Coil-Globule Phase Transition in a Single Polystyrene Chain in Cyclohexane

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The first observations of the entire temperature-induced coil-globule transition in a single polystyrene polymer chain in cyclohexane is reported. The position of the coil-globule transition relative to the coexistence curve in the phase diagram of the system is also shown. The transition occurred at 32°C with a width of 5°C for 2.6×10^7–molecular-weight polystyrene with a sharp decrease in hydrodynamic radius from 1250 Å to 500 Å as the temperature was lowered.

The conformations of polymers in solution have long been of interest. Within the last fifteen years, theorists have described a discrete transition in polymer configuration from an extended coil to a collapsed globule state.[1] Recently this laboratory reported the first observations of the complete coil-globule transition of polyacrylamide $[M_w=(5-6)\times10^6]$ in acetone-water solutions.[2] The transition was induced by varying the solvent composition. This three-component system, however, is less desirable for study as the solvent composition within the polymer coils may very well differ from that in the bulk of the solvent, increasing the complexity of any analysis. In this Letter, we report our observation of the coil-globule transition in a binary system: polystyrene in cyclohexane.

The best previous light-scattering measurements[3] of the dimensions of polystyrene in cyclohexane as a function of temperature were made on samples of 4.4×10^7 molecular weight at concentrations down to 2×10^{-5} g ml^{-1}. The authors were only able to observe the beginning of the transition before interpolymer aggregation occurred. They concluded that it would be unlikely for the single-globule state to exist before aggregation began. Others,[4] using neutron scattering techniques, have also succeeded in observing the onset of the transition using 2.9×10^4–molecular-weight polystyrene at a concentration of 3.4×10^{-3} g ml^{-1}. From our observations of the position of the coil-globule transition relative to the coexistence curve (shown later), it is clear why these workers were unable to observe the complete transition. Much lower concentrations are required to ensure existence of the globular state before the polymers aggregate. In this experiment, for 2.7×10^7–molecular-weight polystyrene, concentrations as low as 10^{-7} g ml^{-1} were necessary to observe the globule state.

At such low concentrations, the portion of signal in excess of background scattering is very small. The classical technique of determining polymer dimensions with use of measurements of the angular dependence of the scattered-light intensity becomes extremely difficult. This technique requires an accurate determination of a small change in a very small signal. However, even with such a low signal-to-noise ratio, one is able to use the technique of photon correlation spectroscopy to make a straightforward measurement of polymer dimensions.

The translational diffusion coefficient of particles in solution, D, is related to the hydrodynamic radius, a, of the particles by the Stokes-Einstein relation,[5] $D=k_BT/(6\pi\eta a)$, where k_B, T, and η are Boltzmann's constant, temperature, and viscosity of the solution, respectively. The diffusion coefficient is obtained through the decay rate of the photon correlation function of the scattered-light intensity.[5]

Samples were prepared with use of 2.7×10^7–molecular-weight polystryene (Polysciences lot no. 3-1761, $M_w/M_N=1.3$), and high-quality cyclohexane (Fisher 99-Mol% pure), both used as supplied with no additional purification. All glassware and sample cells were very carefully cleaned and handled to prevent contamination by dust or other impurities. The solution temperature was controlled with an accuracy of better than ± 0.05 °C and monitored with use of an immersible Teflon-encased thermistor (YSI-702).

The source of incident light was an argon-ion laser (Spectra-Physics 164-00) operated at 5145 Å and intensities between 200 and 1200 mW. Scattered light was detected with a photomultiplier (RCA 8850) at an effective forward angle of 23°. A digital photon correlator (Nicomp Instruments) accumulated the correlation function of the scattered light. The logarithm of the correlation function was fitted by use of the method of cumulants.[6] From the fit, the diffusion coefficient and the hydrodynamic radius were readily calculated.

We also made measurements of a portion of the

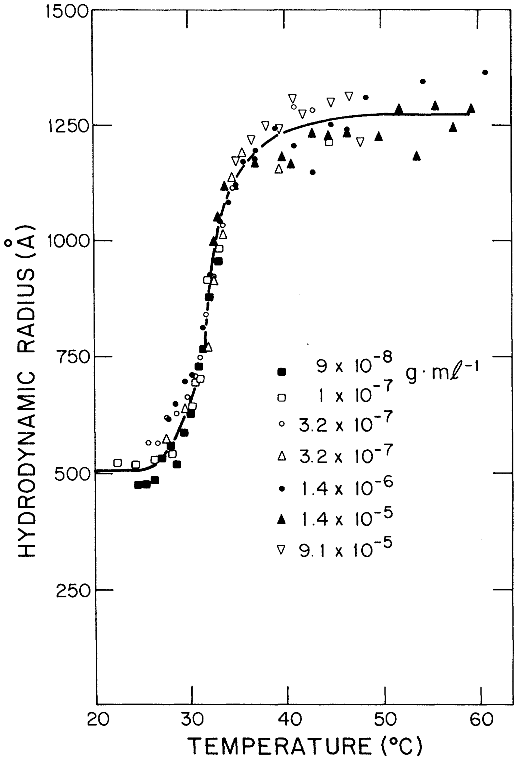

FIG. 1. The temperature dependence of the hydrodynamic radius of polystyrene $M_W = 2.7\times10^7$ in cyclohexane is plotted for several concentrations of polystyrene. A collapse in radius occurs at 32°C. The transition width is approximately 5°C. At higher concentrations the polymers aggregated into clusters preventing measurement of single-polymer dimensions at lower temperatures. At each concentration before the onset of aggregation, though, the radius follows approximately the same temperature dependence.

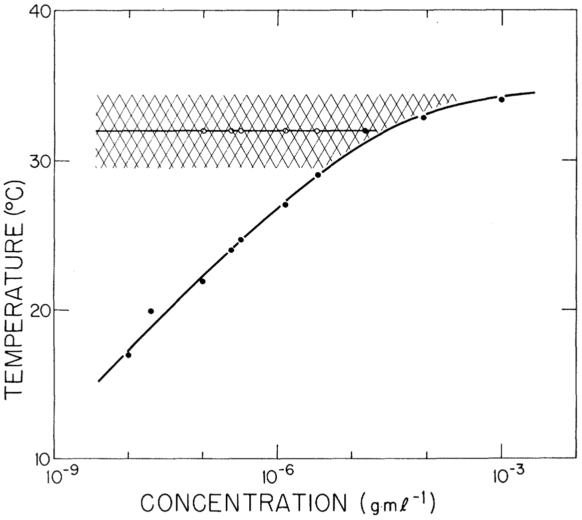

FIG. 2. A portion of the phase diagram of polystyrene in cyclohexane is shown. The coil-globule transition temperature is plotted as a function of concentration (open circles). The transition region is shaded. The phase separation temperatures for several concentrations are also plotted (solid circles). The concentration axis is logarithmic; the phase separation temperature falls quite slowly with decreasing concentration. At the lowest concentrations indicated on the coexistence curve the coil-globule transition could not be measured because the signal had become too weak.

coexistence curve of the polystyrene-cyclohexane system. The coexistence curve is defined by the states of temperature and solute concentration at which the segment-segment attractions just begin to dominate the segment-solvent attractions, and the polymers phase separate, forming aggregates. We monitored the intensity of the scattered light to determine the temperature at which this aggregation occurs. At the phase separation temperature both the intensity and the magnitude of the intensity fluctuations increased because of the increase in size of the scatterers. At higher concentrations, the increase in size was confirmed by the hydrodynamic radius measurements. At the lowest concentrations, the correlation function became difficult to measure, but intensity measurements were sufficient to detect the increase in particle size.

Figure 1 shows the hydrodynamic radius of the polymer chains as a function of temperature for several concentrations of polystyrene. The extended coil has a hydrodynamic radius of about 1250 Å, and collapses at 32 °C to the globular state having a radius of about 500 Å. The width of the transition is about 5 °C. Although most measurements were made while lowering the temperature of the solution, the transition could be reversed upon raising the temperature. The solid circles in Fig. 2 indicate the states of temperature and concentration at which phase separation occurred by interpolymer aggregation. The open circles indicate the coil-globule transtion temperature measured for several concentrations. The transition occurred at approximately the same temperature for each concentration. In taking into account the logarithmic scale of the concentration axis, it is apparent that the coexistence curve is remarkably flat. Very low concentrations are, indeed, necessary in order to reach the region of globule states below the coil-globule transition line and above the coexistence curve.

In addition to the correlation in the scattered photons due to the translational diffusion of the scattering molecules, there can be a large correlated signal resulting from scattering associated with intramolecular motion.[7] This signal would make the apparent diffusion coefficient, calculated under the assumption that the scattered-light intensity fluctuated only because of translational diffusion of the polymer, larger than its actual value. By going to a forward-scattering angle, the contribution to the correlation function due to scattering from the internal motion can be reduced. For a 23° forward-scattering angle, the contribution is estimated to be less than 10%. It will be of interest to make use of the scattering associated with the internal motions of the polymers to determine the amplitude and relaxation time of the internal modes as the polymer undergoes collapse.

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