

Viscosity study of polystyrene in cyclohexane

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The intrinsic viscosities of five different molecular weight polystyrenes in cyclohexane were measured at different temperatures. The temperatures cover three regions: above the θ point, at the θ point and below the θ point. The data were analysed with the theoretical framework on critical phenomena as a guide line. Although the collapsed region and the totally collapsed region vary with the range of molecular weight, the scaling law appears to be valid. There is a one-to-one correspondence of an observable in one regime to another regardless of the number of links. © 1997 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Intrinsic viscosity data of polystyrene in cyclohexane have been reported over several decades^{1–9}. The emphasis in most of the papers was usually on the study of chain configuration of the polymer molecule in solution above the θ temperature with the mean field theory¹ or two-parameter theory^{3,7} as the underlying guideline. The data reported in this paper cover the temperatures in all three regions: below θ , at θ and above θ , with emphasis on the range at θ and below θ . The underlying guideline, as was reported previously^{8,9}, is the scaling law. An experimental advantage now exists in the availability of samples with lower polydispersity compared with those used by our predecessors.

The temperature T and the number of links in a polymer molecule N were chosen as scaling variables, whereas the intrinsic viscosity $[\eta]$ as the observable which is directly or indirectly related to the position vector R .

EXPERIMENTAL

Polystyrene samples were obtained from Waters Associates. They were products of Toyo Soda with polydispersity ranging from 1.01 to 1.05 with exception of the molecular weight 2.0×10^7 sample for which the polydispersity was not given. Cyclohexane, 99.99% pure, was obtained from J. T. Baker Co. It was further distilled with a special setup of distilling apparatus. A stock solution was prepared by dissolving about 40 mg (accurately weighed) of polystyrene in 25.0 ml of solvent. A 10.0 ml sample was placed in the viscometer. After each measurement, the solution was diluted with 5.0 ml solvent until the final volume was 25.0 ml. The same pipette was used throughout the experiment. The concentration range for each sample is 0.016–0.040 g dl⁻¹. In mixing the polymer and solvent,

precaution of mechanical degradation was taken seriously by minimizing any disturbance, including swirling.

A Cannon-Ubbelohde capillary viscometer, model E 50-788, was used for the measurement. At least five flow times for each polymer solution were recorded. The viscometer containing the sample was immersed in a water bath for about 30 min before measurement to ensure that equilibrium was achieved. The temperature was controlled to within ± 0.05 – 0.01°C of the stated value. The viscosity apparatus was located in an isolated area of the laboratory for the purpose of minimizing turbulent air streams which often make flow time increase exponentially with temperature. The experimental points of reduced viscosity *versus* concentration are on a straight line which was extrapolated to zero concentration to obtain the intrinsic viscosity value.

Prior to using this particular viscometer, a four-bulb spiral capillary viscometer was tried. Viscosity shear-rate effect correction was estimated according to the method suggested by Schurz and Immergut¹⁰. The correction value was found to be negligibly low. For this reason, the viscosity values are reported without any correction for shear-rate effects⁵.

RESULTS

Table 1 lists the intrinsic viscosity values in the unit dl g⁻¹ of the five polystyrene samples in cyclohexane at different temperatures. For the low molecular weight polystyrene ($M 3.84 \times 10^4$), measurement can be carried out to as low as 7°C , whereas, for the high molecular weight sample ($M 2.06 \times 10^7$), measurement can be carried out only two degrees below the θ point (35°C). In Table 2 some of the literature values are listed to compare with our values. Within the experimental uncertainty, the agreement is generally satisfactory. For that reason, no analysis was performed on experimental data to obtain Huggins k' values for further comparison.

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Table 1 Intrinsic viscosity (dl g^{-1}) of polystyrene in cyclohexane

Temperature $^{\circ}\text{C}$	Molecular weight				
	3.79×10^4	3.55×10^5	1.09×10^6	3.84×10^6	2.06×10^7
7.0	0.136				
7.2	0.137				
8.0	0.139				
9.0	0.142				
10.0	0.144				
20.0	0.154				
21.0	0.159				
24.0		0.411			
24.2		0.415			
24.5		0.417			
25.0		0.423			
29.0			0.780		
29.2			0.785		
29.5			0.792		
30.0		0.480	0.806		
31.0				1.48	
31.2				1.49	
31.5				1.55	
32.0		0.503	0.876	1.61	
32.5			0.884	1.67	
33.0		0.509	0.896	1.69	
33.2					3.15
33.5			0.937	1.75	3.18
33.8					3.22
34.0		0.530	0.956	1.81	3.28
34.5			0.967	1.86	3.56
34.8				1.88	
35.0	0.162	0.535	0.968	1.89	3.88
36.0				1.90	
40.0	0.162	0.601	1.14	2.26	5.26
43.0	0.163	0.644	1.19	2.33	5.63

Table 2 Comparison of some viscosity data for polystyrene in cyclohexane

Molecular weight	Temperature ($^{\circ}\text{C}$)	$[\eta]$ (dl g^{-1})	
		This paper	Literature
3.55×10^5	35.0	0.535	
4.11×10^5	34.5		0.550 ⁵
1.05×10^6	34.8		0.86 ³
1.09×10^6	35.0	0.968	
1.30×10^6	34.5		0.990 ⁵
1.56×10^6	34.8		1.06 ²
3.20×10^6	34.2		1.22 ¹
	35.0		1.42 ²¹
	38.2		1.47 ¹
3.84×10^6	35.0	1.89	
2.06×10^7	35.0	3.88	
2.30×10^7	34.5		4.35 ⁵

In *Figure 1* we plot the data to observe if the Mark-Houwink equation holds

$$[\eta]_{\theta} = KM^{1/2}$$

Because all five points fall on a straight line with a slope 0.50, the law does hold. The K value is found to be

7.9×10^{-4} , which (for $10^4 < M < 10^7$) is smaller than the value 8.8×10^{-4} reported by Einaga *et al.*⁵ but higher than the value 7.5×10^{-4} (M range not given) in the 'Polymer Handbook'¹¹. The discrepancy may occur if the plot is in the form of $[\eta]/M^{1/2}$ versus $M^{1/2}$. However, we believe our K value is reasonably reliable within experimental error.

In *Figure 2* we grouped the $[\eta]$ values of the five polystyrene samples together for visual inspection. According to Cragg *et al.*¹², for a linear polystyrene with molecular weight 9.75×10^4 , there is a very small change in intrinsic viscosity over the temperature range between 25° and 65°C regardless of whether the polymer is dissolved in a good solvent such as benzene ($[\eta]$, 2.54–2.57) or dioxane ($[\eta]$, 2.11–2.14), or in a poor solvent such as cyclohexanone ($[\eta]$, 1.97–1.98). Only when the molecular weight exceeds one million (e.g. 1.3×10^6), does the intrinsic viscosity of linear polystyrene increase rapidly with temperature. Our observation, as expressed in *Figure 2*, is in agreement with this generalization. The curves in *Figure 2* may be divided into two regions, one above the θ point and the other below the θ point. In the region above the θ point, there is almost no change in the viscosity for the 3.79×10^4 molecular weight

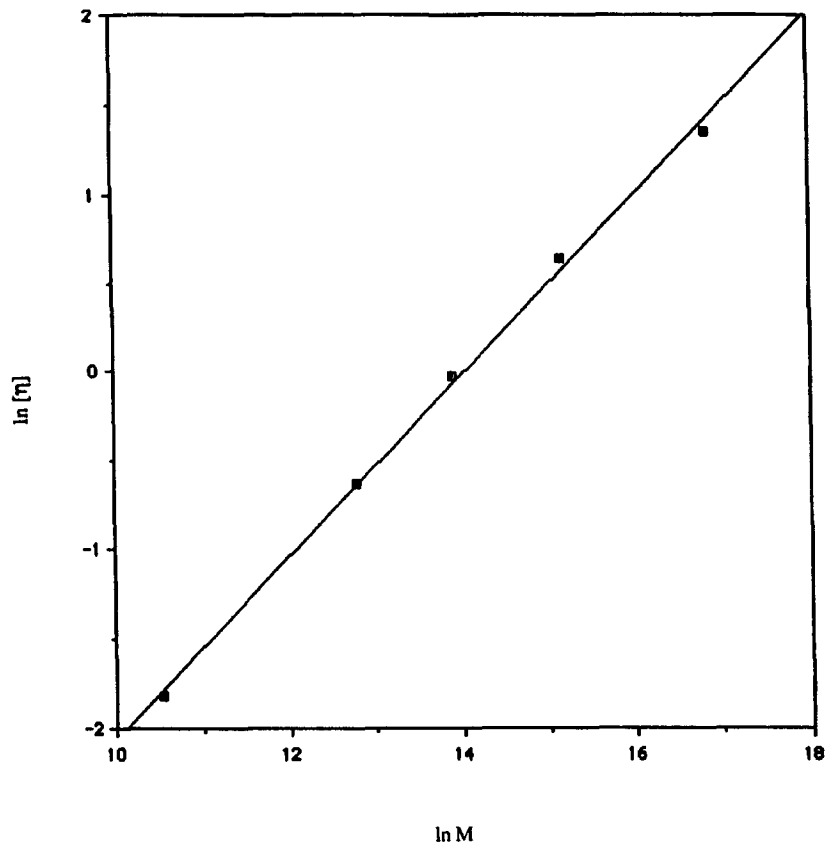


Figure 1 Plot of $\log [\eta]$ versus $\log M$ at $T = \theta$ for polystyrene in cyclohexane to test Mark-Houwink equation

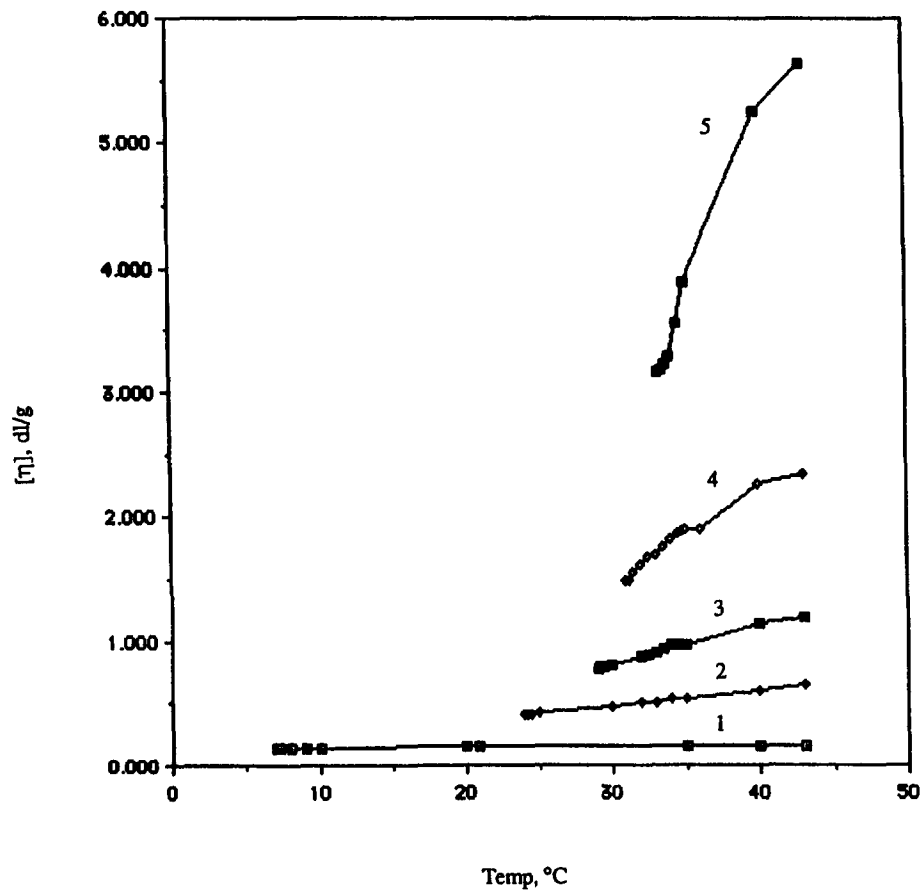


Figure 2 Intrinsic viscosity of polystyrene in cyclohexane as a function of temperature. Molecular weight: (1) 3.79×10^4 , (2) 3.55×10^5 , (3) 1.09×10^6 , (4) 3.84×10^6 , (5) 2.06×10^7

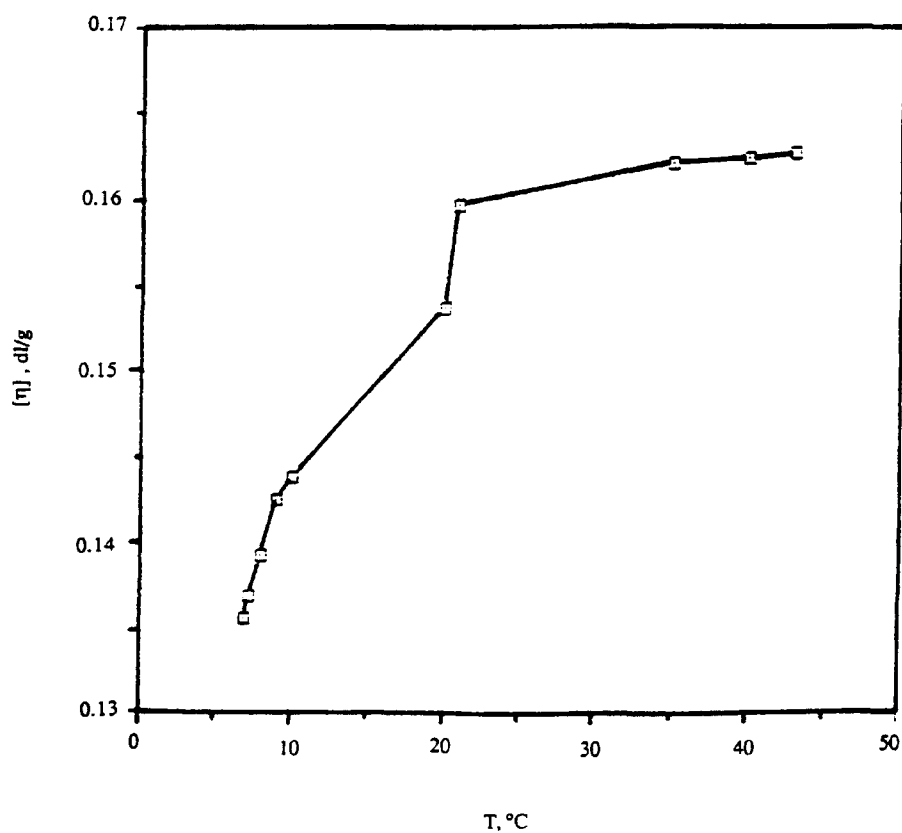


Figure 3 The intrinsic viscosities of a polystyrene in cyclohexane at temperatures below and above the θ point ($M = 3.79 \times 10^4$)

polystyrene. The change occurs only for the molecular weight sample 3.55×10^5 and above. The higher the molecular weight, the steeper is the curve. For the 2.06×10^7 molecular weight polystyrene, the asymptote

appears to be too remote to be reached. In the region where the temperature is below the θ point, almost in all cases the change is drastic. Even for the 3.84×10^4 molecular weight sample we see some change though it is

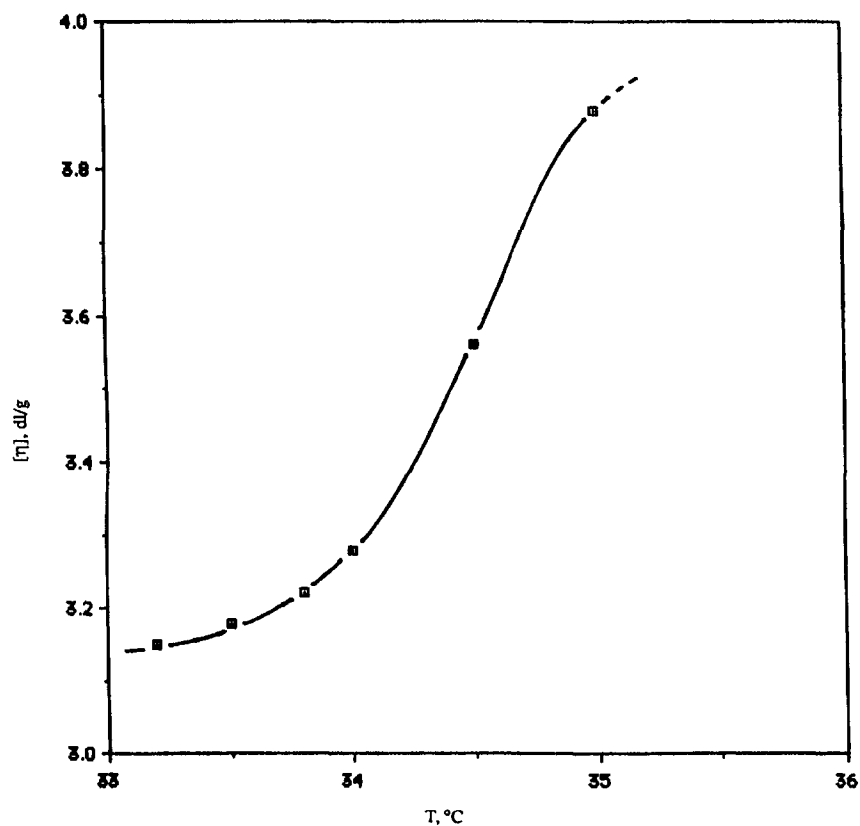


Figure 4 The intrinsic viscosities of a polystyrene in cyclohexane at temperatures below the θ point ($M = 2.06 \times 10^7$)

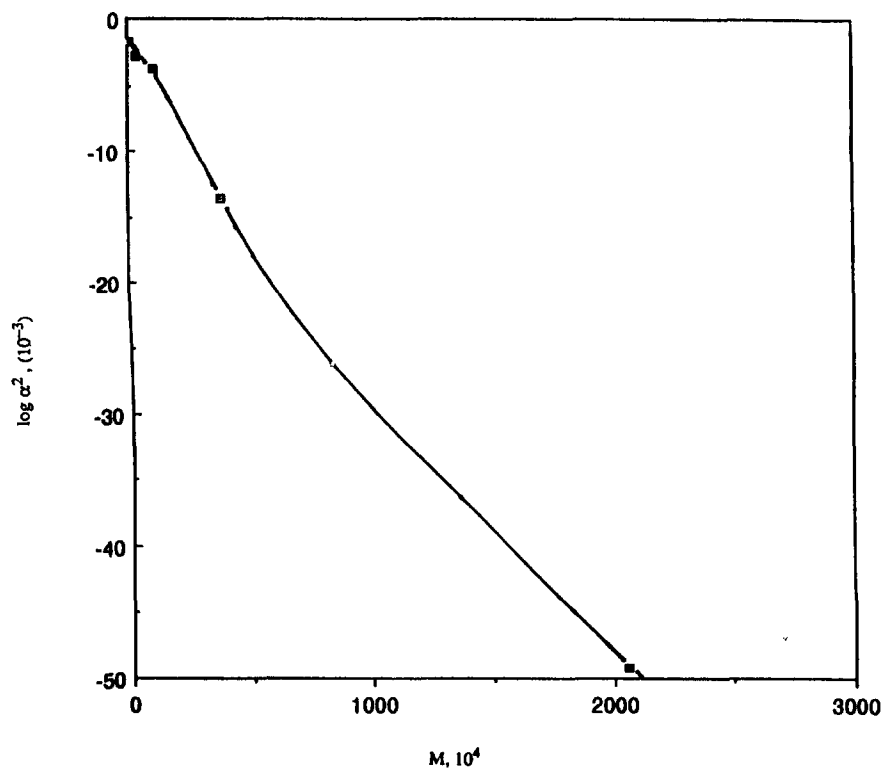


Figure 5 The contraction of polystyrene in cyclohexane as a function of molecular weight at 34.0°C

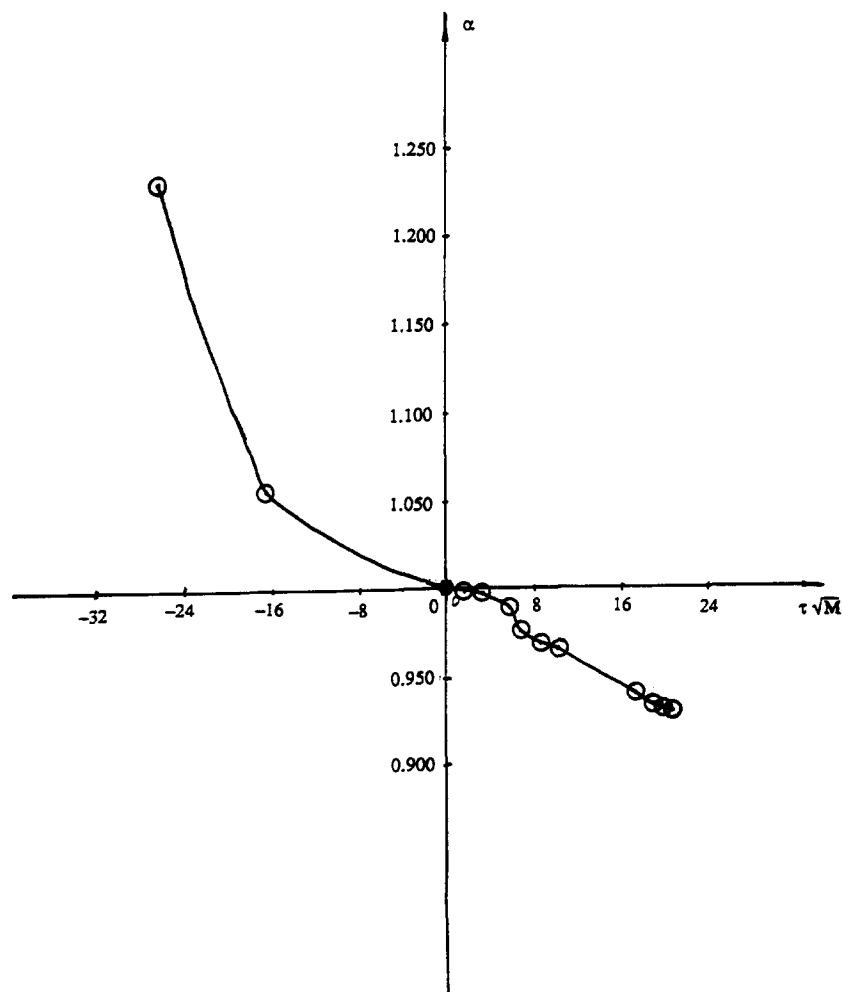


Figure 6 The plot of the expansion factor α versus $\tau\sqrt{M}$ for a polystyrene in cyclohexane ($M = 1.09 \times 10^6$)

obscured in the scale we used. The fact that there is a relatively slow change in all the cases at the temperature below 35°C indicates the existence of a collapsed state in each of the polymer solutions. We discuss this in the next section.

ANALYSIS

The renormalization group theory suggests that the coil-globule transition in the collapsed state follows the scaling law^{13,14}

$$R \sim N^{1/3} \tau \text{ for } T < \theta \text{ or } R \sim N^{1/3} \tau^{-1/3} \text{ for } \tau \sqrt{N} \gg 1$$

where R is the magnitude of position vector \vec{R} , τ is the reduced temperature defined as

$$\tau = \frac{\theta - T}{T}$$

The scaling law is also expressed in the equation

$$\alpha \sim \tau \sqrt{N}$$

where α is the expansion factor, which is considered as characterizing the configuration of a real chain¹⁵. In our analysis, we consider α and α_η (the viscosity expansion factor) as equivalents.

Coil-globule transition in general

Among the five samples, we first analysed the viscosity

behaviour as a function of the temperature for the lowest molecular weight, 3.79×10^4 , and for the highest molecular weight, 2.06×10^7 , respectively. Figure 3 shows the behaviour of the lowest molecular weight and Figure 4 the highest molecular weight. The viscosity behaviour of polystyrene ($M 3.79 \times 10^4$) in cyclohexane, as shown in Figure 3, is almost identical to the behaviour of polystyrene ($M 2.9 \times 10^4$) in deuterated cyclohexane, as reported in the small-angle neutron scattering measurement¹⁶. Both viscosity data and neutron scattering data indicate that at the temperatures between 20°C and the θ point, the change is very small, whereas in the range between 20°C and 11°C, an abrupt change occurs. For the 2.06×10^7 sample there is a similarity between our data and those obtained using the photon correlation spectroscopy technique¹⁷. The temperature dependence of the hydrodynamic radius of polystyrene, $M = 2.7 \times 10^7$, in cyclohexane for several concentrations of the polymer shows a curve similar to that shown in Figure 4. The curve falls steeply below the θ point. Thus, there is a drastic contrast in behaviour between the lowest molecular weight and the highest molecular weight in our samples.

We now compare the change in dimensions of the five polystyrene samples at the temperature 34°C, near the θ point. For intrinsic viscosity data the dimensional change is appropriately represented by the quantity α^2 which is defined as $\alpha^2 = \langle R^2 \rangle^2 / \langle R^2 \rangle_0^2$. The two

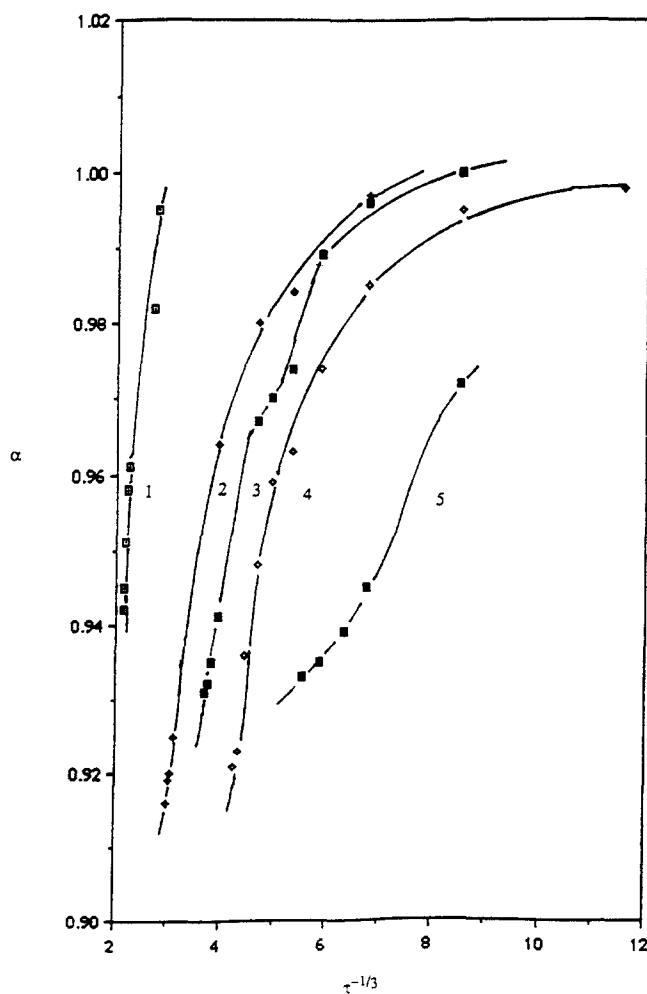


Figure 7 Inspection of the scaling law $\alpha \sim \tau^{-1/3}$ for different molecular weights: (1) 3.79×10^4 , (2) 3.55×10^5 , (3) 1.09×10^6 , (4) 3.84×10^6 , (5) 2.06×10^7

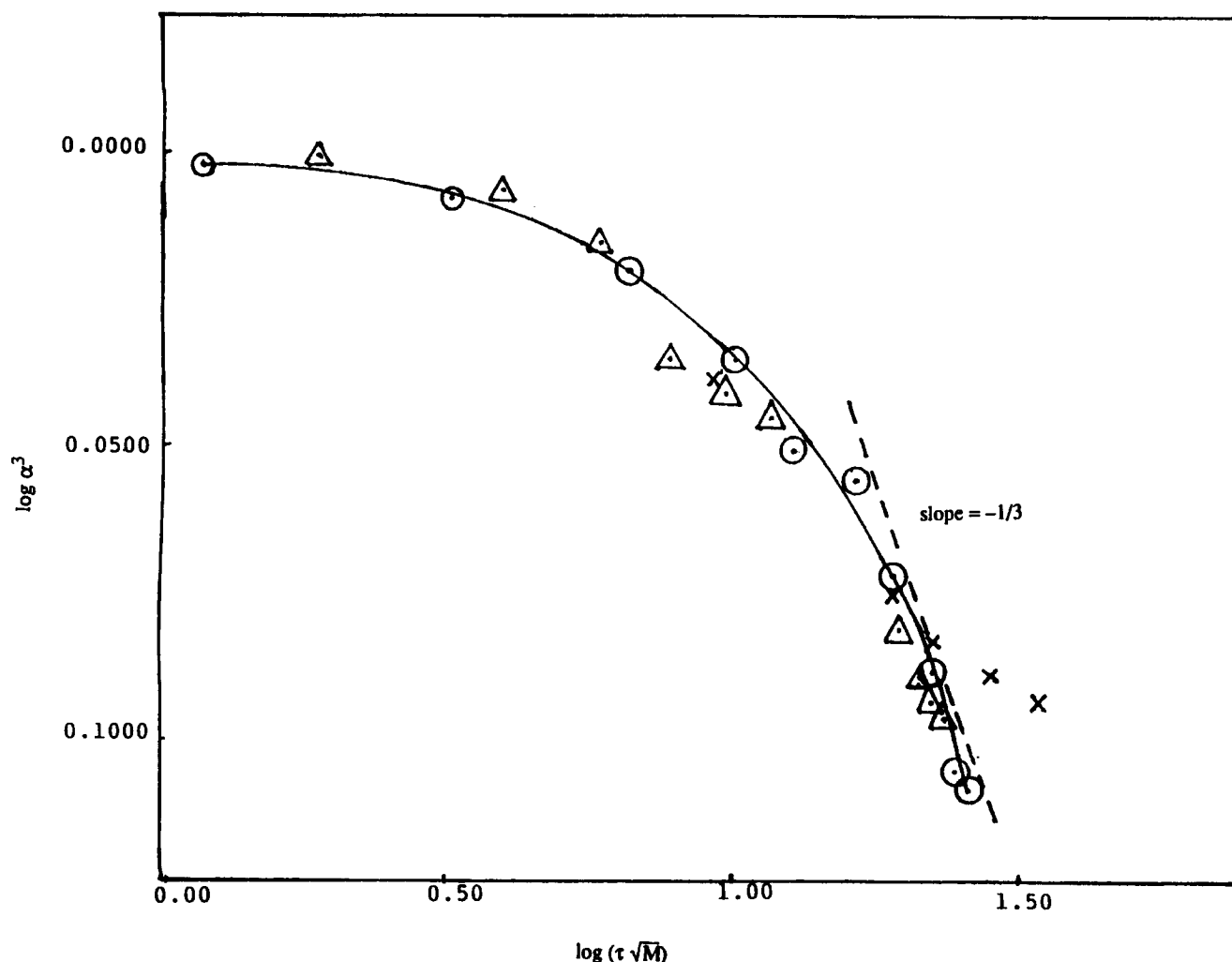


Figure 8 Log-log plot of $\alpha^3 = [\eta]/[\eta]$ versus $\tau\sqrt{M}$ for three molecular weights. Symbols: Δ , 1.09×10^6 ; \odot , 3.84×10^6 ; \times , 2.06×10^7 . The scales have been adjusted: \odot , taken as the master curve; Δ , x-bar shifted by a factor of -0.1 ; \times , x-bar shifted by a factor of -0.2 .

terms, $\langle R^2 \rangle$ and $\langle R^2 \rangle_0$ are the mean-square radii of gyration of linear flexible polymer in the perturbed and unperturbed state, respectively.

Figure 5, in which the values of $\log \alpha^2$ are plotted versus M , shows the drastic contraction of polystyrene in cyclohexane with increasing molecular weight. A similar curve was found for the contractions at 32°C , the temperature which is below the critical point.

Figures 3, 4 and 5 suggest that, for a high molecular weight polystyrene the coil-globule transition is smooth but rapid, whereas for a low molecular weight polystyrene the transition is abrupt but slow. Too sudden a change and too slow a change may lead to the conclusion that it would be unlikely for a single-globule state to exist before phase separation begins¹⁸. Our data further indicate that the hydrodynamic radius of the high molecular weight polystyrene (2.7×10^7) in cyclohexane depends not only on temperature but also on concentration¹⁷.

The θ domain

The θ domain is the region around the θ point in which the coil dimensions of a polymer chain remain constant over a range of temperature¹⁹. A prediction was made in that within this domain the variation of the expansion factor α with τ is linear for $\tau < \tau_c$, and nonlinear for $\tau > \tau_c$, where τ_c is the critical temperature.

The diffusion coefficient data obtained from photon correlation spectroscopy showed that in θ domain ($0 \leq \tau\sqrt{M} \leq 10$), α is a linear function and the linearity is symmetrical with respect to θ ⁸. In Figure 6 the viscosity data are plotted also in the form of α versus $\tau\sqrt{M}$ for molecular weight 1.09×10^6 . The shape of the curve in Figure 6 is similar to that with diffusion coefficient data⁸. According to Bauer and Ullman²⁰, the data of α versus $\tau\sqrt{M}$ should fall on the same master curve. The diffusion coefficient data plot showed that for two samples, $M = 1.71 \times 10^5$ and $M = 1.26 \times 10^6$, the experimental points do fall on the same master curve. Our viscosity data of five samples of different molecular weight, however, do not fall on the same master curve. For that reason we do not include the data of other samples in Figure 6. Furthermore, as shown in Figure 6, there is no symmetry of the curve with respect to θ and the θ domain on the linear portion of globule state is narrower. For diffusion coefficient data the range is $0 \leq |\tau\sqrt{M}| \leq 10$, whereas for viscosity data the range is $0 \leq |\tau\sqrt{M}| \leq 6$. However, in a separate plot for different samples (not all shown in this paper), the three different molecular weights (1.09×10^6 , 3.84×10^6 , 2.07×10^7) fall on the same range, $0 \leq |\tau\sqrt{M}| \leq 6$.

Figure 7 compares the θ domain in the form of α versus $\tau^{-1/3}$ according to the scaling law. It is clearly seen that only those three samples with molecular weights in the

range of 10^6 show the levelling-off of the curve as the temperature approaches the θ point. The θ domain is too long for the 3.84×10^4 molecular weight polystyrene and too short for the 2.06×10^7 molecular weight polystyrene to reach the asymptotic region. This observation was explained elsewhere²¹ that for a polymer with a relatively smaller molecular weight (3.84×10^4) a collapsed state may occur before the totally collapsed state, whereas for a polymer with a relatively larger molecular weight (2.06×10^7), a collapsed state may not occur before a totally collapsed state.

Coexistence curve

The coexistence curve is plotted in the form of α^3 versus $\tau\sqrt{M}$ (Figure 8) on log-log scale to compare with the data obtained by Perzynski *et al.*⁸. A slight difference in this plot is that whereas Perzynski *et al.*⁸ plotted the data directly on the log-log paper, this is a linear plot of $\log \alpha^3$ versus $\log \tau\sqrt{M}$. The two curves have similar shapes that both have two asymptotes. The asymptote at the temperature not too far from the θ point has a slow slope. This represents the region in which the polymer chain gradually collapses. The other asymptote at the temperatures farther from the θ point has a steep slope. This represents the region in which the polymer chain is totally collapsed²². In Figure 8 a dotted line is drawn next to the curve around $d \log \alpha^3 / d \log M$, the totally collapsed region. The slope is $-1/3$ in contrast to Perzynski's graph where the slope is -1 ; this appears to depend upon the position where the slope is drawn. The aim in this study was to make the experimental points close to the slope as many as possible in the totally collapsed region.

It should be pointed out, as indicated in the legend of Figure 8, that for the three different molecular weights the experimental points from viscosity data fall on the same master curve only after they are normalized. This appears to lend support to S. T. Sun's comments²³. They criticized the Nierlich experiment¹⁶ for overlooking the fact that the coil-globule transition is broadened as the value of N decreases. That is, the scaling law is observed only when the asymptotic condition is strictly met, namely, $N \rightarrow \infty$. We believe that our observation on three samples of different molecular weight falling on the same master curve only after normalization is perhaps more realistic.

Using the viscosity data analysis, the following conclusion may be drawn. Whether the coil-globule transition is smooth or abrupt depends on molecular weight. For polymers with high molecular weights, e.g.,

10^7 , the transition is smooth, because the contraction is drastic as the temperature is lowered below the θ point. For polymers with low molecular weight, e.g., 10^4 , the molecule contracts slowly below the θ point until a certain critical point is reached. The region of θ domain is small for large molecular weight polymer and large for small molecular weight polymer. Thus, if universality, as often stressed in the scaling concept of polymer chain²⁴, means strictly independent of molecular weight (i.e., material systems or regimes), then the condition of universality does not appear to have been met in viscosity measurement. Conversely, if universality means a one-to-one correspondence of observables with different material systems, our data appear to support reasonably well the prediction of the scaling law as demonstrated in Figure 8.

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