Communications to the Editor

Small-Angle Neutron Scattering from a Living Polymer Solution: Preliminary Experiment

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I. Introduction. One can view the onset of reversible, equilibrium polymerization in "living" polymers as the temperature is lowered through the ceiling temperature, T_p,[1,2] as a phase transition and treat it either with a classical mean field theory[3,4] or with the $n \to 0$ limit of the n-vector model of a magnetic phase transition.[5,6] The application of such theories to the prediction of thermodynamic and transport properties of living polymer solutions is an object of active investigation.[7,8]

Small-angle neutron scattering (SANS) is an appropriate tool for studying such living polymer solutions. Previously, SANS studies have been made on sulfur during its equilibrium polymerization in solution.[9] No SANS studies have ever been reported for a "living", organic, polymer solution. The impediment to such work has probably been the diffculty in preparing samples that will remain unterminated for long periods of time. We have learned how to make samples which are essentially stable.[7,8] We present here preliminary SANS measurements on samples of living poly(α-methylstyrene) in deuterated tetrahydrofuran, using sodium naphthalide as the initiator.[10] We compare the experimental data to a new equation for the scattering intensity of a living polymer solution as a function of temperature.[11] This equation is based on the $n \to 0$ magnet model in the mean field approximation and is able to account for the essential features of the scattering data.

II. Theory. In 1980 the limit $n \to 0$ (where n is the dimension of the order parameter) of a dilute n-vector model of magnetism in a small external magnetic field was introduced to describe equilibrium polymerization in a solvent, with applications to sulfur solutions[12] and to living polymer solutions.[6] In the mean field approximation, this theory corresponds to the Flory theory of polymer solutions.[13] The theory in its mean field limit can be extended to the study of the concentration structure function, $S(q)$, directly related to the neutron scattering intensity, $I(q)$, where q is the wavenumber.[11] The application of the full, unapproximated, theory is not yet possible; we nonetheless use the magnetic terminology rather than the Flory terminology because we expect the full power of the more general formulation to be available in the future and because this terminology emphasizes the connection of equilibrium polymerization to phase transitions.

We discuss here only the results for the limit as $q \to 0$ of $S(q,T)$, where T is the temperature, which we call $S(0,T)$ and which is related to the concentration susceptibility. From eq 5.14 and 5.15 of Wheeler and Pfeuty,[12] we get

$$[S(0,T)]^{-1} = \left[\left(\frac{\partial x_m{}^*}{\partial \tilde{\Delta}}\right)_p\right]^{-1} = -\hat{K} + \frac{1}{1 - x_m{}^*} + \frac{h}{m}\left[\frac{K_p m + h}{h + \left(K_p m + \frac{h}{2}\right)(K_p m + h)^2}\right] \quad (1)$$

where T is the temperature, $x_m{}^*$ is the initial mole fraction of monomer, $1 - x_m{}^*$ is the initial mole fraction of solvent, and $\tilde{\Delta}$ is related to the chemical potentials of the solvent and the monomer. Here $\hat{K} = 4T_1/T$ is a measure of the solvent–monomer interaction energy and is related to the Flory interaction parameter,[13] χ; T_1 is the temperature of the upper critical solution point of the solvent–monomer solution. For the living polymer systems considered here

$$K_p = \exp\left[\frac{-\Delta H_p{}^\circ + T\Delta S_p{}^\circ}{RT}\right] \quad (2)$$

where K_p is the equilibrium constant for polymerization, $\Delta H_p{}^\circ$ and $\Delta S_p{}^\circ$ are the enthalpy and entropy of polymerization, respectively, and R is the gas constant. The "magnetic" quantities h (the external magnetic field) and m (the magnetization) are related[6] to the total mole fraction of polymers, x_p, and to the mole fraction of initiators, x_i:

$$h = \frac{2N_p}{m} = \frac{x_i}{m} \quad (3)$$

$$m^2 = 2x_m(x_m{}^* - x_m) \quad (4)$$

with the quadratic equation for x_m

$$x_m = x_m{}^* - \frac{x_p}{1 - K_p x_m} \quad (5)$$

where x_m is the mole fraction of unreacted monomer at equilibrium and $x_p = x_i/2$ for this system.

III. Experimental Methods. A. Sample Preparation. The starting materials were 99.5% deuterated tetrahydrofuran (TDF) from Sigma Chemical Co., 99.97% pure tetrahydrofuran (THF) from Aldrich Chemical Co., 99% pure α-methylstyrene from Aldrich Chemical Co., 99% pure naphthalene from Baker Chemical Co., and 99.95% pure sodium from Aldrich Chemical Co. Our purification and handling techniques are described in detail in refs 7 and 8. The sodium naphthalide initiator, prepared in THF, was diluted with TDF before use, and then only a small amount was used in preparing (in TDF) each sample, so the amount of THF in the final sample was insignificant.

The sample mixture was made by putting the required amount of dilute initiator solution into a reaction vessel attached to the neutron scattering cell,[8] adding first clean TDF, and then adding clean α-methylstyrene. This
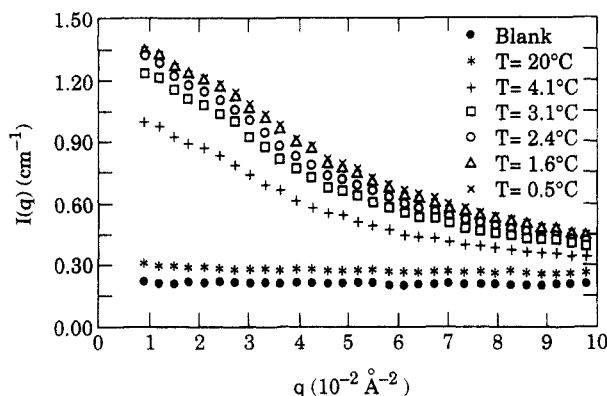
Figure 1. Neutron scattering intensity, $I(q)$, as a function of wavenumber, q, and temperature, T, for the first cooling of the sample of living poly(α-methylstyrene) in TDF, initiated by sodium naphthalide. The initial mole fraction of monomer is 0.12, and the molar ratio of initiator to monomer is 1.7×10^{-3}.

solution was degassed while in the reaction vessel by freezing with liquid nitrogen, pumping off residual gases, and thawing; this procedure was repeated three times. The solution was then poured from the reaction vessel into the cell, and the cell was permanently sealed. The sample on which we report here has a mole fraction of initial monomer $x_m{}^* = 0.12$ and a mole ratio of initiator to monomer, r, of 1.7×10^{-3}.

The neutron scattering cell (made by Hellma Co.) consists of two quartz disks of 0.5-mm thickness, separated by a distance (neutron path) of 2.5 mm; the diameter of the sample is 21.5 mm. The cells were held in a copper block, the temperature of which was controlled to ± 0.1 K using circulating water.

B. Data Acquisition and Treatment. The experiment was run on the spectrometer PACE in the reactor Orphée at the Laboratoire Léon Brillouin (CEA–CNRS), Saclay, France. The incident wavelength λ obtained via a mechanical selector was 6.56 Å $\pm$ 10%. The q range of the collimated beam was 3.92×10^{-2} to 0.98×10^{-1} Å^{-1}.

For the sample with $x_m{}^* = 0.12$, T_p was around 4 °C. Thus it had never polymerized, other than in the freeze–pump–thaw procedure during preparation; if it had never been polymerized, then it could not contain very much "dead" polymer. We started from room temperature, much above T_p, for the first progressive cooling. On subsequent heating and cooling, hysteresis effects appeared, which we will present in detail later. We report data only on the first cooling. The scattering from a "blank" sample, made of monomer and solvent with no initiator, was measured at 3 °C.

For each temperature, the evolution of the scattering was observed and showed stabilization within 30 min. All subsequent spectra were then summed. The neutron scattering intensity $I(q)$ as reported here is corrected for sample thickness, counting time, and empty cell scattering and is scaled by the scattering cross-section of 1 mm of water, taken[14] to be 0.87 cm^{-1}.

IV. Results and Discussion. Figure 1 shows $I(q)$ for the sample of living poly(α-methylstyrene) in TDF ($x_m{}^* = 0.12$, $T_p = 4$ °C) at six temperatures on the first cooling. Note the lack of slope in the scattering for the blank sample and the very small slope of the initiated sample at 20 °C. That the initiated sample at 20 °C scatters more than the blank could be due to the presence of some dead oligomers. The scattering intensity of the initiated sample then increases dramatically as the temperature is decreased, reflecting the growth of the living polymers.
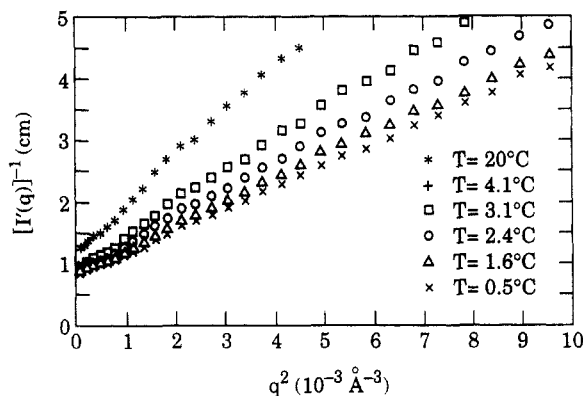

Figure 2. Zimm plot of the same data as in Figure 1. $I'(q)$ is $I(q)$ for the sample minus $I(q)$ for the blank (see text).
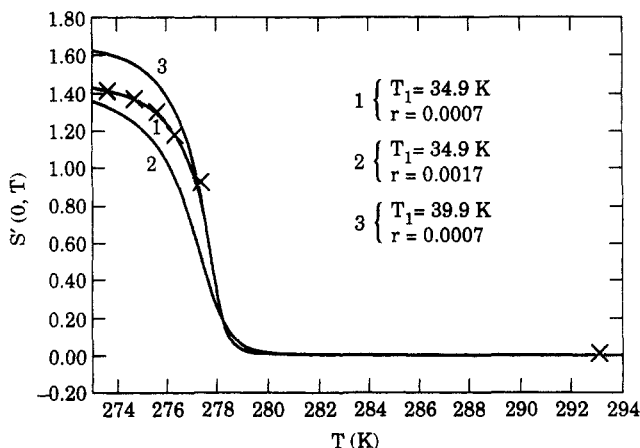

Figure 3. $S'(0,T)$, the concentration structure function at $q = 0$, as a function of temperature for the same living polymer solution as in Figures 1 and 2. The prime indicates that $S(0,T)$ for the blank has been subtracted (see text). The experimental data are indicated by "X"; the uncertainty is about ± 0.01. The solid lines are theoretical curves using various values for the parameters.

$I(q)$ still requires small corrections for incoherent scattering, inelastic scattering, and multiple scattering, which are difficult to estimate. Thus we calculate $I'(q) = I(q) - I_{\text{blank}}(q)$, where $I_{\text{blank}}(q)$ is the spectrum obtained from the blank sample. In this way we subtract not only incoherent scattering but also the background scattering corresponding to the solvent and monomer. We then obtain

$$S'(q,T) = S(q,T) - S_{\text{blank}}(q, 3\ °C) = \frac{I'(q,T)}{\kappa} \qquad (6)$$

where $S(q,T)$ and $S_{\text{blank}}(q, 3\ °C)$ are the concentration structure functions for the mixture with and without initiator. The quantity κ is the contrast, given by[15]

$$\kappa = \frac{1}{V}\left[b_2\frac{V_1}{V} - b_1\frac{V_2}{V} \right]^2 \qquad (7)$$

where V_1 and V_2 are the respective molecular volumes for α-methylstyrene and TDF, V is the mean molecular volume ($V = x_m{}^* V_1 + (1 - x_m{}^*) V_2$), and b_1 and b_2 are the molecular neutron scattering amplitudes. We estimate $\kappa = 0.83$ cm^{-1}.

To extrapolate better to $q = 0$, we plot $[I'(q)]^{-1}$ versus q^2 in Figure 2. The data are nearly linear in this Zimm plot, allowing us to obtain $I'(0)$ from the graph. The values of $I'(0)/\kappa = S'(0)$ are compared in Figure 3 to the theoretically predicted behavior. For the theory, we used $\Delta H_p{}° = 34.8$ kJ/mol[16] and $\Delta S_p{}° = 107$ J/(mol K).[17,18] We found it necessary to adjust not only T_1 but also r to have eqs 1–5 describe the data; the best fit was achieved with $T_1 = 34.9$ K and with $r = 0.0007$.

The value of T_1 deduced from the best fit to the data seems reasonable, TDF being a moderately good solvent for α-methylstyrene. The value of r deduced from the best fit is smaller than the experimental value (0.0017). A possible explanation could be the deactivation of some of the initiator molecules or the termination of some of the polymer molecules.

The Zimm plots also permit us to estimate the Ornstein–Zernike correlation lengths[19] to be 7.5, 22.5–25, 22.5–25, 21.3, 20.7, and 20.2 Å at 20, 4.1, 3.1, 2.4, 1.6, and 0.5 °C, respectively. We will pursue this issue in more detailed experiments.

V. Conclusions. We report here the first study by SANS of a living polymer system, evolving as a function of temperature and presenting a polymerization transition. The preliminary results are in reasonable qualitative agreement with the behavior expected from a mean field theory modeling the polymerization as a phase transition.

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Registry No. Poly(α-methylstyrene), 25014-31-7.