

Insight Into Chain Dimensions in PEO/Water Solutions

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Received 4 March 2007; accepted 9 April 2007

DOI: 10.1002/polb.21221

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Small-Angle Neutron Scattering has been performed from poly(ethylene oxide) in deuterated water at temperature ranging from 10 to 80 °C. A simple fitting model was used to obtain a correlation length and a Porod exponent. The correlation length L characterizes the average distance between entanglements in the semidilute region and is proportional to the individual coil sizes in the dilute region. L was found to increase with temperature in the semidilute region but it decreases with temperature in the dilute region. This decrease is the precursor to the single-chain collapse which applies to very dilute polymer solutions. © 2007 Wiley Periodicals, Inc. *J Polym Sci Part B: Polym Phys* 45: 2196–2200, 2007

Keywords: neutron scattering; phase behavior; solution properties

INTRODUCTION AND EXPERIMENTAL

Poly(ethylene oxide) (PEO) is the simplest water-soluble polymer. Its chemical structure—(CH₂CH₂O)—contains the just right balance between hydrophobic and hydrophilic interactions to make it dissolve in water for a wide range of temperatures and concentrations. The PEO/water system has been the subject of much research interest.^{1–15} The literature is full of extensive studies, focusing on the various aspects of clustering and solvation in PEO/water solutions. Many methods (including dynamic light scattering and small-angle neutron scattering) have been employed and are described elsewhere. This article has been kept short and to the point and focuses solely on chain dimensions as measured through the correlation length.

The single-chain polymer collapse has attracted much attention over the years. Studies were made on polystyrene in cyclohexane.¹⁶ Further studies were made on water-soluble PNIPAM solutions.¹⁷ All chain collapse studies were made on very high molecular weight and low polydispersity polymers at very low concentrations.

Small-Angle Neutron Scattering (SANS) is a valuable technique for the characterization of polymers in solution. When used with a deuterated solvent (*d*-water in this case), SANS can determine structure and phase miscibility in dilute and semidilute PEO/*d*-water solutions.¹⁵ SANS measurements have been taken at the NIST Center for Neutron Research using standard (low- Q and high- Q) instrument configurations and experimental conditions.

PEO of molecular weight $M_w = 41,500$ g/mol ($M_n = 36,500$ g/mol) has been purchased from Aldrich and used with high purity *d*-water. SANS data have been taken from PEO/*d*-water solutions of 0.3, 0.5, 1, 2, and 4% mass fraction for a range of temperatures from 10 to 80 °C (at 10 °C intervals). The overlap polymer fraction (boundary between dilute and semidilute solutions) has been estimated in the literature using

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Journal of Polymer Science: Part B: Polymer Physics, Vol. 45, 2196–2200 (2007)
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many criteria.¹⁸ The overlap mass fraction is estimated to be between 0.5 and 2% in our case depending on what criterion is used. Our PEO/*d*-water solutions were mixed separately and measured 2 days after preparation.

Figure 1 shows the reduced SANS data for the 1% mass fraction PEO/*d*-water solution.

POLYMER SOLUTION THEORY

A generic model that reproduces the main scattering features observed in the variation of the scattered intensity $I(Q)$ with the scattering variable Q is used to fit the SANS data. The functional form for this model is as follows:¹⁵

$$I(Q) = \frac{C}{1 + (QL)^m} + B$$

Here C is a Q -independent constant representing the scattering scale, L is a correlation length, m is the Porod exponent, and B is a Q -independent (mostly incoherent scattering) background. The special case corresponding to $m = 2$ is the well-known Lorentzian function. Note that in this case ($m = 2$) the radius of gyration can be estimated as $R_g \sim \sqrt{3}L$ at low- Q and $R_g \sim \sqrt{2}L$ at high- Q .

The mean field theory of polymer solutions¹⁴ (due to Flory) describes polymer chains as random walks. When interactions between mono-

mer–monomer and monomer–solvent molecules are equivalent, the solution is in the theta-condition and the random walk is unbiased. In this case, the radius of gyration R_g follows a simple scaling dependence on the degree of polymerization N and statistical segment length b as: $R_g = b\sqrt{N/6}$. When monomer–monomer (slightly) repulsive interactions are favored, chain statistics follow a self avoiding random walk, and polymer chains are swollen. When monomer–monomer (attractive) interactions are favored over monomer–solvent interactions, chain statistics follow a self-attractive random walk leading to the onset of “chain collapse.” These cases are summarized through the scaling relation $R_g^2 = \frac{b^2 N^{2\nu}}{(2\nu+1)(2\nu+2)}$ where ν is the excluded volume exponent that takes on the following values: $\nu = 3/5$ for fully swollen chains, $\nu = 1/2$ for Gaussian chains, and $\nu = 1/3$ for fully collapsed chains. The Porod exponent m obtained from SANS measurements is related to the Flory excluded volume exponent ν as $m = 1/\nu$.

Polymer solutions phase separate either upon heating yielding a Lower Critical Solution Temperature (LCST) or upon cooling leading to an Upper Critical Solution Temperature (UCST). Water-soluble polymers tend to be characterized by an LCST. The PEO/water system is known to phase separate upon heating.¹⁵ A plot of the inverse of the scale intensity with inverse temperature in absolute temperature ($1/C$ vs. $1/T(K)$) shows a linear behavior. Extrapolation of this linear variation to $1/C = 0$ (i.e. when the SANS intensity “diverges”) yields an estimate of the spinodal temperature T_s . When T_s is crossed, the polymer solution starts undergoing spinodal phase separation.

Many PEO solution studies focused on the effect of clustering, which appears as a low- Q SANS feature. The present study focuses on the high- Q SANS data only. The low- Q clustering part discussed elsewhere¹⁵ is weak for dilute solutions.

RESULTS AND DISCUSSION

Fits to the SANS data show expected results such as the intensity (parameter C) increase with increasing temperature pointing to an LCST behavior and the increase of the Porod exponent (parameter m) with temperature going from m values around $5/3$ (fully swollen coils) to

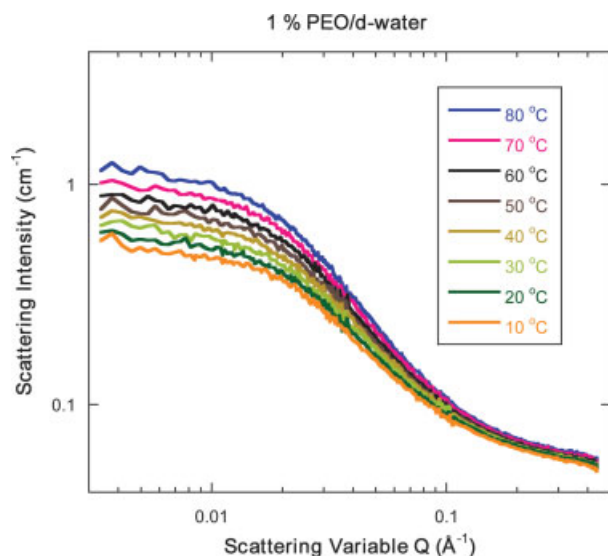


Figure 1. Variation of the SANS intensity with temperature for the 1% mass fraction PEO/*d*-water sample.

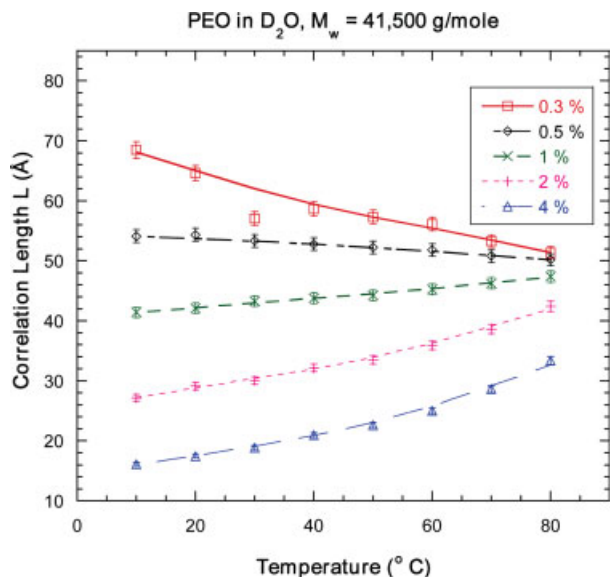


Figure 2. Variation of the correlation length L with increasing temperature for the various PEO/ d -water samples measured. L is seen to increase with temperature for semidilute solutions, but it decreases with temperature for dilute solutions. Statistical error bars have been included. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

values around 2 (Gaussian chains). Figure 2 shows the variation of the correlation length L with temperature. L is seen to increase with temperature for semidilute solutions but decreases with temperature for dilute solutions. L is expected to increase when approaching the spinodal temperature for semidilute solutions because of the growing concentration fluctuations. L becomes comparable to the coil dimension at the overlap mass fraction ϕ^* . Based on the observed trends, the overlap mass fraction is estimated to be between 0.5 and 1%. Below ϕ^* , it is interesting to note that chains are shrinking slightly with temperature. This is reminiscent of the chain collapse transition observed for extremely dilute solutions that have a very long (and narrow) molecular-weight distribution.¹⁷ In dilute solutions, the solvent quality is becoming poorer. This observation of chain shrinking in dilute solutions agrees with the Flory theory, which predicts $R_g \sim bN^\nu$ with $\nu = 0.6$ in good solvent condition and $\nu = 0.5$ in the theta-solvent condition. The low temperature corresponds to the good solvent condition and the high temperature is close to the theta-condition. Note that the theta-temperature is equivalent to

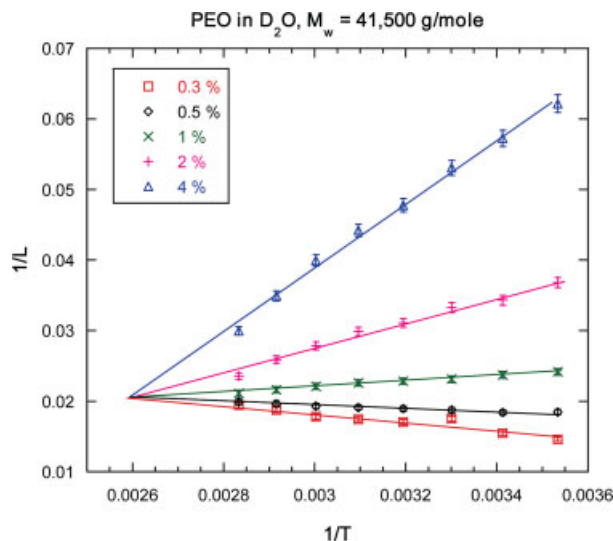


Figure 3. Variation of $1/L$ versus $1/T$ (in absolute temperature). The linear variations converge to a value independent of mass fraction. Statistical error bars are small. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the spinodal temperature in the limit of infinite molecular weight.

At the theta-condition, single-coil scattering is given by the so-called Debye function $P(U) = 2[\exp(-U^2) - 1 + U]/U^2$ where $U = Q^2 R_g^2$

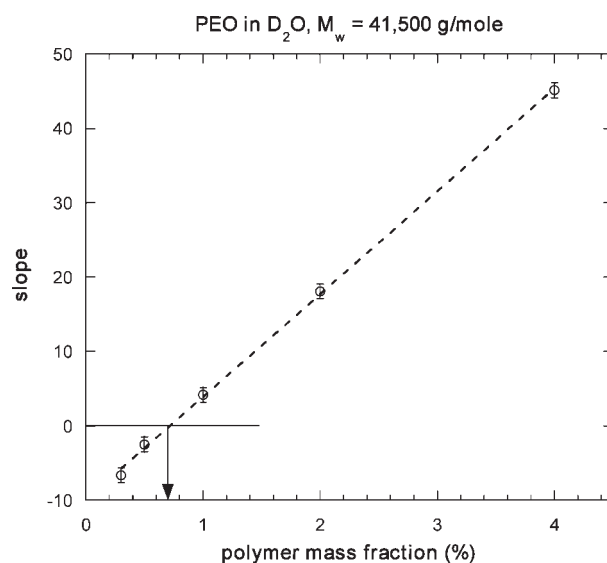


Figure 4. Linear variation of the slope of the plot $1/L$ versus $1/T$ with mass fraction (%) PEO in d -water). The mass fraction corresponding to zero slope defines the experimentally measured overlap mass fraction ϕ^* ($= 0.7\%$ in this case).

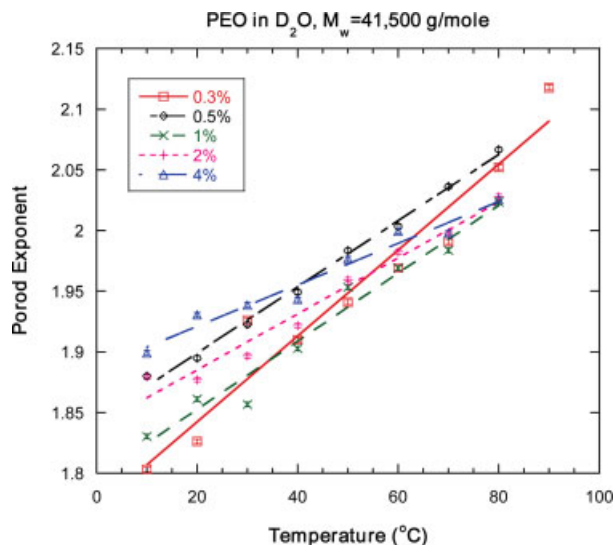


Figure 5. Variation of the Porod exponent m with increasing temperature for the various PEO/ d -water samples measured. Polymer chain statistics are seen to vary from swollen chains with m between $5/3$ and 2 (at low temperatures) to Gaussian coils with m around 2 (at high temperatures). Variation is not uniform for the different samples. Statistical error bars are small. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

$= Q^2 N b^2 / 6$. Its high- Q expansion is given by $P(U \rightarrow \infty) = 2/Q^2 R_g^2 \sim 1/Q^2 L^2$. This gives a relationship $L^2 = R_g^2 / 2$. The case closest to the theta-condition corresponds to the 0.3% PEO/ d -water sample at 80°C . For this case, $L = 51 \text{ \AA}$ and $\nu = 0.487$ yielding the following estimates for $R_g = 72 \text{ \AA}$ and $b = 5.8 \text{ \AA}$ (here $N = 943$ has been used).

It is interesting to note that the plot of $1/L$ versus $1/T$ (in absolute temperature) shown in Figure 3 yields linear behavior of the form $1/L = E + F/T$ where E is the intercept and F is the slope.

Note that the slope F changes sign when the overlap mass fraction ϕ^* is crossed, and that the various linear variations converge to a spot. Plotting the variation of the slope F with mass fraction ϕ also shows a linear behavior (Fig. 4) of the form $F = -9.59 + 13.7 \phi$. The experimentally measured overlap mass fraction ϕ^* is obtained for $F = 0$ and corresponds to $\phi^* = 0.7\%$ in our case. Putting all dependencies together yields the following variation for the correlation length with mass fraction ϕ and temperature T .

$$\frac{1}{L} - \frac{1}{L_1} = 13.7 (\phi - \phi^*) \left(\frac{1}{T} - \frac{1}{T_1} \right).$$

Here $\phi^* = 0.7\%$, $L_1 = 49 \text{ \AA}$, and $T_1 = 385 \text{ K}$. Obviously, ϕ^* , L_1 , and T_1 are independent of polymer mass fraction and temperature, but are expected to change with molecular weight.

Figure 5 shows the variation of the Porod exponent for the various measured samples. These exponents vary from around $5/3$ (fully swollen chains) at low temperature to around 2 (Gaussian coils) at high temperature. It is important to note that the full chain collapse is characterized by a Porod exponent of 3 . Porod exponents near 3 have not been observed in our data. Porod exponents increased with temperature consistently, indicating that the solvent quality is getting poorer.

CONCLUSIONS

In conclusion, an interesting shrinking of polymer coils is observed in dilute PEO/ d -water solutions. This maybe the precursor to the known polymer chain collapse observed for very dilute solutions and very high molecular weight polymer.¹⁷ A novel way of measuring the overlap mass fraction is presented. Variation of the correlation length with polymer mass fraction and temperature follows an expression that applies to dilute and semidilute solutions. It would be interesting to find out whether such formula would apply to other polymer solutions (with different parameters) making it universal.

This work is based upon activities supported in part by the National Science Foundation under Agreement No. DMR-0454672. Useful comments and suggestions by Yuri Melnichenko are appreciated.

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