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# Observation of Polymer Chain Contraction near the Overlap Concentration

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Polymer chain dimensions in solution are determined by the solvent quality.[1,2] Isolated polymer chains are expanded relative to their unperturbed size in good solvents owing to excluded-volume interactions between monomers. At the theta condition the repulsive excluded-volume interactions are compensated by attractive monomer−monomer interactions such that the monomer distribution within the chain exhibits Gaussian statistics. At the theta condition the polymer coil size varies with segment number, $N$, as

$$R_g^{\theta} \sim N^{1/2} \tag{1}$$

where $R_g$ is the radius of gyration and $\xi$ denotes the theta condition. Decreasing solvent quality ultimately leads to the formation of polymer globules following chain collapse. While this dilute solution picture has gained wide acceptance,[2,3] chain behavior as a function of solvent quality remains unresolved at concentrations in the near-overlap and semidilute regions. If it is assumed that the overlap concentration is essentially the mixture critical concentration,[1] $c_c$, and that the critical concentration segment number dependence[4,5] is $c_c \sim N^{-0.38}$, scaling arguments predict chain collapse at the critical temperature, $T_c$, and mixture critical concentration[6]

$$R_g^{T_c,c_c} \sim N^{0.46} \tag{2}$$

This result was subsequently derived by more rigorous methods.[7,8] Alternative theoretical approaches based on a molecular theory of single chain collapse[9,10] and a proper accounting of concentration fluctuations and three-body interactions in the familiar Flory−Huggins theory[11] predict collapse only for temperatures less than $T_c$; that is, the chain dimension should remain unperturbed up to the phase boundary.

Recent small-angle neutron scattering (SANS) investigations have considered the behavior of a polymer chain near the mixture-critical concentration in liquid and supercritical fluid solvents.[12−16] These studies report that $R_g$, which is associated with polymer intramolecular correlations, remains essentially $R_g^{\theta}$ as the mixture critical point is approached along an isothermal or isobaric path. The intermolecular correlations characterized by the correlation length ($\xi$) rapidly increase near the mixture critical point and can exceed the magnitude of $R_g$, indicating the presence of strongly interacting unperturbed chains. These previous observations agree with some predictions that polymer chain dimensions remain unperturbed with decreasing solvent quality until incipient phase separation.[9−11] The present authors have also reported similar SANS results for poly(ethylene-*co*-20.2 mol % 1-butene) ($PEB_{10}$)−ethane and $PEB_{10}$−pentane solutions.[17] However, this $PEB_{10}$−alkane solution study was somewhat problematic since the $PEB_{10}$ was not fully deuterated, compromising the isotopic labeling contrast technique efficacy, and protonated ethane was used, resulting in elevated incoherent background scattering. Since careful examination of these SANS results indicated possible polymer chain contraction upon approach to the phase boundary, the experiments were repeated with the following three improvements: deuterated ethane, fully deuterated $PEB_{10}$, and an improved high-pressure SANS cell.[12]

Ethane-$d_6$ (99 at. % D) is obtained from C/D/N Isotopes Inc., and pentane (98 at. % D) is obtained from Cambridge Isotope Laboratories. The h-$PEB_{10}$ and d-$PEB_{10}$ are synthesized via anionic polymerization of butadiene with subsequent saturation by hydrogenation or deuteration as described in detail elsewhere.[18−21] The h-$PEB_{10}$ and d-$PEB_{10}$ are statistically random copolymers with ∼10 ethyl branches per 100 carbon atoms, weight-average molecular weights of 232 500 and 232 800, respectively, and polydispersity indexes of 1.01 and 1.06, respectively. The phase behavior of the $PEB_{10}$−alkane mixtures is determined prior to SANS experiments from cloud-point measurements using equipment and techniques described in detail elsewhere.[22,23] The high-pressure, unibody scattering cell and the experimental scattering technique are described in a previous report.[12] Neutron scattering experiments are performed on the NG-3 30-m SANS spectrometer at the National Institute of Standards and Technology (NIST) located in Gaithersburg, MD. A description of the 30 m SANS instrument at NIST is given elsewhere.[24] The experimental configuration and data reduction are also described in an earlier publication.[12] SANS data are obtained from independent experiments with 2.3 and 4.8 wt % $PEB_{10}$−pentane solutions at 130 °C and 4.8 wt % $PEB_{10}$−ethane solutions at 110 and 130 °C. Values for $R_g$ and $\xi$ are obtained via the isotopic labeling method,[25] taking into account pressure-induced changes in solution density as well as scattering cell path length.[12,17]

Figure 1 shows the typical evolution of the polymer solution microstructure as the pressure is varied along an isotherm. The onset of phase separation in this 4.8 wt % $PEB_{10}$−ethane solution is indicated by the rapid growth of $\xi$ near the phase boundary (see the inset phase diagram in Figure 1 for these $PEB_{10}$−alkane solutions). In addition, the expected crossover of the concentration fluctuation correlation length and chain dimension is observed in accord with similar observations on a wide range of polymer solutions.[12−17] Most interesting is the observed decrease in the chain dimension, $R_g$, upon approach to the phase boundary, in stark

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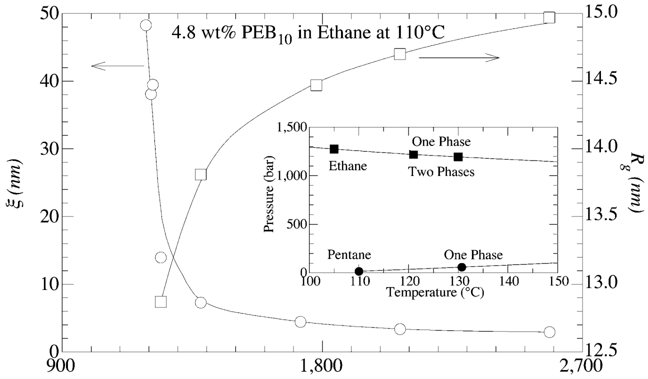

**Figure 1.** Crossover of the polymer chain dimension, $R_g$, and the polymer solution correlation length, ξ, upon approaching the phase boundary for the PEB$_{10}$−ethane system at 110 °C. The inset diagram shows the phase behavior for the PEB$_{10}$−ethane and PEB$_{10}$−pentane systems, each with 4.8 wt % PEB$_{10}$ in solution.

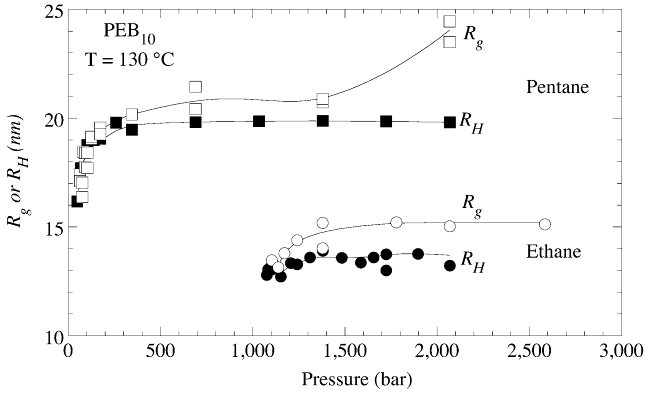

**Figure 2.** Observation of chain collapse following an isothermal pressure reduction path on approach to a phase boundary in PEB$_{10}$−alkane solutions. The $R_g$ data are obtained at finite concentration (see text) while the $R_H$ values are determined at infinite dilution.[26]

contrast to the behavior reported by others including the present authors.[12−17]

Figure 2 compares the SANS-determined $R_g$ and the infinite dilution hydrodynamic radii ($R_H$) of PEB$_{10}$ chains dissolved in both ethane and pentane as reported in a complementary dynamic light scattering (DLS) study.[26] The chains contract to ~80% of their unperturbed chain dimension upon approach to the phase boundary. Additional polymer molar masses would have to be considered to determine the validity of eq 2. While the observed variation in chain size with pressure is qualitatively similar for both solvents, it is readily apparent that ethane is a much poorer solvent than pentane.[17,26] Although the close agreement in the observed contraction in the finite-concentration $R_g$ and infinite-dilution $R_H$ might suggest that the chain concentrations are not high enough to yield the constant $R_g$ values previously observed[12−17] and theoretically predicted by some,[9−11] several experimental observations are offered here, suggesting that solution concentration alone cannot explain these experimental observations.

Overlap concentrations will depend on the pressure via changes in the solvent density for the compressible solutions considered in the present study. The overlap concentrations, $c^*$, are estimated to be 4.5−5.4 and 1.4−1.8 wt % for PEB$_{10}$ in ethane and pentane, respectively, based on the $R_g$ values measured by SANS and accounting for changes in solution density. Therefore, for the SANS study with the two PEB$_{10}$−pentane solutions, one concentration is just slightly larger than $c^*$ while the other is 2−3 times larger than $c^*$. Likewise, the PEB$_{10}$−ethane solutions are essentially at concentrations equal to $c^*$ for SANS measurements at 110 and 130 °C. In fact, the concentration ranges used in the present study are similar to those used in a SANS study reported by Melnichenko and co-workers for poly(styrene) (PS)−cyclohexane and PS−acetone solutions. However, these PS chains do not collapse upon approach to a phase boundary when the temperature is isobarically reduced.[13,15] Perhaps the change in chain dimensions is a result of the path used to approach the phase boundary since, in the present study, the phase boundary is approached by isothermally reducing the pressure. This explanation is not likely since Melnichenko and coworkers also used an isothermal pressure reduction path on approach to the phase boundary for poly(dimethylsiloxane) (PDMS)−CO$_2$ solutions where $c \cong c^*$ and observed that the PDMS chains do not collapse along such a path.[16] In fact, similar observations on chain dimensions are reported by the present authors and shown in Figure 3 for PEB$_{10}$−dimethyl ether solutions.[12,27] Once again, there is strong agreement between finite-concentration $R_g$ (SANS) and infinite-dilution $R_H$ (DLS) values where both radii indicate that chain dimension remains unchanged upon approach to a phase boundary. Hence, the present authors have observed *both* chain collapse and unperturbed chains for an isothermal pressure reduction path to the phase boundary using SANS and DLS techniques. The relatively close quantitative agreement between the two size measurements, $R_g$ and $R_H$, is because they are evaluated at different concentrations.[1,2] Normally $R_H$ is expected to be less than $R_g$ when both quantities are determined at infinite dilution.

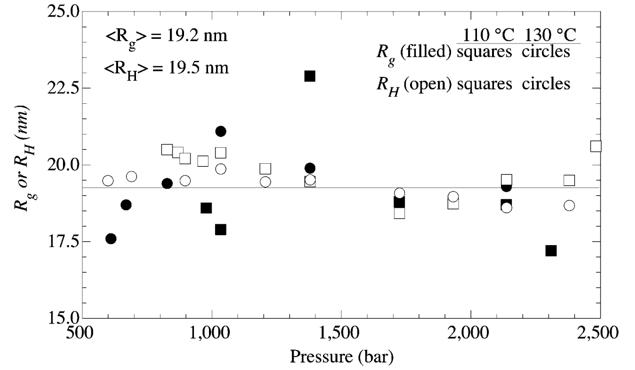

**Figure 3.** Chain collapse is not observed upon decreasing pressure along an isotherm to a phase boundary in PEB$_{10}$−dimethyl ether solutions. The reported $R_g$ were measured at finite concentrations (see text) while $R_H$ values were determined at infinite dilution.[27]

It appears that, under some conditions near the critical concentration, chains may collapse slightly relative to their unperturbed dimension, thereby avoiding significant interpenetration while at other times concentration fluctuations may drive the formation of polymer-rich microdomains. Recent DLS investigations of single-chain diffusion in these systems indicates that remarkable differences exist between the various PEB$_{10}$−solvent pairs near the phase boundary.[26,27] The concentration dependence of the translational diffusion coefficient provides access to $A_2$ via the so-called dynamic second virial coefficient, $k_D^\phi$, since $k_D^\phi \propto A_2/R_H{}^3$.[28] The DLS studies show that phase separation occurs for sub-theta-solvent quality for $PEB_{10}$−simple alkane solutions,[26] while phase separation occurs *before* the onset of theta-solvent quality in the case of $PEB_{10}$−dimethyl ether solutions.[27] Behavior of the latter sort has been accounted for by Wolf and co-workers within a modified Flory−Huggins framework where chain connectivity and conformation effects are determined.[29−32] This observation illustrates the unique character of polymer solution phase separation induced by pressure reduction along an isotherm when the solvent is very compressible. Such a path leads to a large decrease in the fluid density, which in turn can lead to a decrease in the mixing enthalpy sufficient to induce macroscopic phase separation. That is, even if the monomer−solvent interactions are nominally favorable, the solvent density is not sufficient to effectively screen intramolecular monomer−monomer and ultimately intermolecular polymer−polymer attraction.[29,33−35]

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## References and Notes

(1) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(2) Rubinstein, M.; Colby, R. H. *Polymer Physics*; Oxford University Press: Oxford, 2003.
(3) Chu, B.; Ying, Q.; Grosber, A. *Macromolecules* **1995**, *28*, 180.
(4) Izumi, Y.; Miyake, Y. *J. Chem. Phys.* **1984**, *81*, 1501.
(5) Lhuillier, D. *J. Phys. II* **1992**, *2*, 1411.
(6) Cherayil, B. J. *J. Chem. Phys.* **1994**, *100*, 4655.
(7) Sanchez, I. C. *J. Phys. Chem.* **1989**, *93*, 6983.
(8) Widom, B. *Physica A* **1993**, *194*, 532.
(9) Raos, G.; Allegra, G. *J. Chem. Phys.* **1996**, *104*, 1626.
(10) Ganazzoli, F.; Raos, G.; Allegra, G. *Macromol. Theory Simul.* **1999**, *8*, 65.
(11) Muthukumar, M. *J. Chem. Phys.* **1986**, *85*, 4722.
(12) DiNoia, T. P.; van Zanten, J. H.; Kline, S. R.; Garach-Domech, A.; McHugh, M. A.; Wright, P. J.; Fetters, L. J. *Macromolecules* **2003**, *36*, 7372.
(13) Melnichenko, Y. B.; Anisimov, M. A.; Povodyrev, A. A.; Wignall, G. D.; Sengers, J. V.; Van Hook, W. A. *Phys. Rev. Lett.* **1997**, *79*, 5266.
(14) Melnichenko, Y. B.; Wignall, G. D. *Phys. Rev. Lett.* **1997**, *78*, 686.
(15) Melnichenko, Y. B.; Wignall, G. D.; Van Hook, W. A.; Szydlowski, J.; Wilczura, H.; Rebelo, L. P. *Macromolecules* **1998**, *31*, 8436.
(16) Melnichenko, Y. B.; Kiran, E.; Wignall, G. D.; Heath, K. D.; Salaniwal, S.; Cochran, H. D.; Stamm, M. *Macromolecules* **1999**, *32*, 5344.
(17) DiNoia, T. P.; Kirby, C. F.; van Zanten, J. H.; McHugh, M. A. *Macromolecules* **2000**, *33*, 6321.
(18) Rachapudy, H.; Smith, G. G.; Raju, V. R.; Graessley, W. W. *J. Polym. Sci., Part B: Polym. Phys. Ed.* **1979**, *17*, 1211.
(19) Kirgas, T. M.; Carella, J. M.; Struglinski, M. J.; Crist, B.; Graessley, W. W. *J. Polym. Sci., Part B: Polym. Phys.* **1985**, *23*, 509.
(20) Balsara, N. P.; Fetters, L. J.; Hadjichristidis, N.; Lohse, D. J.; Han, C. C.; Graessley, W. W.; Krishnamoorti, R. *Macromolecules* **1992**, *25*, 6137.
(21) Fetters, L. J.; Graessley, W. W.; Krishnamoorti, R.; Lohse, D. J. *Macromolecules* **1997**, *30*, 4973.
(22) Meilchen, M. A.; Hasch, B. M.; McHugh, M. A. *Macromolecules* **1991**, *24*, 4874.
(23) Mertdogan, C. A.; Byun, H.-S.; McHugh, M. A.; Tuminello, W. H. *Macromolecules* **1996**, *29*, 6548.
(24) Glinka, C. J.; Barker, J. G.; Hammouda, B.; Krueger, S.; Moyer, J. J.; Orts, W. J. *J. Appl. Crystallogr.* **1998**, *31*, 430.
(25) Williams, C. E.; Nierlich, M.; Cotton, J. P.; Jannink, G.; Boue, F.; Daoud, M.; Farnoux, B.; Picot, C.; de Gennes, P.-G.; Rinaudo, M.; Moan, M.; Wolf, C. *J. Polym. Sci., Polym. Lett. Ed.* **1979**, *17*, 379.
(26) Kermis, T. W.; Li, D.; Guney-Altay, O.; Park, I.-H.; van Zanten, J. H.; McHugh, M. A. *Macromolecules* **2004**, *37*, 9123.
(27) Li, D.; McHugh, M. A.; van Zanten, J. H. *Macromolecules* **2005**, *38*, 2837.
(28) Cotts, P. M.; Selser, J. C. *Macromolecules* **1990**, *23*, 2050.
(29) Bercea, M.; Cazacu, M.; Wolf, B. A. *Macromol. Chem. Phys.* **2003**, *204*, 1371.
(30) Wolf, B. A. *Macromol. Chem. Phys.* **2003**, *204*, 1381.
(31) Stryuk, S.; Wolf, B. A. *Macromol. Chem. Phys.* **2003**, *204*, 1948.
(32) Wolf, B. A. *Macromolecules* **2005**, *38*, 1378.
(33) Luna-Barcenas, G.; Gromov, D. G.; Meredith, J. C.; Sanchez, I. C.; de Pablo, J. J.; Johnston, K. P. *Chem. Phys. Lett.* **1997**, *278*, 302.
(34) Luna-Barcenas, G.; Meredith, J. C.; Sanchez, I. C.; Johnston, K. P.; Gromov, D. G.; de Pablo, J. J. *J. Chem. Phys.* **1997**, *107*, 10782.
(35) Gromov, D. G.; de Pablo, J. J. *Fluid Phase Equilib.* **1998**, *150*, 657.

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