Pressure- and Temperature-Induced Transitions in Solutions of Poly(dimethylsiloxane) in Supercritical Carbon Dioxide

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ABSTRACT: Supercritical fluids (SCFs) have great technological potential for minimizing the organic wastes associated with polymer manufacturing and processing. However, significant challenges remain for developing the same level of understanding of the behavior of polymers in SCFs as has been reached for polymers in traditional organic solvents. Small-angle neutron scattering was used to study the effect of pressure and temperature on the phase behavior of poly(dimethylsiloxane) (PDMS) in supercritical carbon dioxide (SC CO_2). It was demonstrated that PDMS−SC CO_2 solutions reproduce all main features of the temperature−concentration phase diagram for polymers in organic solvents. Moreover, because of their continuously adjustable solubility, SCFs exhibit novel effects, such as a pressure-induced transition to the Θ point and to the good solvent domain, in addition to a polymer−solvent demixing at a lower critical solution pressure.

A supercritical fluid (SCF) is a substance at a pressure and temperature above the liquid−vapor critical point where the coexisting liquid and vapor phases become indistinguishable. The physical properties of SCFs are similar to those of dense gases, although when highly compressed, their density may be comparable to that of the subcritical liquids. SCFs in general and supercritical carbon dioxide (SC CO_2) in particular have emerged as an attractive alternative to the organic solvents used for polymer manufacturing and processing. One key advantage of SCFs is the possibility of continuously tuning the solvent quality by varying the pressure (P) in addition to the temperature (T), which offers an unparalleled means for controlling polymer solubility. Despite recent progress in many specific areas of SCF science and technology (see e.g. refs 1 and 2 and references therein), significant challenges remain for developing the same level of understanding of the behavior of polymers in SCFs as has been reached for polymers in traditional organic solvents. Here we address the effect of temperature and pressure on the phase behavior of poly(dimethylsiloxane) (PDMS) in SC CO_2. We apply small-angle neutron scattering (SANS) to extract information on the concentration fluctuations and the dimensions of polymer chains at different conditions and find that the supercritical solutions reproduce all salient features of the temperature−concentration phase diagram for polymers in liquid solvents.[3] Moreover, because of their continuously adjustable properties, SCFs exhibit novel effects, such as a pressure-induced transition to the Θ point and to the good solvent domain, in addition to a polymer−solvent demixing at a lower critical solution pressure.

At the phenomenological level, liquid solvents for polymers are divided into three classes, namely poor, theta (Θ), and good solvents. The solvent quality is directly related to the ability of the solvent molecules to mediate the attractive intrachain forces responsible for the polymer−solvent demixing. Poor solvents can hardly impede the intrachain interactions and hence can dissolve only short-chain (or low molecular weight M_W) polymers with a limited number of contacts between the segments. The pairwise attractive and repulsive interactions compensate at the Flory or the "Θ temperature" (T_Θ) which is defined as the upper critical solution temperature (UCST) for a polymer with infinite molecular weight $M_W = \infty$.[4,5] At $T = T_\Theta$ the radius of gyration $R_g(T_\Theta)$ of polymer chains is unperturbed by excluded-volume effects and is also independent of the long-range critical concentration fluctuations. In the good solvent domain $T > T_\Theta$ the repulsive forces between the segments work to expand R_g above the unperturbed dimensions at $T = T_\Theta$.

The dimension of polymer chains R_g and the correlation length of the concentration fluctuations ξ in polymer solutions may be determined at different (P,T) using SANS combined with a high concentration isotope labeling method.[6] The coherent scattering intensity, I, for a mixture of identical hydrogenated and deuterated polymer chains in a solvent is

$$I(Q,x) = K^* S_s(Q) + L^* S_t(Q) \qquad (1)$$

where $S_s(Q)$ is the single-chain structure factor which contains information on the dimensions (R_g) of the polymers. Similarly, $S_t(Q)$ is the total scattering structure factor which contains information on the correlation length of the concentration fluctuations, ξ. The scattering vector is given by $Q = 4\pi\lambda^{-1} \sin \theta$, where 2θ is the scattering angle and λ is the neutron wavelength.

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The prefactor $K^* \sim (b_H - b_D)^2 x(1 - x)$ in eq 1 is a function of the neutron scattering lengths of the hydrogenated (b_H) and deuterated (b_D) monomers as well as on the mole fraction (x) of hydrogenated polymers. If all chains are hydrogenated ($x = 1$), $K^* = 0$, and one can obtain $\xi(T,P)$ directly from $I(Q,x=1) \sim S_t(Q)$ using the Ornstein−Zernike formula

$$S_t(Q) = S(0)/(1 + Q^2\xi^2) \tag{2}$$

In addition to b_H and b_D, the prefactor $L^* \sim [b_H x + (1 - x)b_D - b_s']^2$ in eq 1 depends on the scattering length b_s' of a solvent normalized via the ratio of the specific volumes of the monomer and the solvent molecule. For PDMS−CO_2 mixtures, $b_H = 0.086 \times 10^{-12}$ cm, $b_D = 6.33 \times 10^{-12}$ cm, and $b_s' = 1.47 \times 10^{-12}$ to 3.76×10^{-12} cm in the range between the critical ($\rho_{CO_2} = 0.469$ g/cm^3) and the liquid-state densities ($\rho_{CO_2} = 1.2$ g/cm^3). For a given combination of the neutron scattering lengths ($b_H < b_s' < b_D$), it is possible to make the prefactor L^* zero at any density of SC CO_2 by choosing an appropriate concentration (x) of hydrogenated PDMS (e.g., $L^* = 0$ at $x = 0.512$ and $\rho_{CO_2} = 0.95$ g/cm). In this case, eq 1 gives the single chain (intramolecular) scattering directly, and the R_g may be obtained by fitting $I(Q)$ with the Debye function:[7,8]

$$S_s^D = (2/y^2)(y - 1 + e^{-y}), \quad y = Q^2 R_g^{\ 2} \tag{3}$$

For solutions of nonoverlapping polymer chains[9] under the Θ condition, eq 3 yields in the limit of small Q[7,8]

$$S(Q) = \frac{S(0)}{1 + Q^2\xi^2(\Theta)}, \quad \xi(\Theta) = R_g(\Theta)/\sqrt{3} \tag{4}$$

Thus, the SANS measurements of ξ vs T (or P) may be used to determine the Θ temperature (or the Θ pressure) using eq 4.[10]

The experiments were performed on the 30 m SANS spectrometer at the Oak Ridge National Laboratory over the Q range of $0.005 < Q/\text{Å}^{-1} < 0.05$ ($\lambda = 4.75$ Å). The data were radially averaged and converted to an absolute coherent cross section (in units of cm^{-1}) using procedures described elsewhere.[11] The structure factors $S_s(Q)$ and $S_t(Q)$ were obtained from eq 1 and used to calculate ξ and R_g at different thermodynamic conditions using eqs 2 and 3. Polymer samples of PDMS-*h* ($M_W = 22\,500$, 47 700, and 79 900 of polydispersity $M_W/M_N \leq 1.03$) and PDMS-*d* ($M_W = 27\,600$, $M_W/M_N \leq 1.11$) were synthesized and characterized at the Max Planck Institute for Polymer Research, Germany. PDMS-*d* (75 600, $M_W/M_N \leq 1.3$) was purchased from Polymer Standards Service GmbH, Mainz, Germany. All solutions were prepared at the overlap concentration[9] ($C^* = 0.1397$, 0.0959, and 0.0741 g/mL for $M_W = 22\,500$, 47 700, and 79 900, respectively). H−PDMS or isotopic mixtures of ($h + d$) PDMS at $x = 0.512$ were loaded into a stainless steel cylindrical cell which was fitted with optically polished sapphire windows virtually transparent to neutron radiation. The samples were pressurized at $T = 50$ °C to 45.7 MPa (i.e., at $\rho_{CO_2} = 0.95$ g/cm^3) with CO_2 (SFC purity 99.99%, Matheson Gas Products, Inc.) and stirred thoroughly until a transparent homogeneous solution was obtained. After completing the temperature scans $\xi(T,P)$ or $R_g(T,P)$ at constant density ($\rho_{CO_2} = 0.95$ g/cm^3), the variation of $\xi(P,T=\text{const})$ or $R_g(P,T=\text{const})$ was measured with pressure at isothermal conditions.

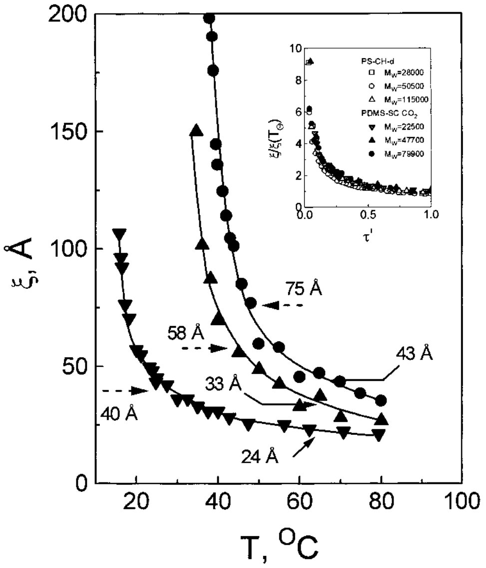

Figure 1. $\xi(T)$ for *h*-PDMS with $M_W = 22\,500$ (▼), 47 700 (▲), and 79 900 (●). $\rho_{CO_2} = 0.95$ g/cm^3. Dashed and solid arrows show the value of $R_g(\Theta) = 0.267 M_W^{1/2}$ [ref 16] and $\xi(\Theta) = R_g(\Theta)/\sqrt{3}$ (eq 4), respectively. The inset shows the variation of the reduced correlation length vs the reduced temperature $\tau' = [T_\Theta/(T_\Theta - T_C)](T - T_C/T)$ for solutions of PS in CH-*d* [ref 17] and PDMS in SC CO_2. In the latter case, the parameters used for calculations are $T_\Theta = 65$ °C, $T_C = 12.2$ °C ($M_W = 22\,500$), $T_C = 31.8$ °C ($M_W = 47\,700$), and $T_C = 36.1$ °C ($M_W = 79\,900$).

The temperature variation of ξ in PDMS−SC CO_2 solutions at constant density $\rho_{CO_2} = 0.95$ g/cm^3 is shown in Figure 1. As monitored by the intermolecular correlation length, the concentration fluctuations diverge ($\xi \Rightarrow \infty$) as T approaches the critical temperature of phase demixing T_C. The intermolecular correlations decline rapidly with the temperature, become comparable to the dimension of polymer chains at $(T - T_C) \sim 12$−16 °C, and reach the theoretical value $\xi(\Theta)$ for each M_W (eq 4) at $T = T_\Theta = 65 \pm 5$ °C. To our knowledge, this is the first experimental observation of the temperature-induced transition to the Θ point in polymer solutions in SCFs. In the inset in Figure 1 we compare the temperature variation of the concentration fluctuations in supercritical CO_2 and in organic solvents [i.e., polystyrene (PS) in the Θ solvent cyclohexane-*d* (CH-*d*)]. The reduced correlation lengths $\xi/\xi(T_\Theta)$ for both systems fall on the same master curve when plotted vs the reduced temperature $\tau' = [T_\Theta/(T_\Theta - T_C)](T - T_C/T)$, which accounts for the temperature distance from both T_Θ and T_C. A typical variation of ξ vs $(T - T_C)$ in PDMS−SC CO_2 solutions is shown in Figure 2. As is seen, the critical index ν in a scaling law for the correlation length $\xi \sim (T - T_C)^{-\nu}$ exhibits a sharp crossover from the mean-field value ($\nu = 0.5$) in the Θ region to the Ising model value ($\nu = 0.630 \pm 0.001$[12]) in the critical region around T_C. Accordingly, the critical index $\gamma = 1.23 \pm 0.02$ for the susceptibility (i.e., the osmotic compressibility) in $\chi \sim (T - T_C)^{-\gamma}$ at $T \Rightarrow T_C$ for all solutions studied agrees within experimental errors with the Ising model value (1.239 ± 0.002[12]). The crossover takes place when $\xi \sim R_g$ and thus reproduces the main features of the crossover observed in solutions of PS in CH-*d* (see the inset in Figure 2).[13,14] These observations delineate an intrinsic analogy between the temperature behavior of polymers in SCFs and in liquid Θ solvents in the vicinity of the UCST and show that

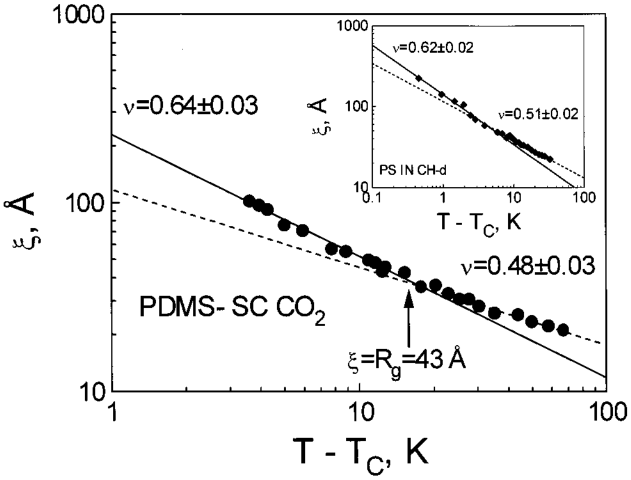

Figure 2. Variation of ξ as a function of $(T - T_C)$ for solution of PDMS ($M_W = 22\,500$) in SC CO_2. $\rho_{CO_2} = 0.95$ g/cm^3. The slope gives the value of the critical index ν. The inset shows ξ vs $(T - T_C)$ for PS−CH-*d* solution with a similar $M_W = 28\,000$ of the polymer.

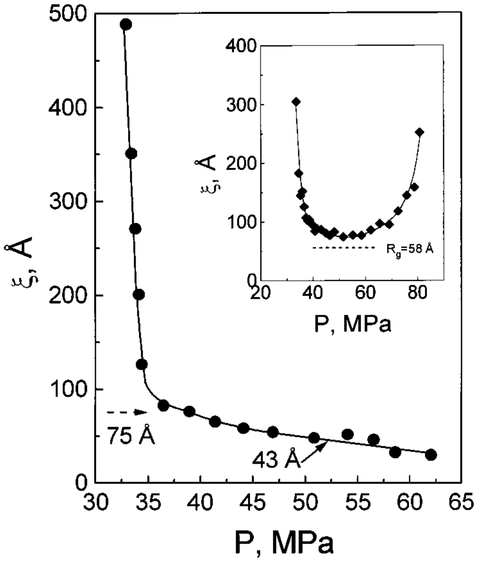

Figure 3. Variation of the correlation length ξ as a function of pressure for PDMS ($M_W = 79\,900$) in SC CO_2 at $T = 50$ °C. Dashed and solid arrows show the value of $R_g(\Theta)$ and $\xi(\Theta)$ (eq 4), respectively. The inset shows $\xi(P)$ for solution of PDMS ($M_W = 47\,700$) in SC CO_2 at $T = 32$ °C close to the UCST for this solution ($T_C = 31.8$ °C). The extrapolation of $\xi^{-1}(P)$ to zero gives $P_C \cong 32$ MPa and $P_C \cong 90$ MPa for the UCSP and the LCSP, respectively.

polymer solutions in SCFs belong to the universality class of the Ising model.

The effect of pressure on the thermodynamic condition of PDMS−SC CO_2 solutions is illustrated in Figure 3. The concentration fluctuations diverge as P approaches the upper critical solution pressure (UCSP) P_C where the system exhibits pressure-induced phase demixing. The solvent quality increases rapidly with P in the range $(P - P_C) \leq 7$ MPa and more gradually after ξ becomes comparable to the radius of gyration of polymer chains $R_g(\Theta) = 75$ Å. At $P_\Theta = 52 \pm 4$ MPa the correlation length becomes equal to the theoretical value $\xi(\Theta) \cong 41$ Å (eq 4), which indicates that the Θ condition has been reached. This is the first experimental observation of the pressure-induced transition to the Θ point in polymer solutions in SCFs, the existence of which was predicted earlier in ref 15. It is interesting that the effect of pressure may be quite opposite at less favorable thermodynamic conditions. If the experiment is performed at a temperature close to a UCST, $\xi(P)$ goes through the minimum after which the lower critical solution pressure (LCSP) is approached (see the inset in Figure 3). The best solvent quality is reached close to the Θ pressure $P_\Theta = 52$ MPa, though the correlation length $\xi(P_\Theta) \cong 74$ Å is still much larger than the dimension of polymer chains in the solution $R_g(\Theta) = 58$ Å. This indicates that pressure alone may not always be capable of moving supercritical polymer solutions out of the poor solvent domain. The situation is similar to polymer solutions in poor organic solvents (e.g., PS in acetone) where the intermolecular correlations never decrease below the dimension of the constituent polymer.[10] We are not aware of previously published data on the pressure-induced demixing upon an increase in pressure in supercritical polymer solutions and believe this result to be the first experimental observation of the LCSP.

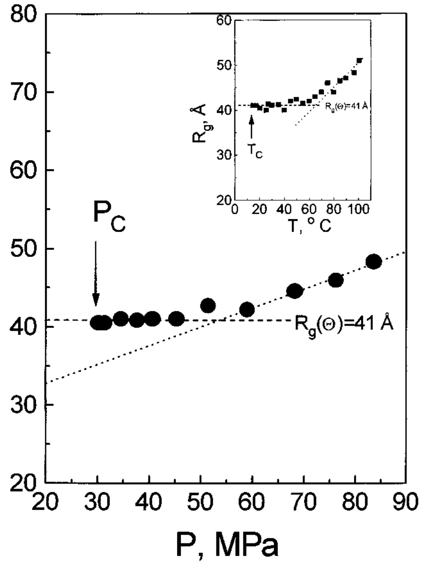

Figure 4. Variation of the radius of gyration for PDMS with $M_W = 22\,500$ in solution of $(h + d)$ PDMS in SC CO_2 vs pressure at $T = 70$ °C. The inset shows R_g as a function of temperature at $\rho_{CO_2} = 0.95$ g/cm^3.

Figure 4 illustrates the behavior of the radius of gyration of PDMS in SC CO_2 with P and T. As is seen, R_g of the polymer remains invariant during both pressure and temperature quenches which extend to the immediate vicinity of the (T,P) polymer−SCF demixing locus and agrees well with the dimension of unperturbed chains with ($R_g = 0.267 M_W^{1/2} \cong 40$ Å[16]). This observation indicates the universality of the constancy of R_g in semidilute polymer solutions below T_Θ and P_Θ which was previously demonstrated for liquid solvents[10,17] and has now been shown to extend to supercritical fluids. At $P > P_\Theta$ and/or $T > T_\Theta$ the dimensions of polymer chains increase due to the excluded-volume effects, as was observed in PS−CH-*d* solutions at $T > T_\Theta$,[18] indicating that SC CO_2 is becoming a good solvent for PDMS in this range of the thermodynamic parameters.

In conclusion, the experiments demonstrate universality between the structure and thermodynamic properties of the liquid and supercritical polymer solutions. In the latter case, the threshold of unlimited miscibility (the Θ point) may be reached by varying either the pressure or the temperature. The experimental data agree with the results of Monte Carlo simulations which indicate that polymer chains may adopt unperturbed and expanded conformations at high densities.[19] This provides a foundation for a better understanding the underlying physics of SCF–polymer assemblies.

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