Notes

Coil−Coil Interactions for Poly(dimethylsiloxane) in Compressible Supercritical CO_2

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Investigations of the solvent quality of a supercritical fluid solvent (SCF), such as CO_2, has attracted academic and industrial interest for processing polymers.[1,2] Reliable applications of supercritical CO_2 technology require information on polymer−CO_2 phase behavior and on the solvent quality of CO_2 as a function of pressure or density. One measure of solvent quality is the second osmotic virial coefficient, A_2, which also provides information on the behavior of isolated polymer chains in solution.[3,4] As the solvent density is adjusted, A_2 is anticipated to change from negative values at low densities and poor solvent quality where polymer chains contract slightly relative to their unperturbed size to positive values at high densities and good solvent quality where polymer chains expand relative to their unperturbed size. At the theta condition, where A_2 is zero, repulsive excluded-volume interactions compensate attractive monomer−monomer interactions, and the polymer adapts its unperturbed size.

While A_2 is typically determined by osmotic pressure or static light scattering (SLS) methods, both techniques are problematic to implement in a high-pressure environment with a highly compressible solvent. Our research group has utilized dynamic light scattering (DLS) to probe coil−coil interactions[5,6] since it is easier to identify and resolve potential artifacts associated with high-pressure scattering cells.[6,7] Coil−coil interactions are ascertained via the concentration, c, dependence of the polymer translational diffusion coefficient, D[8]

$$D = D_0[1 + k_D c + ...] \tag{1}$$

where D_0 is the infinite dilution diffusion coefficient and k_D is the dynamic second virial coefficient. Both thermodynamic and hydrodynamic (i.e., frictional) interactions are accounted for in k_D[9,10]

$$k_D = 2A_2M - k_s + \frac{RT\kappa_T}{M} \tag{2}$$

where M is the polymer molar mass, k_s is the friction coefficient associated with the collective sedimentation coefficient,[10] R is the gas constant, T is the absolute temperature, and κ_T is the solution isothermal compressibility.[9] The third term is $\sim O(10^{-6})$ and is neglected relative to the other terms.[5]

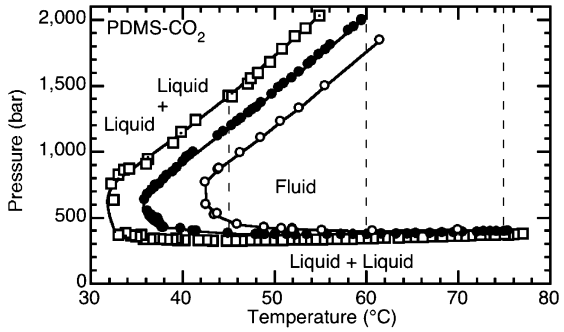

Figure 1. Phase behavior of 0.077 wt % (squares), 1.01 wt % (solid circles), and 7.0 wt % (open circles) PDMS in supercritical CO_2. Lines through the data are to guide the eye, and the vertical dashed lines show the isothermal paths used for DLS measurements. The data have an accumulated error and reproducibility of ±15 bar and ±0.2 °C, except where the cloud-point curve changes slope, and it is more difficult to distinguish the phase-transition pressure.

Cotts and Selser performed a particularly illustrative exposition of coil−coil interactions utilizing SLS and DLS with polymer covering a wide range of molecular weights.[11] To compare their study with related DLS investigations, it is more convenient to consider the polymer volume fraction, ϕ, dependence of D to account for the effect of polymer molar mass

$$D = D_0[1 + k_D^{\phi}\phi + ...] \tag{3a}$$

where

$$k_D^{\phi} = k_D \frac{M}{N_A V_H} \tag{3b}$$

Here, N_A is Avogadro's number and V_H is an equivalent hydrodynamic hard-sphere volume calculated with experimental values of the hydrodynamic radius R_H. Cotts and Selser[11] report the best estimate of the theta condition is $k_D^{\phi} = -2$, and the limit for good solvent conditions is $k_D^{\phi} \cong 2$.

Recently, Andre and co-workers investigated coil−coil interactions for poly(dimethylsiloxane) (PDMS)−CO_2 solutions[12] where they report that A_2, and the corresponding solvent quality, increase and appear to reach a maximum as the pressure is increased just near the pressure limit of their experimental apparatus. They were unable to probe the single-phase region shown in Figure 1 near the high-pressure, upper critical solution temperature (UCST) boundary of the PDMS−CO_2 system measured by the present authors. To the authors' best knowledge, this is the first time the high-pressure branch of the UCST has been reported for this system although Xiang and Kiran[13] reported on the low-pressure UCST branch up to ~620 bar as well as the lower critical solution temperature boundary and the minimum in the boundary. The PDMS−CO_2 phase behavior

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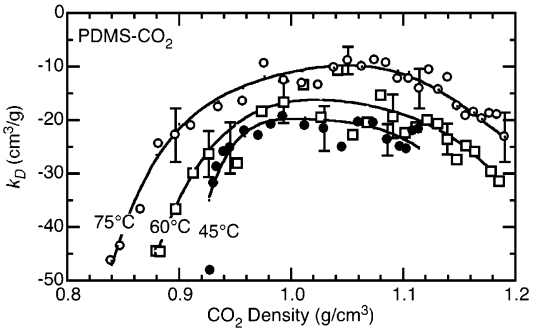

Figure 2. Dependence of the dynamic second virial coefficient on CO_2 mass density at 45 °C (solid circles), 60 °C (squares), and 75 °C (open circles). The representative error bars shown here are the error associated with the fit of the data to eq 2.

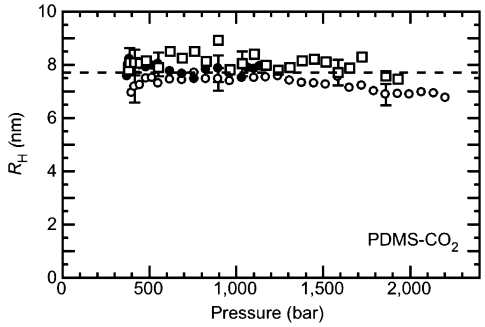

Figure 3. Dependence of the PDMS hydrodynamic radius on pressure at 45 °C (solid circles), 60 °C (squares), and 75 °C (open circles). The dashed line represents R_H averaged for all three temperatures. The representative error bars account for the error in D_0 and in the viscosity of pure CO_2.

is similar to that of the poly(ethylene-*co*-1-butene) (PEB_{10})−dimethyl ether (DME) system previously reported by the present authors.[6] Interestingly, DLS measurements for the PEB_{10}−DME system revealed that solvent quality continually increases as the pressure is increased, starting at the low-pressure phase boundary and ending at the high-pressure UCST boundary, in contrast with the apparent maximum in solvent quality reported by Andre and co-workers[12] for the PDMS−CO_2 system. In this Note the existence of maximal solvent quality at intermediate pressures (densities) in the PDMS−CO_2 system is unequivocally demonstrated with DLS measurements over a wide pressure (CO_2 density) range at 45, 60, and 75 °C near both high- and low-pressure phase boundaries shown in Figure 1.

PDMS (M_w = 75 800, M_w/M_n = 1.11) is obtained from Polymer Source, Inc., and CO_2 (99.999%) is obtained from BOC Gases. Details are given elsewhere[5,6] on the high-pressure scattering cell, DLS apparatus, and method of data analysis taking into account any pressure-induced changes in polymer concentration, solution viscosity, and solution refractive index. Teflon O-rings are used to seal the windows, and a spring-energized Teflon O-ring is used to seal the piston to avoid introducing contaminants that CO_2 can leach from hydrocarbon O-rings. Also, pure CO_2 rather than water is used as the pressurizing fluid to move the floating piston again to avoid introducing a contaminant into the polymer solution. The milklike scattering pattern of the laser beam at 90°, rather than the pattern from a conventional light source, provides a precise determination of the cloud point. D is obtained from autocorrelation functions via the cumulant method, and D_0 and k_D are obtained from a linear, least-squares analysis of D as a function of concentration. The Supporting Information Section provides details on the determination of k_D from D vs c plots. R_H is obtained via the Stokes−Einstein relation, $D_0 = kT/(6\pi\eta R_H)$, where k is Boltzmann's constant and η is the viscosity of CO_2.[14]

Figure 2 shows experimentally determined k_D values as a function of CO_2 density at 45, 60, and 75 °C. The existence of a fairly broad maximum in k_D at densities intermediate to those at the phase boundaries is readily apparent in contrast to the k_D values reported by Andre and co-workers.[12] There are two significant differences between the present study and that of Andre and co-workers. First, the present study explores a much larger CO_2 density range, 0.84−1.19 g/cm^3 vs 0.97−1.04 g/cm^3. This large density range is used at all temperatures in the present study to better elucidate the behavior of k_D. Second, a higher molar mass PDMS is used in the present study which accounts for the larger values of k_D observed here. The maximum in k_D observed in the present study demonstrates unequivocally the existence of maximal CO_2 solvent quality for the PDMS−CO_2 system at intermediate densities in close agreement to the "apparent" maximum of A_2 reported by Andre and co-workers.

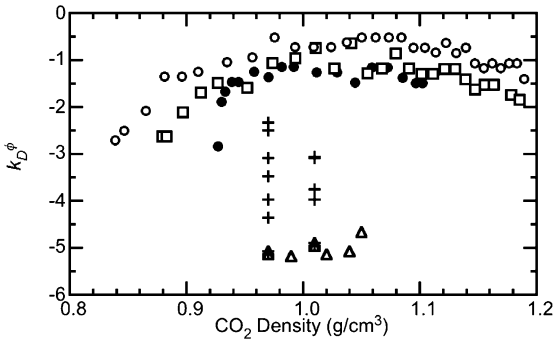

Figure 4. Dependence of the volume fraction-based, dynamic second virial coefficient, k_D^ϕ, on CO_2 density at 45 °C (solid circles), 60 °C (squares), and 75 °C (open circles) obtained in this study. k_D^ϕ measurements of Andre and co-workers for a 31.3K molar mass PDMS are shown for 25 °C (triangles) and temperatures ranging from 30 to 54 °C for a density of 0.97 g/cm^3 and 30 to 42 °C for a density of 1.01 g/cm^3 (crosses).

Figure 3 shows that R_H is invariant with pressure (density). Although it may be argued that there is a weak maximum in R_H at intermediate pressures at 75 °C, this observation might simply be due to the precision of the experimental measurement (i.e., the polymer chains are not large enough to determine relative size changes). However, it is also plausible that slight changes in coil conformation may be offset by slight changes in coil draining characteristics. The invariant behavior of R_H of PDMS in CO_2 is in agreement with that observed by Andre and co-workers. Our research group has observed essentially the same behavior for the PEB_{10}−DME system where R_H was independent of temperature or DME density even though a higher molar mass polymer was considered.[6]

As noted previously, it is more convenient to consider the polymer volume fraction dependence of D as a means of accounting for the effect of polymer molar mass when comparing measurements made on different polymer samples. In Figure 4, k_D^ϕ values as a function of CO_2 density obtained in the present study are compared with those estimated from the data of Andre and co-workers[12] for a 31.3K molar mass PDMS. The greatly enhanced density range and easily discerned k_D^ϕ maximum associated with the current study are immediately apparent. While the lower k_D^ϕ values of Andre and co-workers are primarily a result of lower molar mass polymers and temperatures, the potential role of end effects being more prevalent in their samples cannot be entirely discounted. Also, the larger

molar mass PDMS investigated here provides greater sensitivity for the measured concentration dependence of D that is particularly important when the concentration dependence is weak.

The concentration dependence of D provides access to the second osmotic virial coefficient, A_2, since both the thermodynamic and hydrodynamic interactions are functions of A_2/R_H^3.[11] Therefore, the observed maximum in k_D^ϕ corresponds to a maximum in A_2. On the basis of a previous observation of $k_D^\phi = -2$ at the theta condition,[11] it is apparent that the low-pressure phase boundary occurs at sub-theta conditions since the measured $k_D^\phi < -2$ at this low-density phase boundary. The k_D^ϕ values estimated from the data of Andre and co-workers indicate sub-theta conditions in accordance with their measured negative A_2 values.[12] Earlier high-pressure DLS studies with compressible solvents indicate that phase separation also occurs at sub-theta solvent quality for PEB_{10}−simple alkane solutions,[5] while phase separation occurs *before* the onset of theta-solvent quality in the case of PEB_{10}−DME solutions[6] at the low-pressure phase boundary. It is likely that the low-pressure phase boundary results from a solvent whose density is not sufficient to effectively screen intramolecular monomer−monomer and, ultimately, intermolecular polymer−polymer attraction[15−17] even in the presence of favorable polymer−solvent interactions. Phase separation at the high-pressure UCST for the PDMS−CO_2 system appears to occur at marginal solvent conditions ($-2 < k_D^\phi < -1$), albeit not as favorable conditions as the PEB_{10}−DME[6] system. Also, here k_D^ϕ is observed to be decreasing upon approach to this phase boundary while k_D^ϕ was increasing in the PEB_{10}−DME system.[6] In both cases, phase separation at the high-pressure UCST occurs for a solvent quality that is most definitely not sub-theta or poor, indicating that diminishing free volume in a high-density, compressible solvent plays a significant role in fixing the location of the phase boundary.

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Supporting Information Available: Details on the determination of k_D from D vs c plots. This material is available free of charge via the Internet at http://pubs.acs.org.

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