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Solution Properties of a CO_2-Soluble Fluoropolymer via Small Angle Neutron Scattering

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Many nonionic, low molar mass organics are soluble in liquid and supercritical carbon dioxide,[1,2] but only two classes of polymers—amorphous (or low melting) highly fluorinated polymers and silicones—exhibit significant solubility in dense carbon dioxide at readily accessible conditions ($T < 100$ °C and $P < 500$ bar).[2−7] Understanding the solution characteristics of these CO_2-philic polymers is of primary importance for quantifying their growing role in polymer synthesis and processing.[5,6] In this communication, we report the first characterization of solutions of a high molecular weight polymer in supercritical CO_2 by small-angle neutron scattering (SANS).

We have shown that fluorinated acrylate polymers, such as poly(1,1-dihydroperfluorooctyl acrylate) [poly(FOA)], are soluble in supercritical CO_2 and can be synthesized to high conversion (>95%) by free radical solution polymerization methods at high solids (>60 w/v %).[3] Using SANS, we are able to monitor the conformation of poly(FOA) in CO_2 solution as reflected by its R_g and second virial coefficient. Scattering curves generated from poly(FOA) in CO_2 are analyzed using traditional methods for polymers in a good solvent.[8−11]

Various characterization techniques have been applied to polymer solutions in CO_2 including X-ray scattering, UV and IR spectroscopy, and viscometry.[12−16] Conventional light scattering experiments are difficult since there is insufficient difference in the refractive indices of fluorinated polymers and CO_2 (or fluorocarbon and chlorofluorocarbon solvents).[12,13] In the case of SANS, however, scattering contrast is expressed in terms of scattering length density (SLD) differences, which, in turn, are obtained from summing the corresponding atomic scattering lengths over the different molecules.[11] For the fluorinated acrylate repeat unit ($C_{11}H_5O_2F_{15}$), we find $SLD_{poly(FOA)} = 3.36 \times 10^{10}$ cm^{-2}. For the solvent, $SLD_{CO_2} = \rho(2.498 \times 10^{10}$ cm$^{-2})$, where ρ is the density of CO_2.[17] More importantly, the polymer SLD is sufficiently different from that of CO_2 to enable the use of SANS to monitor polymer solution characteristics over a range of densities (i.e., solvent strengths) in this highly compressible medium.

Two samples of poly(FOA) were prepared by solution free radical polymerization methods in supercritical CO_2 under conditions specifically designed to produce different molecular weights.[18]

SANS Data Acquisition and Analysis. Neutron scattering experiments were performed at the W. C. Koehler 30 m SANS spectrometer at the Oak Ridge National Laboratory.[19] The neutron wavelength was 4.75 Å ($\Delta\lambda/\lambda \approx 5\%$). The sample to detector distance and corresponding range of momentum transfer varied for the low M_w and high M_w polymer solutions.[20] Conversion of the neutron intensities to absolute differential cross sections and correction for detector efficiency and background have been previously described.[21,22] Experiments were conducted by placing a precise amount of a poly(FOA) sample in a 2.5 mL, 316 stainless steel high-pressure cell equipped with 1.0 cm thick sapphire windows (>90% transparency for neutrons). The scattering cell is identical in design to the high-pressure reaction cell we have used extensively for polymer synthesis in CO_2.[3,5,6] The cell was then pressurized with CO_2, heated to the desired temperature, stirred for ~10 min, and aligned in the SANS beam. Spectra were taken directly after the sample cell was mounted, and the transmission of the sample was recorded.[23]

Analysis of the SANS curves generated from poly(FOA) solutions in CO_2 is based on the average of two techniques—the Zimm approximation at low scattering vector (Q)[24] and fitting of the scattering curve to a Debye coil model calculated with a gaussian distribution of chains.[9−11,25] Values for the z average radius of gyration (R_g) and the differential cross section at zero scattering vector ($d\Sigma/d\Omega(0)$) are obtained for each solution. The weight average molecular weight (M_w) and the second virial coefficient (A_2) are obtained by extrapolation of $d\Sigma/d\Omega(0)$ for a series of dilute solutions to zero concentration.

SANS data were obtained for a concentration series of the high molecular weight poly(FOA) ($M_w = 1.4 \times 10^6$ g mol^{-1}) in CO_2 (at 60 °C and 395 bar, 65 °C and 340 bar, and 40 °C and 340 bar); the low molecular weight polymer ($M_w = 1.1 \times 10^5$ g mol^{-1}) was analyzed at 60 °C and 340 bar.

Figure 1a shows representative scattering data ([c] = 0.015 g cm^{-3} for high M_w poly(FOA) in CO_2 at 65 °C and 340 bar) and the line from Debye coil fitting along with the background scattering of pure CO_2 at the same conditions. Figure 1b shows the analysis of the low Q region of the same curve using the Zimm approximation. The radius of gyration for each set of

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(20) For the high M_w polymer solutions, the sample to detector distance varied from 7.0 to 10.0 m, giving a range of momentum transfer, $0.0027 < Q = 4\pi\lambda^{-1} \sin \theta < 0.081$ Å^{-1}, where 2θ is the angle of scatter. For the low M_w polymer solutions, the sample to detector distance was 3.0 m, giving a range of momentum transfer, $0.0091 < Q < 0.193$ Å^{-1}.

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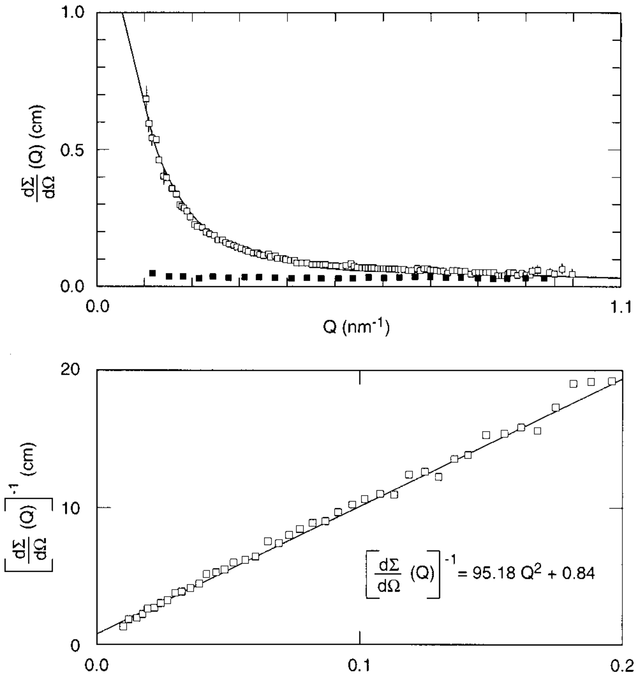

Figure 1. (a) Scattering curve of 0.015 g cm^{-3} solution of high M_w poly(FOA) in supercritical CO_2 at 65 °C and 340 bar (□) and the signal for CO_2 background at the same conditions (◆). Note the differential cross section of pure CO_2 is 0.03 cm^{-1} over $0.15 < Q < 0.4$ nm^{-1} and is 0.02 cm^{-1} at $Q > 0.05$ nm^{-1}. (b) $d\Sigma/d\Omega(Q)^{-1}$ vs Q^2 of the low Q region of the same curve and the results from linear regression.

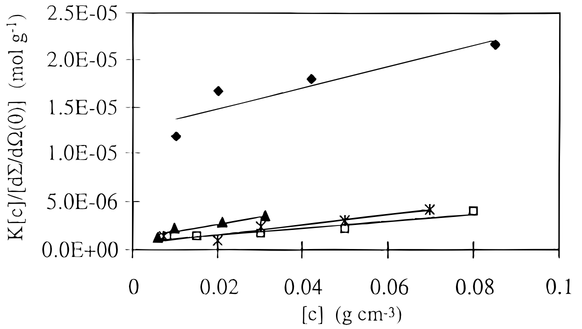

Figure 2. Linear regression fitting of $K[c]/[d\Sigma/d\Omega(0)]$, where $K = (\Delta SLD)^2/(\rho)(N_a)$, vs [c] for high M_w poly(FOA) at 60 °C and 340 bar (□), high M_w poly(FOA) at 65 °C and 395 bar (△), high M_w poly(FOA) at 40 °C and 340 bar (*), and low M_w poly(FOA) at 65 °C and 395 bar (◆).

conditions (Table 1) remains essentially constant ($R_g \approx 110$ Å) with concentration, affirming that all experiments were done in the dilute regime ($0.005 < [c]$ (g cm^{-3}) < 0.08).

Results for the four systems studied are shown graphically in Figure 2, where the values of $d\Sigma/d\Omega(0)$ are obtained from Debye coil fits. Weight average molecular weights and second virial coefficients calculated from the average (of Zimm analysis and Debye coil fits) intercepts and slopes are shown in Table 1.

The measured molecular weight results for the two polymers are consistent with those anticipated from the conditions at which each was synthesized. For the high molecular weight sample, the average value of M_w (1.4×10^6 g mol^{-1}) is within the experimental error of individual experiments. The values for A_2 are approximately the same order of magnitude as those found for polymers dissolved in a thermodynamically good solvent.[26]

The R_g (av $R_g \approx 110$ Å) did not change within the experimental error of individual measurements over the range of densities studied ($0.842 < \rho$ (g cm^{-3}) < 0.943). However, related studies of the phase behavior of polymers in CO_2 have confirmed that the solvation of polymers by CO_2 is linearly related to solvent density.[27] Future experiments shall focus on polymer solutions over a wider range of CO_2 densities, where trends should be more dramatic.

Table 1. SANS Results for Concentration Series of Poly(FOA) in CO_2 at Various Conditions

poly(FOA) sample	P (bar)	T (°C)	ρ^a (g cm^{-3})	R_g (Å)	A_2 ($\times 10^5$ cm^3 mol g^{-2})	M_w ($\times 10^{-6}$ g mol^{-1})
low M_w	395	60	0.888	35 ± 0.15	9.5 ± 0.5	0.113 ± 0.006
high M_w	340	65	0.842	120 ± 13	1.9 ± 0.4	1.5 ± 0.4
high M_w	395	60	0.888	100 ± 6	4.1 ± 0.8	1.2 ± 0.3
high M_w	340	40	0.934	114 ± 9	2.5 ± 0.3	1.6 ± 0.3

[a] Density of pure CO_2 at these conditions.[17]

Comparison of the results for the two molecular weight samples studied allows for preliminary discussion concerning the effect of polymer molecular weight on solution characteristics in CO_2. The second virial coefficient for poly(FOA) in CO_2 is a decreasing function of molecular weight, as observed in conventional polymer solutions. When the range of M_w is narrow, i.e., 1−2 decades, the M_w dependence of A_2 can be empirically described by the proportionality $A_2 \ \alpha \ M_w^{-\delta}$, where $\delta = 0.3$ applies in various systems.[28] Data for poly(FOA) solutions in supercritical CO_2 yield $\delta = 0.4 \pm 0.1$. The radius of gyration also scales with M_w: $(R_g^2/M_w)^{1/2} = 0.10 \pm 0.03$ Å mol$^{1/2}$ g$^{-1/2}$ for both low M_w and high M_w samples. This value is in agreement with literature precedent.[8,11,29] Future experiments shall focus on a series of different molecular weight poly(FOA) samples obtained by fractionation and will further elucidate the molecular weight dependence of both R_g and A_2.

In summary, small-angle neutron scattering gives key molecular parameters of an amorphous fluoropolymer in supercritical CO_2, i.e., the molecular weight, radius of gyration, and second virial coefficient, and thereby gives insights into a polymer chain's behavior in this unique solvent. The positive sign of the second virial coefficients indicate that this medium is a good solvent—there is no evidence of a collapsed chain conformation. In fact, we conclude from the SANS data that, in CO_2, the poly(FOA) chain dimensions are expanded relative to those characteristic of its melt.

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Supporting Information Available: Details of poly(FOA) synthesis (1 page). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(26) By comparison, poly(styrene) ($M_w = 7.65 \times 10^5$ g mol^{-1}) in cyclohexane at 60 °C ($T_\Theta = 34.3$ °C) has an A_2 of 9.3×10^{-5} mL mol g^{-2}. Yamamoto, A.; Fujii, M,; Tanaka, G.; Yamakawa, H. *Polym. J.* **1974**, *15*, 682.

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