as the diffusion time increases the slope at large values of α also increases. This effect is not observed for the diffusion of small molecules in CO_2 under identical conditions and is opposite to that expected in the presence of restricted diffusion. Also, the curvature and Δ dependence is not observed for 8% PS-*b*-PFOA in Freon-113, which is a good solvent for both PS and PFOA.

A distribution of diffusion times for polydisperse PS-*b*-PFOA can also give rise to curvature, but the curvature should not be dependent on the diffusion time.[15] Finally, we note that a distribution of longitudinal relaxation times (T_1) can produce trends similar to those observed; however, for flexible polymers in solution, proton T_1's depend on segmental motions and are insensitive to total molecular weights.[16] To confirm this we measured the relaxation curves for the protons in PS-*b*-PFOA and found that they were described by single exponential decays. We conclude that the observed diffusion time dependent results are produced by chemical exchange of block copolymers between fast and slow diffusive modes, e.g., unassociated free copolymers and slowly moving micelles, thus giving additional evidence for a density-induced micellization transition.

The effects of chemical exchange in PFG-NMR and in diffusion ordered NMR spectroscopy (DOSY) have previously been investigated.[17,18] In the case of two diffusive modes (two-site case with identical chemical shifts), the signal intensity versus α depends on four parameters, the fast and slow diffusion coefficients D_f and D_s, the fraction of spins in the slow site X_s, and the exchange rate $k_s = 1/\tau_s$, where $k_s/k_f = (1 - X_s)/X_s$. The four parameters for PS-*b*-PFOA were determined by simultaneously fitting all seven sets of data to eq 12 of ref 18 by means of the Marquardt–Levenberg algorithm as implemented in SigmaPlot 4.0. The resulting best fit parameters were found to be $D_f = 4.4 \times 10^{-5}$ cm^2/s, $D_s = 2.1 \times 10^{-6}$ cm^2/s, $X_s = 0.74$, and $k_s = 11$ s^{-1}. Curves calculated using these parameters are also shown in Figure 1 with the appropriate diffusion times. In addition, the limiting curves calculated for $\Delta = 0$ and $\Delta = \infty$ are shown. The two-site model is certainly an approximation since the unassociated copolymers are polydisperse; however, as noted above, PFG-NMR diffusion measurements on the copolymers in Freon, where aggregation does not occur, give little indication of polydispersity.[9]

The polymer concentration of 8% (w/v) corresponds to the region of overlap where data interpretation is difficult. Naive use of the uncorrected Stokes–Einstein equation yields hydrodynamic radii of 5.5 and 11.5 nm for the fast and slow components, respectively. We note that a recent dynamic light scattering study of the related block copolymer PVAC-*b*-poly-(1,1,2-tetrahydroperfluorooctyl acrylate) (PTAN) (10.3k/60.4k) in CO_2 at 45 °C ($\rho = 0.82$ to 1.0 g/cm^3) reports radii of 4.0 and 15.3 nm for unimers and micellar aggregates, respectively. The PVAC-*b*-PTAN radii were found to be relatively independent of CO_2 density and copolymer concentration.[4] Exchange rates have not previously been measured for surfactants in CO_2; however, the rate found here is very slow compared with ordinary surfactant micelles but fast compared with exchange rates for block copolymer micelles.[19,20] The mole fraction for the slow site is low compared with recent SANS results but is not unreasonable.

Additional evidence for the exchange model described here is provided by the block copolymer system, PVAc-*b*-PFOA (10k/43k), which is expected to form micelles only at low CO_2 densities.[21] Data for a 8% (w/v) sample at 293 K and three different pressures is shown in Figure 2 (a–c) for Δ ranging from 20 ms (●) to 140 ms (◆). At 241 bar there is little dependence on Δ, and the polymer chains are well solvated. At 96.9 bar some dependence on Δ is becoming evident, and at 90.0 bar the full effects of exchange can be seen. Unfortunately, the S/N ratios in this data set do not permit a full analysis of diffusion coefficients and exchange rates.

We have shown that PFG-NMR is sensitive to the presence of block copolymer based micelles in liquid CO_2. This experiment makes use of the variable diffusion time permitted by NMR. More accurate analyses, especially at lower polymer concentrations, will require higher S/N ratios. The present work was limited by very low filling factors, resulting from the use of fine capillary sample tubes. We plan to pursue this work in the future with capillary pressure cells in a higher frequency spectrometer and in toroid cavity probes[22] that permit the use of much larger samples.

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