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# Hydrodynamic Radius of Polystyrene around the Θ Temperature. 2

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ABSTRACT: The diffusion coefficient of five narrow-fraction polystyrenes ($\bar{M}_w = 1.80 \times 10^5$ to $5.05 \times 10^6$) in cyclohexane has been studied as a function of temperature $T$ and concentration in the dilute regime, in order to extend a previous investigation of a low-$\bar{M}_w$ sample (37 000). Measurements were made by photon correlation spectroscopy from the precipitation point through the Θ temperature (34.5 °C) to about 60 °C. In all cases the hydrodynamic radius of the polymer coil increased smoothly with temperature; the rate of expansion was an increasing function of $\bar{M}_w$ and decreasing function of $T$. These results agree well with several theoretical predictions for the expansion of the radius of gyration, but the subchain ("blob") theory for the polymer coil does not appear to be helpful in the dilute regime.

## Introduction

In a recent contribution[1] to the current debate about the coil–globule transition, we reported a smooth change in the hydrodynamic radius $R_h$ of a low molecular weight polystyrene over a wide temperature excursion about the Θ temperature. The diffusion coefficient $D$ of a narrow-fraction polystyrene ($\bar{M}_w = 37\,000$) dissolved in cyclohexane ($\Theta = 34.5$ °C) was measured as a function of concentration in dilute solution from 6 to 60 °C by photon correlation spectroscopy. The behavior observed for $R_h$ followed closely the theoretical temperature variation of the radius of gyration $R_g$ predicted by mean-field theory[2] and computer simulation studies.[3,4] However, it contrasted with the interpretation of small-angle neutron scattering measurements on a similar system by Nierlich, Cotton, and Farnoux.[5] They concluded that the coil dimensions remain almost constant over a finite temperature region about the Θ point before collapsing at lower temperatures: such behavior was suggested by Daoud and Jannink[6] using scaling law theory.

We have extended our investigation with a further five narrow fractions up to $\bar{M}_w = 5.05 \times 10^6$, specifically to study the molecular weight dependence of the variation in size with temperature. It turns out that the present work has, in part, overlapped the recently reported investigation of Bauer and Ullman,[7] who have studied the identical system over a similar molecular weight range, but only for temperatures below the Θ point. We believe the present work is of interest not only because it extends the temperature range up to 60 °C and beyond but also because of the reproducibility and precision of the measurements (0.3%). When very small changes in coil dimensions are studied, it is crucial that all the measurements are of a consistently high accuracy in order to provide an adequate and sensitive test of the theories.

Nose and Chu[8,9] have investigated both the static and dynamic properties of two narrow-fraction polystyrenes in *trans*-decalin around the Θ temperature ($\Theta = 20.5$ °C). The results of their work in dilute solution show that $R_h$ increased linearly with temperature from 20 to 40 °C for the lower molecular weight sample ($\bar{M}_w = 179\,300$), while for the other sample ($\bar{M}_w = 12 \times 10^6$) $R_h$ increased smoothly with temperature, but at a decreasing rate. The results of the present study amplify and confirm these findings, though agreement between the two systems does not appear to be exact in all details.

## Experimental Section

The experimental details have been given in our previous paper[1] and will not be repeated here. Values of $\bar{M}_w$ and $\bar{M}_w/\bar{M}_n$ for the narrow fractions used in this work are given in Table I; the sample used in the previous study is also included for completeness. For each sample, observations were made at four different concentrations, all in the dilute regime well below coil overlap, from the point of precipitation through the Θ temperature to about 60 °C. In practice, this meant that full sets of readings were obtained down to 30 °C for $\bar{M}_w = 5.05 \times 10^6$ and 18 °C for $\bar{M}_w = 180\,000$.

Table I
Characteristics of the Narrow-Fraction Polystyrenes

| $\bar{M}_w$ | $\bar{M}_w/\bar{M}_n$ | $10^7 D_0{}^{\Theta}$, $\mathrm{cm^2\ s^{-1}}$ | $\bar{M}_D$ |
|---|---|---|---|
| $37 \times 10^3$ [a] | 1.06 | 6.95 | $35.5 \times 10^3$ |
| $180 \times 10^3$ [a] | 1.06 | 3.13 | $175 \times 10^3$ |
| $670 \times 10^3$ [a] | 1.15 | 1.65 | $630 \times 10^3$ |
| $1.26 \times 10^6$ [b] | 1.05 | 1.172 | $1.25 \times 10^6$ |
| $2.88 \times 10^6$ [b] | 1.09 | 0.736 | $3.16 \times 10^6$ |
| $5.05 \times 10^6$ [b] | 1.02 | 0.566 | $5.35 \times 10^6$ |

[a] Pressure Chemical Co. [b] Toyo Soda Co.

Correlation functions of the light scattered from the solutions were made at scattering angles sufficiently small that the time-dependent part was a single exponential (with decay rate $2DK^2$, where $K$ is the scattering vector). This is the case if $x = K^2R_g{}^2 \ll 1$, since the light scattered from all parts of an individual molecule is in phase and the molecule is effectively a point particle. For the highest molecular weight studied, measurements were made at angles as low as 15° where $x = 0.03$. The precautions necessary to avoid flare and back-reflected light in low-angle work have been mentioned in a previous paper.[10]

The reproducibility of the values obtained for $D$ after a temperature excursion ranged from 0.2% for the low molecular weight samples to 0.5% for the highest molecular weight sample. The precision is evident in the smoothness of the curves fitted to the data and in the consistency of the results.

## Results and Discussion

A typical set of experimental results is shown in Figure 1, where values of $D$ at four different concentrations are plotted as a function of temperature $T$ for the sample $\bar{M}_w = 1.26 \times 10^6$. These curves provided the basis for the plots of $D$ against concentration $c$ shown at 4 °C intervals in Figure 2, from which values of $D_0$, $D$ at infinite dilution, are obtained. The slope gradually changes from negative to positive as the temperature rises and the solvent changes from poor to good. Although the excluded volume is zero at the Θ point, the slope is always negative there due to the finite volume occupied by the molecules. Zero slope occurs at a higher temperature, where this volume effect is cancelled by the repulsion between the polymer molecules.

The data from all the samples were similarly processed, and the values of $D_0{}^{\Theta}$ ($D_0$ at the Θ temperature) are presented in Table I. Those for the three high molecular weights agree within 1% with values obtained in a previous

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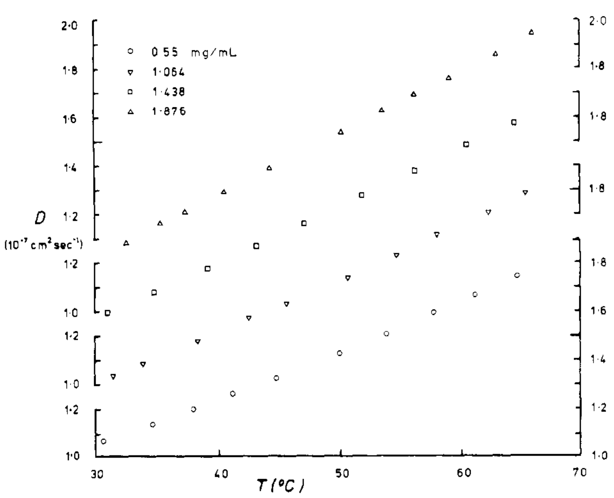

**Figure 1.** Variation of $D$ with $T$ for sample $\bar{M}_w = 1.26 \times 10^6$: (○) $c$ = 0.55 mg/mL; (▽) 1.064; (□) 1.438; (△) 1.876.

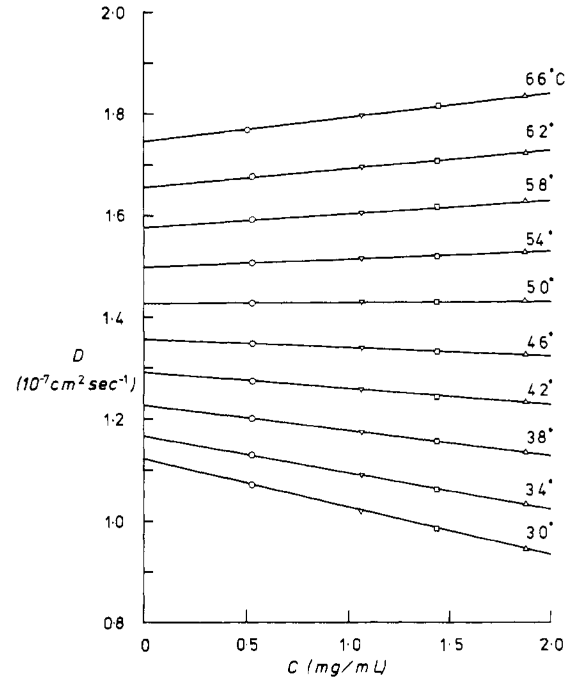

**Figure 2.** Variation of $D$ with $c$ at 4 °C intervals for sample $\bar{M}_w = 1.26 \times 10^6$.

investigation.[10] $D_0$ is usually expressed as a function of the molecular weight $M$ in power law form, $D_0 \propto M^{-b}$, and it is well established both theoretically and experimentally that $b = 0.5$ at the Θ point. The value of $b$ obtained in this work is 0.51 ± 0.01 and a plot of log $D_0^\Theta$ against log $\bar{M}_w$ is shown in Figure 3. The small deviations of some of the points from the line are most likely due to uncertainty in the value of $\bar{M}_w$. The values quoted by the suppliers were determined by conventional light scattering and are probably only accurate to about 5%.

A diffusion molecular weight $\bar{M}_D$ can be assigned to the samples by using the measured value of $D_0^\Theta$ and the average value of $D_0^\Theta \bar{M}_w^{1/2}$ (=$1.309 \times 10^{-4}$ cm$^2$ s$^{-1}$). These are listed in Table I, and it is perhaps significant that the values given to two of the fractions ($\bar{M}_D = 1.25 \times 10^6$ and $3.16 \times 10^6$) are within 2% of estimates from an intrinsic viscosity study of the same samples in cyclohexane by Einaga, Miyaki, and Fujita[11] ($1.27 \times 10^6$ and $3.10 \times 10^6$). Furthermore, if values of $\bar{M}_D$ rather than $\bar{M}_w$ are used, the power law $D_0 \propto M^{-b}$ provides an excellent fit to the measured values of $D_0$ from 30 to 60 °C. The linear relation between log $D_0$ and log $\bar{M}_D$ is thus preserved with the exponent $b$ increasing from 0.490 at 30 °C to 0.510 at 40 °C and 0.523 at 50 °C and 0.530 at 60 °C.

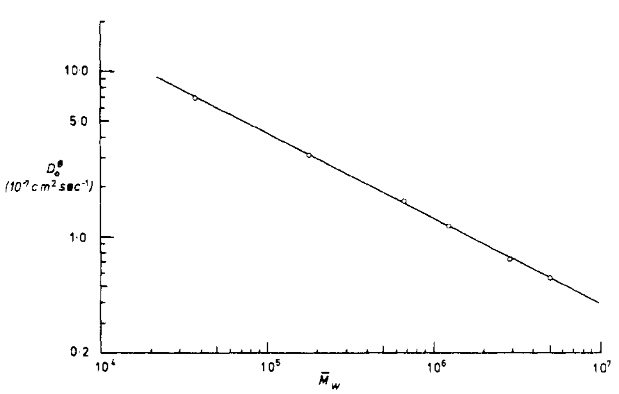

**Figure 3.** Variation of $D_0^\Theta$ with $\bar{M}_w$.

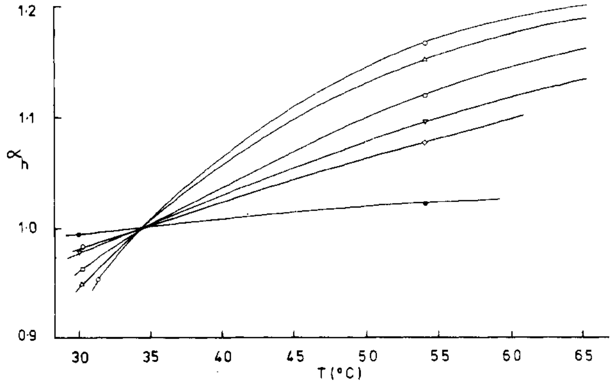

**Figure 4.** Variation of $\alpha_h$ with $T$: (○) $\bar{M}_D = 5.35 \times 10^6$; (△) 3.16 × 10$^6$; (□) 1.25 × 10$^6$; (▽) 630 × 10$^3$; (◇) 175 × 10$^3$; (●) 35.5 × 10$^3$.

Table II

Polynomial Coefficients for the Variation of $R_h$[a] with $T$

| $M_D$ | $10^3 r_1$ | $10^5 r_2$ | $10^7 r_3$ |
|---|---|---|---|
| 35.5 × 10³ | 1.34 | −2.48 | 7.72 |
| 175 × 10³ | 4.23 | −2.47 | 8.24 |
| 630 × 10³ | 5.08 | 1.67 | −13.12 |
| 1.25 × 10⁶ | 7.80 | −8.00 | 9.11 |
| 3.16 × 10⁶ | 10.77 | −15.66 | 1.60 |
| 5.35 × 10⁶ | 12.23 | −18.93 | −8.27 |

[a] $R_h = R_h^\Theta(1 + r_1 t + r_2 t^2 + r_3 t^3)$; $t = T - \Theta$.

Values of the hydrodynamic radius $R_h$ were calculated from the Stokes-Einstein relation $D = kT/6\pi\eta R_h$, where $k$ is Boltzmann's constant and $T$ is the absolute temperature; values of the solvent viscosity $\eta$ were taken from Landolt-Bornstein.[12] The temperature variation of $R_h$ is expressed in Table II as a polynomial expansion about $R_h^\Theta$ at the Θ point. The relation $R_h^\Theta = 0.224_5 \bar{M}_D^{0.500}$ Å is the best fit to the experimental points and agrees within 1–2% with previous investigations in cyclohexane by Jones and Caroline[10] and Gulari et al.[13] However, the values found by Bauer and Ullman[7] are about 5% greater for $\bar{M}_w < 10^6$.

The hydrodynamic expansion coefficient $\alpha_h$ (=$R_h/R_h^\Theta$) is shown in Figure 4 as a function of temperature for each molecular weight. The coil dimensions are seen to change smoothly through the Θ point, and the general pattern is in good qualitative agreement with the theoretical predictions of Sanchez[2] for $\alpha_g$ (=$R_g/R_g^\Theta$). In particular, the slope of the curves, $d\alpha_h/dT$, decreases with increasing $T$, with the lower molecular weights leveling off more quickly. The slope at the Θ point (the coefficient $r_1$ in Table II)

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varies as $\bar{M}_D^{0.42\pm0.04}$, compared with the theoretical variation of $M^{1/2}$.

Scaling law theory, with its descriptive subchain ("blob") model, is enjoying some popularity, but it does not appear to be helpful in interpreting the results of this work in the dilute regime: indeed, there is little support for it. The model supposes that at any temperature there is a characteristic length of polymer chain (blob) over which Gaussian statistics hold. The length is infinite at the Θ point and decreases away from it as a function of $\tau\ (=|T - \Theta|/\Theta)$. One consequence of this simple model, as predicted by Daoud and Jannink,[6] is the existence of a finite Θ region for finite chains. Thus, as shown explicitly by Akcasu and Han,[14] $d\alpha_h/dT$ should be zero at the Θ point, but this is not found to be the case. It appears that perturbation expansions for $\alpha_h$, such as first derived by Stockmayer and Albrecht,[15] offer a more convincing explanation.

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# Lignin. 18. Associative Effects among Organosolv Lignin Components[†]

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ABSTRACT: Organosolv lignins isolated under relatively mild conditions from angiosperms are composed of quite low molecular weight entities. The weight-average and number-average molecular weights of the preparations generally lie within the ranges $\bar{M}_w \sim 2000$–5000 and $\bar{M}_n \sim 800$–1200. Varying degrees of association between the constituent species are characteristic of these samples both in solution and in the solid state. Profiles described by eluting Organosolv lignins from dextran gels with 0.10 M aqueous NaOH represent effective molecular weight distributions which approach those of the discrete components. Under aqueous conditions of pH 13–14, dissociation of Organosolv lignin species occurs in dilute solutions ($\sim$0.5 g L$^{-1}$), while a marked tendency to associate prevails at higher concentrations ($\sim$100 g L$^{-1}$). The extent to which an individual component may participate in association depends appreciably upon the relative proportions of the other species present. Within the bounds of this constraint, the association–dissociation process is reversible and involves at least two kinetically distinguishable steps. Certain counterions and zwitterions reduce the degree of association between Organosolv lignin components. The mechanism may involve the blocking of proton uptake from solution which presumably accompanies the formation of higher molecular weight associated complexes. The relationship between $\bar{M}_w$ and $\bar{M}_n$ for Organosolv lignin samples during association implies that the process is dominated by preferential interactions between lower and higher molecular weight components.

## Introduction

Among the naturally occurring polymers, lignins are second only to cellulose in abundance. They are constituted from ($p$-hydroxyphenyl)propane units by eight different linkages, of which about 50% are $\beta$-0-4 ether structures.[1]

It has been suggested that the widespread disparities between reported molecular weight distributions of by-product lignins (other than the sulfonates) may be due in part to varying degrees of association in different solvents.[2] However, until quite recently,[3] only two exploratory studies seeking to establish that such phenomena may exist had been published.[4,5] On the other hand, association between lignin components can be further complicated by aggregation between the resulting complexes.[6–8]

Marked associative interactions among lignin components are conveniently documented by the striking variations between gel permeation chromatographic profiles observed with different eluants. The effective distributions found when nonaqueous solvents (or nonaqueous solvent–water mixtures in the absence of added salts) are employed exhibit a well-defined multimodal pattern of species extending to very high molecular weights, while those obtained with alkaline aqueous eluants generally consist of a broad envelope of components with distinguishable features apparent only in the lower molecular

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