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# Hydrodynamic Radius of Polystyrene around the $\theta$ Temperature

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ABSTRACT: The diffusion coefficient $D$ of a narrow-fraction polystyrene ($\bar{M}_w = 37\,000$, $\bar{M}_w/\bar{M}_n \le 1.06$) in cyclohexane has been studied as a function of temperature from 6 to 60 °C for four concentrations in the dilute regime. The hydrodynamic radius $R_h$, obtained from the value of $D$ at infinite dilution, increased smoothly with temperature. There was no evidence of a collapse region at low temperatures or of a region of constant coil size around the $\theta$ temperature as has been indicated for the radius of gyration $R_g$ by small-angle neutron scattering.

There has been considerable interest in recent years in the coil–globule transition of a polymer molecule as the temperature $T$ is lowered below the theta point ($\theta$). For example, in a recent paper by Sanchez,[1] where much of the relevant work is cited, mean-field theory was used to calculate the variation of the radius of gyration $R_g$ with temperature for a wide range of chain lengths. The results of this investigation reinforce the conclusions of computer simulation studies:[2,3] $R_g$ decreases smoothly as $T$ is lowered through $\theta$, and the suddenness of the change becomes more marked with increasing chain length.

However, Daoud and Jannink[4] have predicted a more dramatic change. They have deduced the temperature–concentration diagram of polymer solutions and, for dilute solutions, well below coil overlap, have predicted two interesting regions near the $\theta$ state. In the theta region around $\theta$ the coil dimensions remain constant over a range of temperature which is independent of concentration $c$ but decrease with molecular weight $M$ as $M^{-1/2}$. As temperature is reduced further, a collapse region is encountered, sandwiched between the theta region and the coexistence curve, where $R_g$ should vary as $\tau^{-1/3}$, with $\tau = |T - \theta|/\theta$; the extent of this region depends on both $c$ and $M$.

To test this predicted behavior, Nierlich, Cotton, and Farnoux[5] have used small-angle neutron scattering (SANS) to observe the decrease in $R_g$ for a low-molecular-weight polystyrene in deuterated cyclohexane below $\theta$ ($\bar{M}_w = 29\,000$, $\bar{M}_w/\bar{M}_n \le 1.2$, $c = 3.4$ mg/mL). As the temperature was decreased from 38 °C, $R_g$ decreased only slightly down to 20 °C, and this was taken to indicate the extent of the theta region. Between 20 and 11 °C, $R_g$ decreased more rapidly, and the experimental points were shown to vary as $\tau^{-0.32}$, with a choice for $\theta$ of 38 °C, in close agreement with the $\tau^{-1/3}$ variation predicted by Daoud and Jannink for the collapse region. However, the 2% uncertainty in $R_g$ would not preclude a smoother variation throughout the temperature region investigated.

The ability to use photon-correlation spectroscopy to measure diffusion coefficients with great precision presents an opportunity to study the variation of the hydrodynamic radius $R_h$ of polymers in solution around the $\theta$ temperature, and thus a more sensitive test of the theories can be carried out through the dynamic behavior. To this end, we have measured the diffusion coefficient $D$ of a low-molecular-weight polystyrene ($\bar{M}_w = 37\,000$, $\bar{M}_w/\bar{M}_n < 1.06$) in cyclohexane at four different concentrations in the dilute regime. The measurements were made over a wide range of temperature around $\theta$ (34.5 °C) from about 6 to 60 °C.

It is perhaps significant to note that Nishio et al.[6] have recently reported the use of dynamic light scattering to observe the collapse of polyacrylamide ($M = (5\text{–}6) \times 10^6$) when the composition of an acetone–water mixed solvent is varied at around 40 vol % acetone at 25 °C.

**Table I**
**Polynomial Coefficients for the Variation of $D$ with $T$[a]**

$$D = d_0 + d_1T + d_2T^2 + d_3T^3$$

| $c$, mg/mL | $d_0$ | $10^2 d_1$ | $10^4 d_2$ | $10^6 d_3$ |
|---|---|---|---|---|
| 2.58 | 3.60 | 4.49 | 16.2 | −7.5 |
| 5.45 | 2.88 | 8.54 | 6.2 | 0.6 |
| 10.55 | 1.65 | 14.90 | −9.4 | 13.6 |
| 15.36 | 1.25 | 14.49 | −6.5 | 10.7 |

[a] $D$ in $10^{-7}$ cm$^2$ s$^{-1}$, $T$ in °C.

## Experimental Section

Dilute solutions of polystyrene in cyclohexane were prepared at four different concentrations by using a narrow-fraction polystyrene (Pressure Chemical Co., $\bar{M}_w = 37\,000$, $\bar{M}_w/\bar{M}_n < 1.06$) and BDH spectroscopic grade cyclohexane. The concentrations were 2.58, 5.45, 10.55, and 15.36 mg/mL at 34.5 °C, and each solution was clarified by filtering through 0.2-$\mu$m Millipore filters into spectroscopic cells of 10-mm path length.

On the spectrometer, the cells were housed in an enclosure which maintained a temperature constant to 0.05 °C over a range from 6 to 60 °C. The beam from an argon-ion laser operating at 488 nm was focused at the center of the cell, and the light scattered at 90° was detected by an ITT FW 130 photomultiplier tube. The pulses corresponding to individual photoevents were amplified and standardized before being fed to a Malvern K 7023 correlator which computed a 48-point clipped correlation function $G(\tau)$ of the pulse chain. For each solution, correlation functions were recorded at intervals between 1 and 4 °C in the temperature range between about 6 and 60 °C.

For this low $\bar{M}_w$ sample, $K^2R_g^2 \ll 1$, where $K$ is the scattering vector, and theory predicts (see, for example, Berne and Pecora[7]) that the time-dependent part of $G(\tau)$ is a single exponential with decay rate $\Gamma = 2DK^2$. The most efficient use of the data in the fitting procedure was achieved by choosing the time interval between channels on the correlator so that the 48 channels spanned four decay times.

The normalized correlation functions $g^{(2)}(\tau)$ were computer fitted to a function of the form $1 + \alpha \exp(-\Gamma\tau) + \delta$, with $\alpha$, $\Gamma$, and $\delta$ as adjustable parameters; $\alpha$ depends on the optical geometry and $\delta$ is a very small "misnormalization" term[8] which varies from run to run on the same sample.

Above 20 °C, the time-dependent part of $g^{(2)}(\tau)$ was a single exponential as seen in Figure 1, which shows the curve fitted to the data points. The difference between the experimental points and the fitted curve is also shown (×5), and these residuals are seen to be random; the initial point is ignored in the fitting procedure since it is affected by after-pulsing in the photomultiplier tube. Typically, a series of runs at one temperature setting would give a standard deviation of better than 0.1% for $D$, and these values of $D$ were reproducible to 0.2% after a temperature excursion.

## Results and Discussion

The variation of $D$ with $T$ is shown in Figure 2 for the four solutions, together with $D_0$, the value of $D$ extrapolated to infinite dilution. A polynomial of degree 3 was

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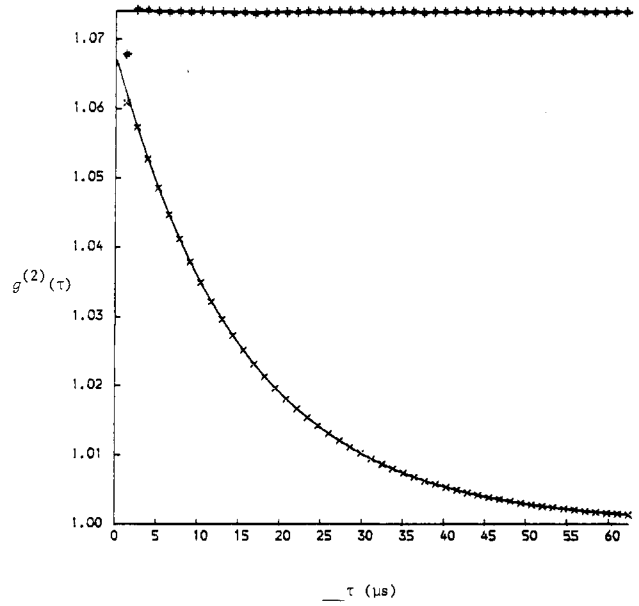

**Figure 1.** Single-exponential fit to data points of correlation function, with residuals (×5) shown above ($\bar{M}_w = 37000$, $c = 15.36$ mg/mL, $T = 25.03$ °C).

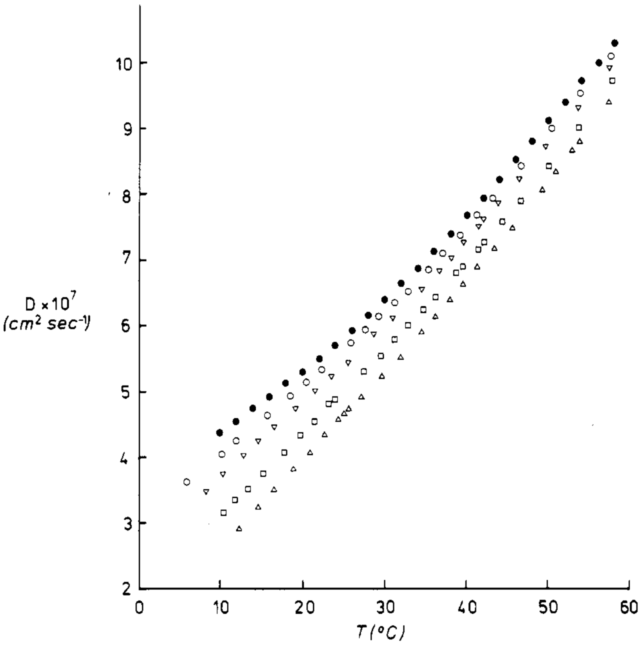

**Figure 2.** Variation of $D$ with $T$: (○) $c = 2.58$, (▽) $c = 5.45$, (□) $c = 10.55$, (△) $c = 15.36$ mg/mL. Filled circles indicate extrapolated values for $D_0$.

fitted to each set of points and the coefficients are given in Table I. From these functions the variation of $D$ with $c$ could be calculated at any temperature, and plots at 5 °C intervals are shown in Figure 3. For these dilute solutions, $D$ varies linearly with $c$: $D = D_0(1 + k_Dc)$, where $k_D$ is the normalized slope.

$R_h$ was calculated as a function of $T$ every 1 °C by using the Stokes–Einstein equation $D_0 = kT/(6\pi\eta R_h)$, where $k$ is Boltzmann's constant; values of the solvent viscosity $\eta$ were taken from Landolt-Bornstein.[9] $R_h$ increases smoothly with $T$, as seen in Figure 4, with minor changes of slope near 33 and 54 °C (for clarity, the points are shown only at 5 °C intervals). There is no indication here of the theta region of constant coil dimension, which should extend down to 20 °C, or of the collapse region below this temperature. Indeed, these features, which formed the

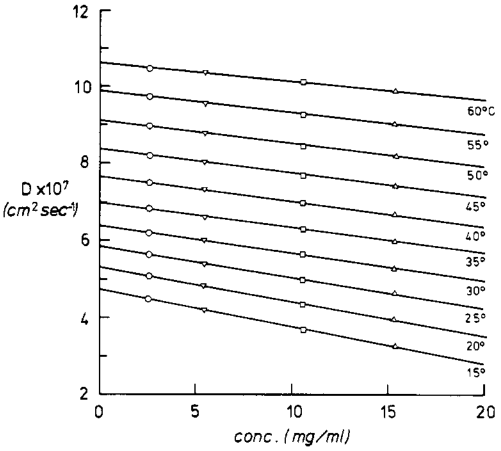

**Figure 3.** Variation of $D$ with $c$ at 5 °C intervals.

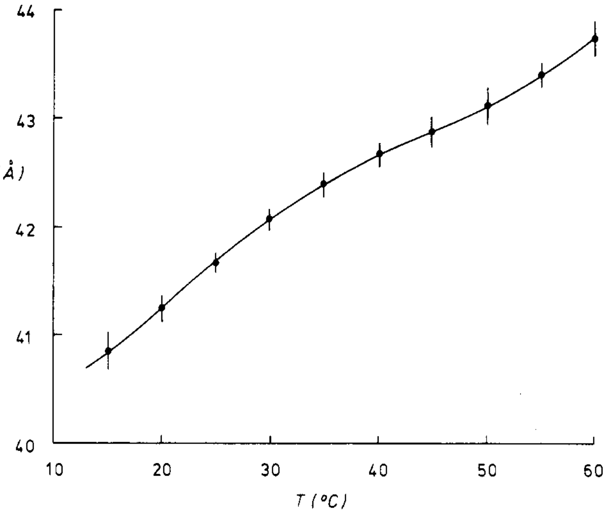

**Figure 4.** Variation of $R_h$ with $T$.

basis of the interpretation of the SANS investigation of Nierlich et al.,[5] are not revealed in the dynamic behavior.

A comparison of these two studies on similar systems shows that around $\theta$ the change in the expansion factor for $R_h$ ($\alpha_h$) with $T$ is less than for $R_g$ ($\alpha_g$): $d\alpha_h/dT = 0.14\%/°C$ while $d\alpha_g/dT \simeq 0.25\%/°C$. This accords with the theoretical result first derived by Stockmayer and Albrecht,[10] who showed that $R_h$ changes more slowly than $R_g$ close to $\theta$. They used a cluster expansion to obtain an exact expression for $\alpha_h$ for small displacements from Gaussian statistics: $\alpha_h = 1 + 0.609z + ...$ and $\alpha_h/\alpha_g = 1 - 0.029z + ...$, where $z$ is the excluded-volume parameter. This difference in the expansion factors has also been investigated recently by Akcasu and Han[11] by the subchain ("blob") theory, but, although they showed that $\alpha_h < \alpha_g$ for $T > \theta$, they did point out the limitations of the theory, particularly near $\theta$. For example, while $d\alpha_h/dT = 0$ at $\theta$ according to the blob theory, it is definitely positive in practice, as the present work shows.

It is worth noting that the temperatures at which precipitation occurred are 4.8, 6.9, and 8.0 °C for the 5.45, 10.55, and 15.36 mg/mL solutions; the 2.58 mg/mL solution froze before precipitation took place. These temperatures are considerably lower than the predicted values of 10.8, 15.0, and 16.6 °C taken from Figure 1 of ref 5 which shows the coexistence curve in the dilute regime.

Small deviations from a single-exponential function were detected in $g^{(2)}(\tau)$ below 20 °C, which increased slightly as $T$ approached the coexistence curve. This could possibly have been caused by the onset of aggregation of the

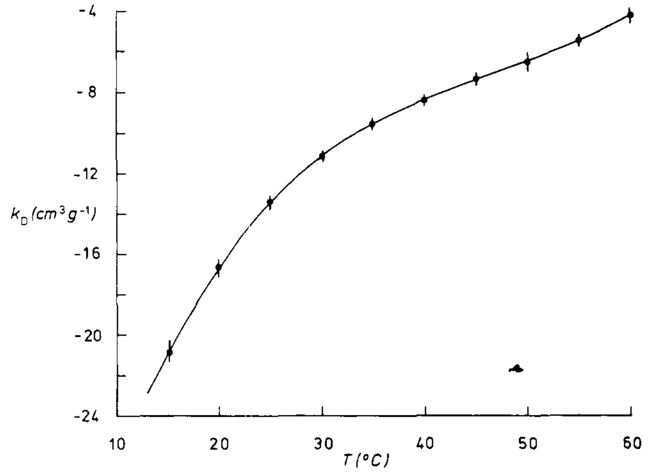

**Figure 5.** Variation of $k_D$ with $T$.

polymer molecules, particularly in the high-$M$ tail of the narrow fraction, thus effectively increasing the polydispersity of the sample. The force-fitted value of $D$ would then be an underestimate in terms of the original distribution, which would lead to an overestimate in $R_h$. At worst, this would be no more than 5%, which is insufficient to give a collapse region with $R_h$ varying as $\tau^{-1/3}$.

The normalized slope of the $D$–$c$ plot, $k_D$, is shown as a function of $T$ in Figure 5 and is seen to be negative over the temperature range investigated; again, the data points are only shown every 5 °C. The theoretical expressions for $k_D$ take the form[12]

$$k_D = (2 - \lambda)A_2M - \rho\bar{v}_h - \bar{v} \qquad (1)$$

where $A_2$ is the second virial coefficient of the solution and $\bar{v}$ is the specific volume of the bulk polymer (=0.92 cm$^3$ g$^{-1}$); $\bar{v}_h$ is the specific hydrodynamic volume, $(4\pi/3)R_h{}^3N/M$, where $N$ is Avogadro's number.

The coefficient $\lambda$ only appears in Yamakawa's theory,[11] where it has a value of 1.345 at the $\theta$ point but decreases slightly for an expanded coil in a good solvent. The coefficient $\rho$ is unity in the theories of Yamakawa[13] and Imai.[14] However, Pyun and Fixman[15] obtained a value of 7.16 for $\rho$ in their "hard-sphere" model; in their "soft-sphere" model, $\rho$ is 2.23 at the $\theta$ point but increases to the hard-sphere value as the coil expands.

At the $\theta$ point (34.5 °C),[16] where $A_2 = 0$, our results give a value for $\rho$ of 1.69 ± 0.08 from eq 1. This lies midway between the soft-sphere case of Pyun and Fixman and the predictions of Yamakawa and Imai. This experimental value corroborates the conclusion reached in a previous investigation[17] with high-$\bar{M}_w$ samples ($\bar{M}_w = 10^6$–$10^7$) and is in excellent agreement with the results of a recent study[18] ($\bar{M}_w$ = 180 000, 670 000, and $1.26 \times 10^6$), which gave a value for $\rho$ of 1.75 ± 0.05.

A complete test of eq 1 would require a knowledge of the variation of $A_2$ with temperature. This could be obtained from a conventional (intensity) light-scattering study, which would also yield values of $R_g$ for comparison with $R_h$.

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