Macromolecules **1983**, *16*, 253-261

Temperature Dependence of the Hydrodynamic Radius of Flexible Coils in Solutions. 1. Vicinity of the Θ Point

Petar Vidakovič[†] and Francis Rondelez*

Physique de la Matière Condensée, Collège de France, 75231 Paris Cedex 05, France.
Received June 3, 1982

ABSTRACT: We have investigated by analytical ultracentrifugation the temperature dependence of the hydrodynamic radius R_H of polystyrene chains in two Θ solvents, cyclohexane (Θ = 35.4 °C) and cyclopentane (Θ = 23.0 °C). The measurements have been performed for $\Theta < T < \Theta + 20$ °C on high molecular weight fractions, $3.8 < 10^{-6}\bar{M}_w < 20.6$. The results thus cover an unusually broad range of N/N_τ, the reduced parameter of the now popular thermal blob theory. It is shown that the asymptotic regime $R_H \sim N^{3/5}(1 - \Theta/T)^{1/5}$ is only reached for N/N_τ values higher than 80. This explains the report by Adam and Delsanti (*J. Phys.* (*Paris*) **1980**, *41*, 713) of an apparent anomalous exponent $R_H \sim (T - \Theta)^{0.034}$ in the same system for $N/N_\tau < 2.7$. For N/N_τ values less than 70, the data can be fit with a semiempirical equation of the Flory type $\alpha_H{}^5 - \alpha_H{}^3 = 0.062(N/N_\tau)^{1/2}$, where $\alpha_H = R_H(T)/R_H(\Theta)$. A small, unexpected, dependence of α_H on molecular weight has also been observed in that latter N/N_τ range. This raises questions on the validity of universal functions and should be further checked. The recent modifications of the original thermal blob theory by Ackasu, Benmouna, and Alkhafaji and by François, Schwartz, and Weill seem to bring no significant improvement to the description of our data.

Introduction

The study of the progressive transition between the Gaussian and excluded volume behaviors of a linear polymer chain is a subject of great current interest. This is usually achieved, although not always, by varying the temperature of the solvent in which the chain has been dissolved. Starting from the Θ temperature of the polymer–solvent system, a crossover is expected to occur from an ideal to a swollen chain as the thermodynamic quality of the solvent gradually improves. In the framework of the scaling theory,[1] Daoud and Jannink[2] have calculated the temperature dependence of the square of the radius of gyration $\langle R_G{}^2\rangle$ for a chain of degree of polymerization N. In the so-called Θ domain (of width $\tau^* \sim N^{-1/2}$) $\langle R_G{}^2\rangle_\Theta \sim N$ while at much higher temperatures $\langle R_G{}^2\rangle \sim N^{6/5}\tau^{2/5}$. τ is the reduced temperature $\tau = 1 - \Theta/T$. These scaling laws coincide with the asymptotic results of the Flory mean-field two-parameter theory, $\alpha_G{}^5 - \alpha_G{}^3 \propto z$, where z is proportional to $N^{1/2}\tau$, and α_G is the expansion coefficient for the chain radius of gyration, $\alpha_G{}^2 = \langle R_G{}^2\rangle_T/\langle R_G{}^2\rangle_\Theta$.[3,4] However, they have the additional advantage of providing a more unified description of polymer statistics. In the scaling law approach, the chain is pictured as a succession of Gaussian blobs, each made of N_τ monomers and with complete excluded volume interaction between the blobs. Close to the Θ temperature, $N/N_\tau < 1$ and the chain obeys purely Gaussian statistics. Far above Θ, an asymptotic regime is reached where the chain is composed of a large number of blobs and the local Gaussian character of the chain is completely lost. The extension of the thermal blob theory to the transition region between these two limiting behaviors has been recently proposed by several authors for both the static[5-7] and hydrodynamic variables.[6,7] Weill and des Cloizeaux have, in addition, pointed out very clearly the difficulty of reaching the predicted asymptotic regime with hydrodynamic variables.[7] Since the spatial crossover within a polymer chain has a much greater influence on hydrodynamic than on static properties, the exponent of the power law for the hydrodynamic radius R_H will converge much more slowly to its critical limiting value $R_H \sim N^{3/5}$ than the static radius of gyration R_G. Very high molecular weight samples will therefore be required to get significative results. Such a difference between static and dynamic properties has already been realized by Stockmayer and Albrecht,[8] as early as 1958, in their calculation of the hydrodynamic expansion factor.

In the static case, the predictions of the thermal blob theory have been substantiated by the direct small-angle neutron scattering observation of a change of statistics for portions of a chain below and above N_τ.[5] Ackasu and Han[6] have also performed a compilation of static light scattering data for the expansion factor of the radius of gyration α_G which seems consistent with the blob hypothesis. However, the experimental data can also be well fitted, if not better, with several approximate theoretical expressions obtained from a direct calculation of the statistical dimensions of a randomly coiled chain with volume exclusion.[9]

In that respect, it is very interesting to check experimentally the predictions of the thermal blob theory in the dynamic case. Indeed, it is the only theory that calculates the expansion factor α_H of the hydrodynamic radius of a single chain over a large range of N/N_τ. The well-known Stockmayer–Albrecht result is only valid for small excluded volume.[8] On the other hand, the extension of the α^5-type equation of Flory to α_H has only been proposed on a semiempirical basis.[10,11] Such a check has been tried very early by Ackasu and Han.[6] Unfortunately, there was only a very limited amount of data at the time and a definite conclusion was difficult to reach. Consequently the need for more extensive data on various polymeric systems has been called upon several times.[9,12]

At least three different experimental groups[13-15] have recently performed light scattering measurements of the temperature dependence of the chain hydrodynamic radius in the vicinity of Θ points. $R_H(T)$ was deduced from the translational diffusion coefficient extrapolated to infinite dilution $D_0 = kT/6\pi\eta_s R_H$, where η_s is the solvent viscosity. This technique is known to generally yield accurate data. However, the necessity of working with large polymer molecular weights makes it extremely cumbersome to apply. Indeed, stray light problems always limit the range of scattering wavevectors accessible to experiments in the forward geometry. As a consequence, contributions from dynamic internal modes become difficult to avoid.[15] This explains why only one data point has been reported with

---

[†] Permanent address: Prirodno-Matematički Fakultet, Odsek za Fizičke i Meteorološke Nauke, 11001 Belgrade, Yougoslavie.

0024-9297/83/2216-0253$01.50/0

a 11.7×10^6 molecular weight sample.[13] All other experiments have been performed in the 10^5–10^6 molecular weight range.[14,15]

In comparison, the ultracentrifugation technique is much better adapted to the problem addressed here. It is thus surprising that very few such measurements of the temperature dependence of the sedimentation coefficient of polymer chains have been reported in the vicinity of Θ points. Nyström, Roots, and Bergman[16] have worked mainly with low molecular weight materials ($\bar{M}_w = 1.1 \times 10^5$ and 3.9×10^5) while Mulderije[11] has only investigated a very narrow range of temperature, $\Theta < T < \Theta + 3$ °C, for one 1.8×10^6 molecular weight sample.

Consequently, we have started a detailed investigation by ultracentrifugation of the temperature dependence of the chain hydrodynamic radius in a large interval from the Θ temperature. We present here data obtained on high molecular weight polystyrene fractions ($3.8 \times 10^6 < \bar{M}_w < 20.6 \times 10^6$) dissolved in two solvents with Θ points around room temperature, cyclohexane and cyclopentane.

We begin by briefly recalling the recent thermal blob theory. Then we describe our sample preparation and experimental setup. The results are presented in a separate part, together with an extensive discussion on the determination of the true Θ temperatures in our polymer solutions. Last we compare our data with the current existing theories: the first-order perturbation calculations of Stockmayer and Albrecht, the hydrodynamic α^5-type equation, and the thermal blob theory and its modified versions.

Theoretical Background

The thermal blob theory permits the calculation of both the equilibrium and dynamic properties of a polymer chain in a self-consistent manner. In this approach, the mean-square distance between two segments i and j along the chain is modeled as

$$\langle |R_n|^2 \rangle = l^2 n, \qquad n \leq N_\tau$$

$$\langle |R_n|^2 \rangle = l^2 N_\tau^{1-2\nu} n^{2\nu}, \qquad n \geq N_\tau$$

where n is a running index corresponding to the chemical distance between i and j, l is the statistical length, and N_τ is a temperature-dependent cutoff to separate Gaussian and excluded volume regimes. The crucial point in these expressions is the introduction of a step change in the statistics of portions of the chain below and above N_τ. It constitutes an extension at any chemical distance $n \leq N$ of a concept originally introduced by Flory[3] for the whole chain in a good solvent. It is indeed well-known that the excluded volume interaction v will swell the coil only if

$$v/l^3 \gg N^{-1/2}$$

By transposition, it is possible to define at any given reduced temperature $\tau = (T - \Theta)/T$, a characteristic chemical distance N_τ such that all distances $\langle |R_n|^2 \rangle$ ($n > N_\tau$) are swollen and all distances $\langle |R_n|^2 \rangle$ ($n < N_\tau$) are unperturbed. N_τ is proportional to $(l^3/v)^2$. Since the binary cluster integral v is usually approximated by $v = v_\infty \tau$ in the vicinity of the Θ temperature, this implies that N_τ depends on temperature as $N_\tau \sim \tau^{-2}$. The proportionality factor depends on the kind of polymer and solvent but not on the chain molecular weight. Unfortunately, it cannot be calculated from first principles and has to be determined from a direct comparison between theory and experiment.

Several authors[5-7] have calculated the complete temperature and molecular weight dependences of the chain radius of gyration R_G for $T > \Theta$ and $N/N_\tau \geq 1$. They all obtain the same expression for α_G, namely

$$\alpha_G{}^2 = \frac{R_G{}^2(T)}{R_G{}^2(\Theta)} = \\ x^2(3 - 2x) + 6x^{1-2\nu}\left(\frac{1 - x^{2\nu+1}}{2\nu + 1} - \frac{1 - x^{2(\nu+1)}}{2(\nu + 1)}\right) \tag{1}$$

where $x \equiv N_\tau/N$.

In the asymptotic limit where the number of subchains (or thermal blobs) is very high ($N/N_\tau \gg 1$), one reaches the simple expression first derived by Daoud and Jannink[2]

$$\begin{aligned}\alpha_G &= \left(\frac{3}{(2\nu + 1)(\nu + 1)}\right)^{1/2}\left(\frac{N}{N_\tau}\right)^{\nu-0.5} \\ &= 0.923(N/N_\tau)^{0.1} \qquad (\nu = 3/5)\end{aligned} \tag{2}$$

Ackasu and Han[6] and Weill and des Cloizeaux[7] have extended this kind of calculation to the hydrodynamic radius R_H, using the Kirkwood–Riseman approach. They obtain the hydrodynamic expansion factor $\alpha_H = R_H(T)/R_H(\Theta)$ as

$$\alpha_H = \frac{4}{x^{1/2}}\left(2(3 - x) + 3\left(\frac{x^{\nu-1} - 1}{1 - \nu} - \frac{x^{\nu-1} - x}{2 - \nu}\right)\right)^{-1} \tag{3}$$

The asymptotic behavior for large N/N_τ is

$$\begin{aligned}\alpha_H &= 4/3(1 - \nu)(2 - \nu)(N/N_\tau)^{\nu-0.5} \\ &= 0.747(N/N_\tau)^{0.1} \qquad (\nu = 3/5)\end{aligned} \tag{4}$$

It remains that these expressions for α_G and α_H cannot be compared directly to experiments since the reduced variable N/N_τ is only known to a proportionality constant $N/N_\tau = B\tau^2$. Ackasu and Han[6] have proposed to derive B by matching the theoretical expression for α_G with the existing experimental data for the radius of gyration at several temperatures. For the polystyrene–cyclohexane system, they obtain

$$N/N_\tau = \frac{\bar{M}_w}{104}\,\frac{\tau^2}{4}$$

Once the value of this adjustable parameter is known, all other dynamic and static parameters can be calculated without any free parameter.

It should be noted that this theory, albeit extremely simple and elegant, cannot give a good description in the transition region centered around $N/N_\tau \sim 1$. The assumption of an abrupt change of statistics is clearly very crude. Several attempts[12,17] have therefore been made to repeat the calculations with a more progressive crossover. However, the mathematical description of the gradual transition between Gaussian and excluded volume statistics is always arbitrary. This introduces extra parameters that make the theory much more model dependent and less universal.[18] We will not write here the corresponding analytical expression for α_H and α_G. Rather we will bluntly use their numerical calculations in the Discussion.

Experimental Section

Materials and Sample Preparation. Narrow molecular weight fractions of polystyrene were obtained from Toyo Soda Co., Japan, and used as received. Their specifications are listed in Table I. Two solvents for polystyrene, with Θ points around room temperature, were selected, namely, cyclopentane and cyclohexane. They were purchased from two different chemical manufacturers, Merck and Aldrich, in the best quality availble (spectrophotometric grade) and used without further purification. All solutions were prepared by dispersing the polystyrene grain by grain into the solvents kept at an elevated temperature. The

Table I
Characteristics of the Narrow-Fraction Polystyrenes

grade	lot no.	nominal mol wt	$\overline{M}_w/\overline{M}_n$
F-2000	TS-33	2060×10^4	
F-850	TS-31	842×10^4	1.17
F-700	TS-32	677×10^4	1.14
F-450	TS-12	4.48×10^6	1.14
F-380	TS-34	384×10^4	1.05
F-126	TS-8	126×10^4	1.05
F-40	TS-6	42.2×10^4	1.04
F-10	TS-20	1.07×10^5	1.01

final working concentrations were always so low ($c \leq 10^{-4}$ g cm^{-3}) that it was not found necessary, contrary to previous experiments,[19] to use an intermediate lyophilization step in benzene in order to achieve good dissolution. The solutions were allowed to equilibrate in the dark between 1 and 2 weeks and were gently shaken by hand only occasionally to avoid possible mechanical degradation. They were then introduced into the sedimentation cell using a syringe equipped with a hypodermic needle.

Sedimentation System. A Spinco Model E analytical ultracentrifuge was used in conjunction with a schlieren optical system. The aluminum cell was a 4° single sector, 12 mm thick and 15 mm long. The displacement of the solvent–solution boundary during the sedimentation run was recorded on a photographic plate and later analyzed with a profile projector. Between 14 and 24 successive pictures were generally taken during which the boundary was allowed to move over the longest possible distance within the cell ($\simeq$10 mm) to improve the measuring accuracy. Precision of the readings was generally better than 1%.

The measured peak positions were fed into a microcomputer (Hewlett-Packard HP 9825) and analyzed using least-squares fitting procedures with both a linear and a quadratic function of the elapsed time t. We have already discussed extensively in ref 19 how the latter fit allows one to take into account (i) the progressive dilution of the solution due to the sector shape of the cell and (ii) the hydrostatic pressure exerted by the column of pure solvent which is gradually formed between the meniscus and the solvent–solution boundary. Its statistical quality is therefore far superior and it was always used in the present experiments.

Most sedimentation runs were performed at rotor speeds of 26 000 and 30 000 rpm. However, speeds up to 46 000 rpm were sometimes used to reduce the spurious broadening of the schlieren peak by diffusion, especially for the lowest molecular weight samples.

The temperature was controlled to ±0.1 °C by an RTIC unit. The rotor was preheated to 43 °C externally and slowly brought to its final temperature after positioning of the sample cell. The Θ temperatures of the polystyrene solutions were found to be 35.4 °C for cyclohexane from Merck, 23 °C for cyclopentane from Merck, and more than 25 °C for cyclopentane from Aldrich. Our criterion was to measure the sedimentation coefficients at maximum dilution S_0 over a large range of molecular weights ($M = 10^5$–2×10^7) and to plot the data on logarithmic scales. At the Θ temperature, all the points should fall on a straight line obeying the relation $S_0 = CM^{0.50}$, where C is a numerical coefficient characteristic of the polymer–solvent system. This procedure will be described in detail in the Results.

Results

We have first performed preliminary experiments to precisely assess the Θ temperatures of our actual polymer solutions. Indeed, for a given polymer–solvent system, there exist large variations between the Θ values reported in the literature. Most experimenters[3] use osmotic pressure

Table II
Sedimentation Velocity Data for Polystyrene in Cyclopentane and Cyclohexane

$10^{-6}\overline{M}_w$	T, K	$10^{13}S_\theta$, s	Q[a]	R_H, Å	α_H	N/N_τ[b]	$10^{-6}\overline{M}_w$	T, K	$10^{13}S_0$, s	Q[a]	R_H,Å	α_H	N/N_τ[b]
Cyclopentane (Θ = 23 °C)													
20.6	296.2	130.01		1033.5	1.00	0	6.77	296.2	74.225		595.0	1.000	0
	298.4	129.06		1067.0	1.032	2.69		301.5	73.67		635.6	1.068	5.03
	299.2	126.57		1097.6	1.062	4.98		303.7	72.52		661.1	1.111	9.93
	300.5	128.29		1098.5	1.063	10.14		307.0	74.82	⩾1	663.6	1.115	20.15
	301.4	131.60		1081.5	1.050	15.02		308.6	76.78		657.5	1.105	26.28
	302.2	125.03		1148.2	1.111	19.53		311.7	76.74		679.2	1.142	40.26
	303.6	127.3	⩾1	1144.9	1.108	29.43		313.2	77.57		682.2	1.147	47.96
	308.2	128.06		1194.7	1.155	75.09		313.9	77.92		684.0	1.150	51.76
	309.2	125.01		1236.6	1.197	87.56		314.8	77.85	⩾1	690.9	1.161	57.00
	311.3	125.49		1258.6	1.218	116.55							
	313.2	127.31		1264.8	1.224	145.94	4.48	296.2	64.06		470.7	1.000	0
	314.2	123.43		1317.7	1.275	162.57		303.7	65.52		484.3	1.062	6.57
	315.2	124.49		1319.6	1.277	179.99		306.2	64.67		503.8	1.105	11.49
								308.2	66.74		498.5	1.093	16.33
8.42	296.2	82.74		663.7	1.000	0		310.2	65.41	⩾1	519.3	1.139	21.94
	299.2	82.39		689.2	1.038	2.04		312.9	67.46		517.5	1.135	30.69
	300.5	82.49		698.3	1.052	4.15		314.2	68.34		517.6	1.135	35.36
	301.4	82.15		708.5	1.068	6.14		315.2	68.72		519.9	1.140	39.14
	302.2	82.50		711.3	1.072	7.98							
	303.6	81.49	⩾1	731.0	1.101	12.03	3.84	296.2	58.21		430.3	1.000	0
	305.2	83.22		728.1	1.097	17.61		306.2	60.69		460.2	1.070	9.85
	308.2	84.13		743.3	1.120	30.69		310.2	61.72	⩾1	471.7	1.096	18.81
	311.3	84.32		765.7	1.153	47.64		314.2	63.21		479.7	1.115	30.31
	313.2	85.60		768.9	1.158	59.65							
	314.2	84.55		786.3	1.185	66.45							
	315.2	86.07		780.2	1.175	73.57							
Cyclohexane (Θ = 35.4 °C)													
20.6	308.6	64.36		1048.3	1.000	0	8.42	308.6	41.19		669.3	1.000	0
	309.6	64.75		1058.1	1.010	0.52		309.6	40.79		686.3	1.025	0.21
	311.0	63.19		1.108.1	1.057	2.95		312.0	40.70	⩾1	713.7	1.066	2.40
	312.0	61.75	⩾1	1151.2	1.098	5.88							
							6.77	308.6	38.02		583.0	1.000	0
								311.7	38.06	⩾1	610.8	1.048	1.61

[a] Q is the fit quality parameter defined by Tournarie (Tournarie, M. *J. Phys.* (*Paris*) **1969**, *30*, 47). Values larger than 1 disprove possible systematic deviations between the experimental data points and the theoretical curve. [b] N/N_τ was calculated from $N/N_\tau = \overline{M}_w\tau^2/416$, with $\tau = (T - \Theta)/T$ according to Akcasu and Han (Akcasu, A. Z.; Han, C. C. *Macromolecules* **1979**, *12*, 276).

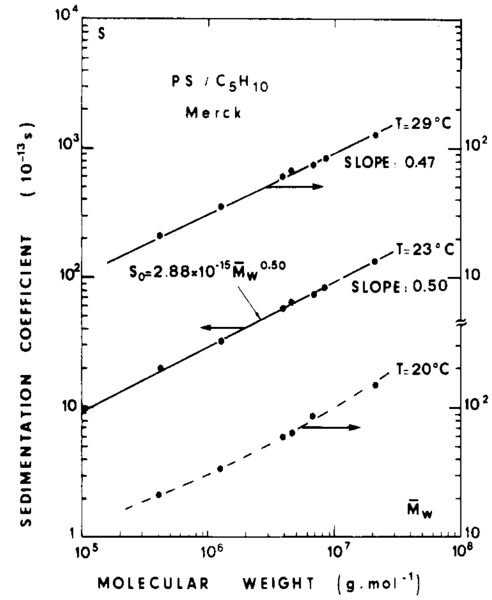

Figure 1. Sedimentation coefficient S as a function of polymer molecular weight $\bar{M}_w$ in logarithmic scales. Polystyrene–cyclopentane solutions are all at $c = 10^{-4}$ g cm^{-3}. Cyclopentane was obtained from Merck.

or light scattering techniques to follow the temperature dependence of the second virial coefficient $A_2(T)$. At $T = \Theta$, $A_2 \equiv 0$. Another approach is to measure at several temperatures the molecular weight dependence of the intrinsic viscosity $[\eta]$ or of the sedimentation coefficient extrapolated at infinite dilution S_0. At the Θ temperature, both $[\eta]$ and S_0 should be proportional to M^α with $\alpha = 0.50$. It is this latter method that has been used here.

For polystyrene in cyclohexane, we have already shown that $S_0 = 1.50 \times 10^{-15}M^{0.50}$ at 35.4 °C[19] and we have therefore adopted this temperature as the Θ temperature in our solutions. Although a similar value has been used by many others,[20-22] it is noteworthy that different temperatures of 34.5[15,23] and 35 °C[14,24] have also been reported. It is generally believed that these variations stem from differences in the water impurity content of the cyclohexane used. Mulderije[11] has reported a 0.01% water concentration for the cyclohexane from Merck.

For polystyrene in cyclopentane, we have performed a series of sedimentation runs over an extended range of molecular weights at different temperatures around the presumed Θ point. The results are shown in Figures 1 and 2 on logarithmic scales for cyclopentane obtained from our two different chemical sources. Only in the case of the Merck product and at a temperature of 23.0 °C do we obtain a straight-line plot over the full range of molecular weights and with the correct 0.50 slope. A least-squres fit yields

$$S_0 = (2.88 \pm 0.5) \times 10^{-15}\bar{M}_w^{0.50\pm0.010}$$

Therefore we will select 23.0 °C as the Θ temperature for this system. At temperatures slightly above or below, no straight lines with the correct slope values of 0.50 can be made to fit our data points. For instance, at 29 °C and with the Merck cyclopentane, the slope has a value of 0.47. With the Aldrich cyclopentane, the Θ temperature is probably higher than 25 °C, as can be noted in Figure 2, where no straight lines can be drawn at 22.7, 23.8, and 24.7 °C. Such a large difference between two solvents otherwise apparently identical should come as no surprise since minute contaminations or impurities can strongly affect the solvent thermodynamic quality. Wolf and Geerissen[25] have observed that the demixing temperature of polystyrene in cyclopentane changes by several degrees between solvents of different origins (Merck and Fluka in their case). Merck does not declare the nature of the remaining impurities while Fluka mentions 2,2-dimethylbutane. In all the following, we have used polystyrene–cyclopentane solutions from Merck since it has the lowest Θ temperature and should therefore be considered to be of a slightly better quality than the cyclopentane from Aldrich. An even lower Θ temperature of 20 °C has been reported by Nyström, Roots, and Bergman[16] using the same sedimentation technique as here. However, they have worked on too limited a range of molecular weights (2×10^4–9×10^5). When we combine their data with ours at 20 °C, we obtain $S_0 = 2.3 \times 10^{-15}\bar{M}_w^{0.517}$ for $2 \times 10^4 < \bar{M}_w < 2 \times 10^7$. The measured exponent value of 0.517 seems too large for the solution to be considered at its Θ temperature at 20 °C. As a supplementary check, we have measured the demixing temperature of our system using the cloud point method. The turbidity of solutions put in a 5 mm light path optical cuvette was monitored at 300 and 280 nm while the temperature was continuously decreased. As the demixing temperature is approached from above, the incident light

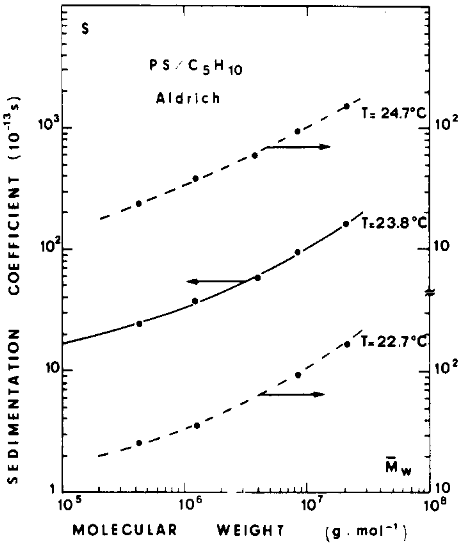

Figure 2. Same as Figure 1 except for the chemical source of the solvent. Cyclopentane used here is from Aldrich.

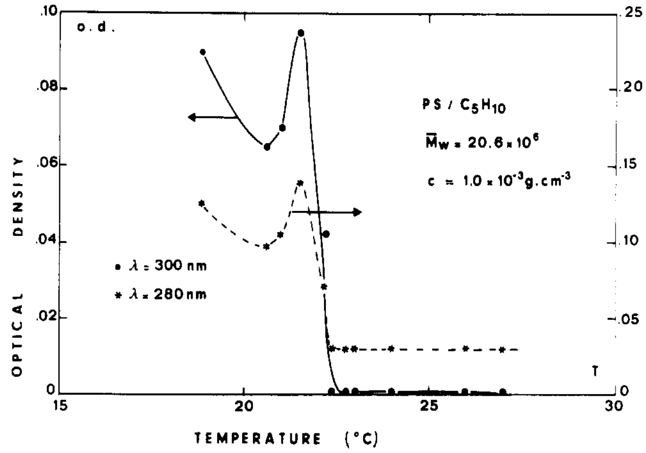

Figure 3. Variation of the optical density of a polystyrene–cyclopentane solution as the temperature is swept from above Θ to below T_d. T_d is the demixing temperature at this particular concentration and can be deduced from the onset of the sharp rise in the optical density curve. $T_d = 22.4 \pm 0.1$ °C. Two different optical wavelengths of 280 and 300 nm have been used for monitoring.

gets scattered by the large aggregates that start to form in the solution.

Figure 3 shows a typical turbidity vs. temperature plot obtained for a 20.6 × 10^6 polystyrene sample. An initial concentration of 1.0 × 10^{-3} g cm^{-3} was chosen so to be in the vicinity of the maximum of the coexistence curve (UCST point).[2] Under such conditions, the demixing temperature should lie just below the Θ temperature (the two temperatures are identical for infinite molecular weight polymer samples). Temperature was swept from 27 °C down to 18 °C at a rate of 1 °C h^{-1} except between 23 and 21 °C, where it was reduced to 0.2 °C h^{-1}. A sharp optical density increase is observed at a well-defined temperature, independent of the monitoring wavelength. It is followed by an optical density decrease at lower temperatures as the large polymer aggregates start to sediment toward the bottom of the cell. This temperature was therefore taken as the demixing temperature T_d of the polymer-solvent solution. Here, T_d is found to 22.4 ± 0.1 °C. Such a value is entirely consistent with a Θ temperature of 23 °C in our polystyrene-cyclopentane (Merck) solutions.

Having accurately determined the Θ points for our solutions, we then measured the sedimentation coefficients of polystyrene chains as a function of temperature and molecular weight. The experiments have been performed exclusively above the Θ temperature. The maximum temperature attainable was 43 °C in all cases, as imposed by our temperature regulation system. The concentrations used were always less than 10^{-4} g cm^{-3}. This was sufficient to ensure that at all molecular weights, the solutions were dilute enough so the chains can be assumed to behave independently.[19] The sedimentation coefficients measured were then assimilated to the sedimentation coefficients at infinite dilution S_0. S_0 is simply related to the hydrodynamic radius R_H of the polymer chain by the Svedberg formula

$$S_0 = \frac{\bar{M}_w(1 - \bar{v}\rho)}{R_H(6\pi\eta_s)}$$

where $\bar{v}$ is the partial specific volume of the polymer and ρ and η_s are the solvent density and viscosity, respectively. The complete numerical results for cyclohexane and cyclopentane solutions are given in table II. We have assumed in the calculations that $\bar{v}$ and ρ are temperature independent, which is certainly correct over the limited temperature range explored.[11,26] Here $\bar{v}$ has been taken to be 0.934[27a] and 0.926[27b] for polystyrene in cyclohexane and cyclopentane, respectively. ρ is given in the tables to be 0.7640 for cyclohexane at 35 °C and 0.7624 for cyclopentane at 23 °C.[26] The temperature variation of the solvent viscosity, which is by no means negligible, has been taken from the literature.[26] For cyclohexane

$$\eta_s(T) = 6.1739 \times 10^{-5} \exp(1.4816 \times 10^3/T)$$

while, for cyclopentane

$$\eta_s(T) = 1.507 \times 10^{-4} \exp(0.9864 \times 10^3/T)$$

where T is expressed in kelvin and η_s in poise units.

Since we are not so much interested in the absolute R_H values than in their temperature variations, we have always directly plotted in the figures the hydrodynamic expansion factor $\alpha_H(T)$.

$$\alpha_H(T) = R_H(T)/R_H(\Theta) \cong (\eta_s(\Theta)S_0(T))/(\eta_s(T)S_0(\Theta))$$

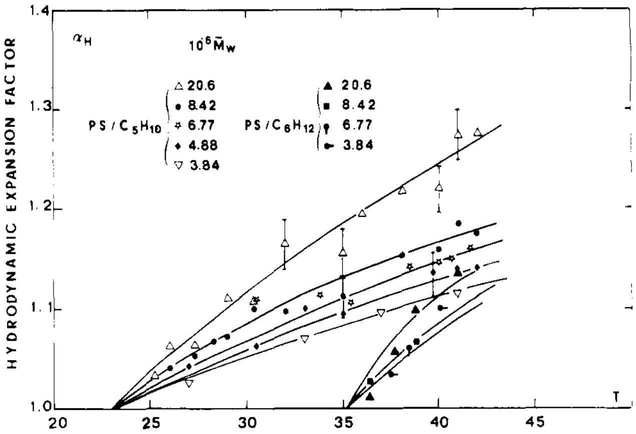

Figure 4. Hydrodynamic expansion factor $\alpha_H = R_H(T)/R_H(\Theta)$ as a function of temperature for dilute polystyrene coils in two different solvents, cyclopentane (C_5H_{10}) and cyclohexane (C_6H_{12}). The solid lines have no physical meaning and are just a guide to the eye to clarify data obtained for five different monodisperse fractions of high molecular weight.

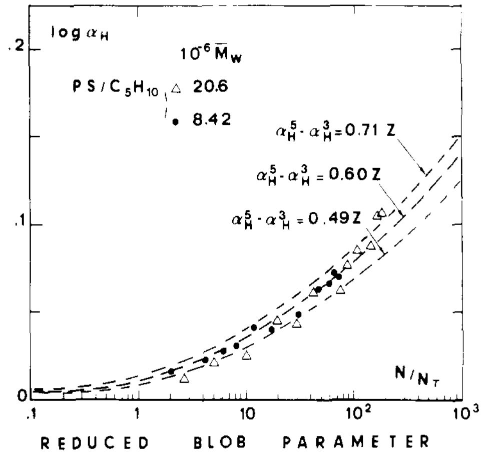

Figure 5. Plot of the logarithm of the hydrodynamic expansion factor α_H as a function of the reduced parameter of the blob theory N/N_τ for two different fractions of polystyrene in cyclopentane. The dashed curves correspond to a tentative fit of the data with an $\alpha_H{}^5 - \alpha_H{}^3 = bz$ Flory equation using three different values of the constant b. z is the excluded volume parameter and is proportional to $(N/N_\tau)^{1/2}$. For polystyrene in cyclohexane, $z = 0.127(N/N_\tau)^{1/2}$ (see text for details).

Figure 4 shows the variation of α_H with temperature for the various molecular weight fractions and in the two different solvents. The temperature range is 4 times more expanded with cyclopentane than with cyclohexane due to the lower Θ temperature of the former solvent. The maximum relative variation in the hydrodynamic radius is 30%. The accuracy on each point is estimated to be ±2%.

It is customary to draw α_H as a function of a reduced unit that is a simple function of temperature and molecular weight. This unit is taken as the excluded volume parameter z in the earliest literature[4] and as the reduced number of thermal blobs within a single chain N/N_τ in the most recent work.[5-7] Both parameters are related to each other by $N/N_\tau = Dz^2$, where D is a constant.[6] In Figure 5, we have reported such a plot of log α_H vs. log (N/N_τ) for the data obtained in cyclopentane with our two highest molecular weight samples, 8.42 × 10^6 and 20.6 × 10^6. To calculate N/N_τ, we have used the expression proposed by Ackasu and Han[6] for polystyrene chains, $N/N_\tau = \bar{M}_w\tau^2/4M_0$. M_0 is the monomer molecular weight. For polystyrene, M_0 = 104 and therefore $N/N_\tau = \bar{M}_w\tau^2/416$

In Figure 6, we have drawn the whole of our results on polystyrene high molecular weight fractions in cyclopentane and cyclohexane. In Figure 7, we have combined all our experimental results with the literature data for

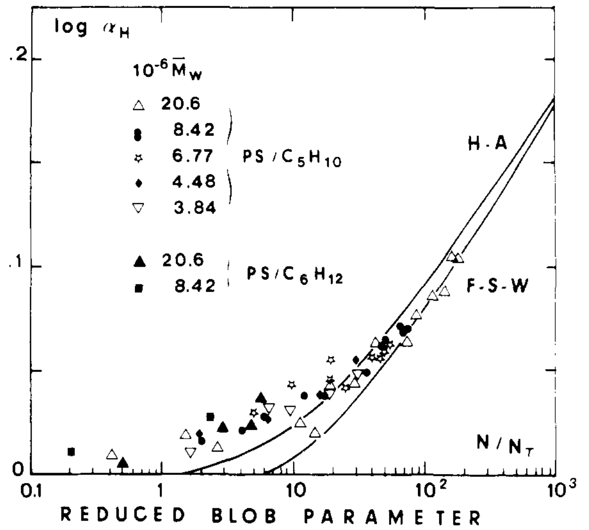

Figure 6. Plot of the logarithm of the hydrodynamic expansion factor α_H as a function of the reduced blob parameter N/N_τ for polystyrene coils in cyclopentane and cyclohexane. The data correspond to five different molecular weight fractions. The two solid lines correspond to the Ackasu-Han (A-H) and to the François, Schwartz, Weill (F-S-W) predictions, respectively.

polystyrene in similar Θ solvents, namely, *trans*-decalin[13] and cyclohexane.[14,15]

A careful examination makes clear that the present data extend the range of N/N_τ explored in such solvents by roughly a factor of 2.

Discussion

We will now compare the experimental data with the various existing theories for the expansion factor α_H of the hydrodynamic radius.

We will discuss in turn the exact first-order perturbation method of Stockmayer and Albrecht,[8] the empirical α^5-type equation of Flory,[3,4] and the thermal blob theory[5-7] and its subsequent modifications.[12,17]

A. Comparison with the First-Order Perturbation Method. This theory is based on the Kirkwood–Riseman approach of polymer hydrodynamics.[28] It is exact to first-order expansion in powers of z and predicts that the hydrodynamic expansion factor α_H should vary as

$$\alpha_H = 1 + 0.609z + ... \qquad (5)$$

Higher order terms have been estimated to be unimportant by Stockmayer and Fixman;[29] however Berry[30] has shown that they start to play a role for $z > 0.4$. We have plotted the Stockmayer–Albrecht (S–A) theoretical law in Figure 7. z was converted to N/N_τ according to $z = 0.127(N/N_\tau)^{1/2}$. This correspondence was derived from the experimental results of Miyaki et al.[9,23,31] for polystyrene in cyclohexane. Let us first recall that $z = [4\pi(\langle R_G^2\rangle_\Theta/M)]^{-3/2}(M^{1/2}/M_0^2)v$, where v, the binary cluster integral, contains the whole temperature dependence of z and M_0 is the monomer molecular weight ($M_0 = 104$ for polystyrene). From the temperature dependence of the radius of gyration,[9] v was measured to be $v = v_\infty\tau$, with $v_\infty = 72 \times 10^{-24}$ cm^3. From static light scattering measurements,[31] $\langle R_G^2\rangle_\Theta/M$ was taken as 8.30×10^{-18} cm^2 mol g^{-1} (a less accurate value of $(8.8 \pm 0.2) \times 10^{-18}$ cm^2 mol g^{-1} had been published previously by the same group[23]). Combining these two data, we then get an expression for z, $z = 6.25 \times 10^{-3}(M\tau^2)^{1/2}$. This value is in relatively good agreement with an older determination by Kato et al.[32] for the nearly similar system of poly(α-methylstyrene) in cyclohexane, $z = 4.5 \times 10^{-3}(M\tau^2)^{1/2}$. To arrive at the desired relationship between z and N/N_τ, one has to use once more the Ackasu–Han formula, $N/N_\tau = \bar{M}_w\tau^2/416$.[6] The final result is

$$z = 0.127(N/N_\tau)^{1/2}$$

which is indeed the expression written above. It should be noted that the value of the prefactor should not be taken too much in earnest. It is probably correct to only ±10% in view of the variation found in the literature between the various experimentalists.

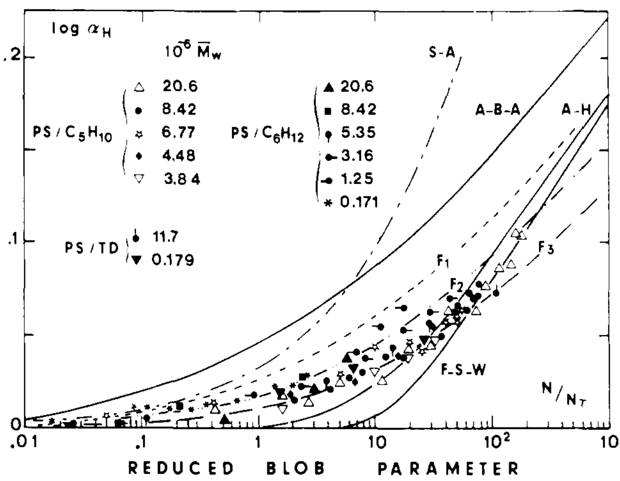

Figure 7. Compilation of results obtained for the hydrodynamic expansion factor of polystyrene in three solvents with Θ points in the vicinity of ambient temperature. For a given molecular weight, the variation of N/N_τ was obtained by changing the temperature of the solution. Data in *trans*-decalin (TD) are from Nose and Chu.[13] Data in cyclohexane (C_6H_{12}) are from this work ($\bar{M}_w = 8.42 \times 10^6$ and 20.6×10^6) and from Pritchard and Caroline[15] for the other $\bar{M}_w$. Data in cyclopentane (C_5H_{10}) are all from this work. The solid curves correspond to the blob theory by Ackasu and Han (A-H) and to its two modifications by Ackasu, Benmouna, and Alkhafaji (A-B-A) and by François, Schwartz, and Weill (F-S-W). The dashed curves correspond to the Flory α_H^5-type expressions for three different values of the b coefficient, $b = 0.71$ (F_1), 0.60 (F_2), and 0.49 (F_3). The dot-dash curve corresponds to the first-order hydrodynamic perturbation theory of Stockmayer and Albrecht (S-A). See text for details.

Comparing the S–A theoretical curve with the experimental data, it is obvious that there is a good fit up to N/N_τ values of about 0.4 (i.e., corresponding to $z < 0.08$). This finding is in good agreement with the single, but very accurate, sedimentation data of Mulderije[11] on 1.8×10^6 polystyrene chains in cyclohexane, 3 °C above the Θ temperature.

For larger N/N_τ values, it is also clear that the predictions of the S–A curve increasingly exceed the experimental points. This comes as no surprise since, as stated earlier, there must be an upper limit to the validity of a linear relationship between α_H and z (or N/N_τ).

Pritchard and Caroline,[15] working on the same polystyrene–cyclohexane system, have used an expansion series to the third power in $(T - \Theta)$ to describe their data obtained with molecular weight fractions up to 5.35×10^6 and for temperatures between 30 and 60° C. In their case, the maximum z was $\simeq 1$ (or $N/N_\tau \simeq 72$). In this high range of z, they have nevertheless claimed that perturbation expansions can still explain their data if enough terms are taken into consideration. We do not think, however, that their data can support this statement. First, they should have used $\tau = (T - \Theta)/T$ instead of $T - \Theta$ in their polynomial expansion, in order to ensure temperature-independent polynomial coefficients. Moreover, the second term of their experimental fit does not have the correct, linear, dependence on molecular weight.

B. Comparison with the α^5-Type Equation of Flory.

Some 20 years ago, Flory proposed a mean-field equation to describe the static expansion factor α_G of the radius of gyration for flexible polymer coils.[3] In its original form, it was written as

$$\alpha_G{}^5 - \alpha_G{}^3 = 2.60z \qquad (6)$$

and was later modified to[4]

$$\alpha_G{}^5 - \alpha_G{}^3 = 1.276z$$

It has sometimes been proposed that such an α^5-type equation can be extended to the description of the hydrodynamic expansion factor α_H. For instance, Noda, Mizutani, and Kato have mentioned that their data for poly(α-methylstyrene) in *trans*-decalin and toluene[10] can be correctly fitted over a wide range of z using

$$\alpha_H{}^5 - \alpha_H{}^3 = 1.22z \qquad (7)$$

The maximum z value attainable in their experiments was $z \simeq 8$, which corresponds to a very large N/N_τ value of 1426 using $z = 9.75 \times 10^{-3}(\bar{M}_w\tau^2)^{1/2}$ for poly(α-methylstyrene) in toluene[30] and $N/N_\tau = \bar{M}_w\tau^2/472$.[4] The number 472 in the denominator, instead of the usual 416, accounts for the difference in molecular weight between poly(α-methylstyrene) and polystyrene.

Despite its apparent excellent agreement with an α^5-type equation, the Noda result must, however, be considered with caution. There is clearly no sound theoretical basis to apply to hydrodynamic variables an equation established for static properties. A point more particular to the Noda experiments is that the Θ temperature for polystyrne in *trans*-decalin is now recognized to be 10 °C higher than originally estimated. Nose and Chu have recently reported a Θ value of 20 °C in the same system.[11]

At any rate, it remains that this compact equation can be a useful tool to try to fit our experimental data over a wide range of z. In Figure 5, three different theoretical curves (F) have been drawn, corresponding to three different values of the prefactor (called b hereafter) in the α^5 equation. b has been taken as 0.71 (curve F_1), 0.60 (curve F_2), and 0.49 (curve F_3). It is immediately apparent that the data points obtained for the 8.42×10^6 molecular fraction can be very precisely described with an α^5-type curve taking $b = 0.60$. On the other hand, the experimental points obtained for the 20.6×10^6 molecular weight fraction, which cover a much more extended N/N_τ range, cannot be satisfactorily fitted with a single value of the b parameter. If it is force-fitted to pass through the data points at small N/N_τ, it underestimates the α_H values at large N/N_τ. For instance, a value of $b = 0.49$ correctly describes the data below $N/N_\tau = 80$ but a much higher b value would be required above. This failure of the α^5-type expression to fit the experiments over a wide range of N/N_τ is already well documented in the work by Miyaki et al. on the same polystyrene–cyclohexane system.[9] Even for the static expansion factor, these authors have shown very conclusively that the best theoretical fit to the data is not given by an equation of the Flory type but rather by an expression of Domb and Barrett.[33] This last empirical formula was constructed so as to agree with the perturbation theory at very small N/N_τ and to approach a simple asymptotic form $\alpha_G{}^2 = 1.53z^{2/5}$, derived from computer data on self-avoiding lattice chains, at large N/N_τ. It would be very interesting to have the hydrodynamic equivalent of this expression in order to see if, as in the static case, it allows for a very close fit to the experimental data over a wide range of N/N_τ. Unfortunately, it represents a formidable task to perform.

Even if α^5-type equations are used to fit the data but over a limited range of N/N_τ, it remains that different values of the b parameter seem to be required according to molecular weight. We have already seen that in the range $2 < N/N_\tau < 70$, the best fit is achieved with $b = 0.60$ for the 8.42×10^6 sample and with $b = 0.49$ for 20.6×10^6 sample. This indicates that the data for this latter material generally lie below those for the former one and cannot be merged into a unique master curve. This point is further confirmed on the other molecular weight fractions between 1.25×10^6 and 8.42×10^6. A close inspection of Figure 7, after allowing for some inevitable ±2% data scattering, reveals that at $N/N_\tau = 18$, for example, α_H is 1.16 for 1.25×10^6,[15] 1.12 for 3.16×10^6,[11,15] and 1.09 for 8.42×10^6 (this work). Therefore, we can say that for a given N/N_τ value, we observe a definite, although small, dependence of the α_H values on the sample molecular weight. This important point should be carefully examined in future works since it raises the whole question of the validity of a universal function to describe all data at various molecular weights. It is therefore relevant not only to the α^5-type approach but to the thermal blob theory as well.

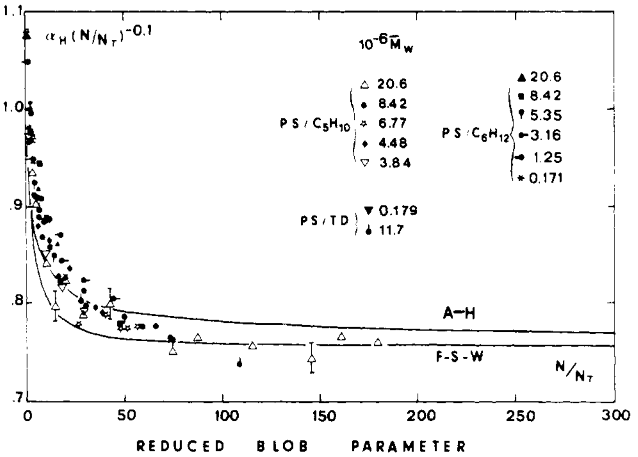

Figure 8. Variation of $\alpha_H(N/N_\tau)^{-1/10}$ as a function of the reduced blob parameter N/N_τ. The data points are the same as in Figure 7. The solid curves correspond to the blob theory by Ackasu and Han (A–4) and to its modification by François, Schwartz, and Weill (F–S–W).

C. Comparison with the Thermal Blob Theory. The temperature blob theory has provided the opportunity to calculate static and dynamic variables in a simple fashion for any N/N_τ values greater than 1. It is, of course, most valid for large N/N_τ since it predicts no swelling of the chain for $N/N_\tau \rightarrow 1$, which is in clear contradiction with the exact perturbation theory. In the asymptotic limit where $N/N_\tau \gg 1$

$$\alpha_H \rightarrow 0.747(N/N_\tau)^{1/10} \qquad (8)$$

In order to check the validity of the blob theory in our experiments, we have therefore plotted the product of α_H times $(N/N_\tau)^{-1/10}$ as a function of N/N_τ. If the asymptotic limit is reached, one expects the data points to fall on a horizontal line, the ordinate intercept of which directly yields the prefactor of eq 8. This seems to be indeed the case in Figure 8 for the data points corresponding to the larger N/N_τ values. The intercept with the ordinate is found to be 0.76 ± 0.02, in excellent agreement with the theoretical value of 0.747. The N/N_τ value below which the experimental points start to deviate from the horizontal line sets the lower limit of the asymptotic regime. Judging from Figure 8 a cutoff value of $N/N_\tau \simeq 80$ can be estimated. To the best of our knowledge, this is the first time that the crossover to the asymptotic regime can be clearly observed in a single solvent for hydrodynamic properties.

In the polystyrene–cyclohexane system, Adam and Delsanti[14] have quite correctly inferred that their observation of an anomalous dynamic exponent $\alpha_H \sim (N/N_\tau)^{0.017\pm0.002}$ was related to their low experimental range of N/N_τ. For their polystyrene fraction of 1.71×10^5, N/N_τ never exceeded 2.7 in their 30 °C temperature interval around the Θ temperature. The data of Pritchard and Caroline[15] have been obtained for higher N/N_τ, up to 75, but it was still not quite sufficient to reach the asymptotic limit. On the other hand, Nose and Chu[13] have published a single data point in the high N/N_τ range ($N/N_\tau = 110$) that roughly agrees with our own measurements.

It would now be interesting to obtain some data with a 40×10^6 molecular weight sample. This would allow extension of the N/N_τ range to 350 and therefore would give a critical check that we have indeed reached the expected asymptotic limit. In the absence of such a measurement, we can only say that the blob theory seems to agree with our experimental data at large N/N_τ, where both the perturbation theory and the Flory empirical equation become clearly inadequate.

In the intermediate range of N/N_τ, $70 > N/N_\tau > 1$, the blob theory does not provide a perfect fit to the experimental data. In Figures 6–8, we have drawn as a solid line (A–H) the complete expression for α_H vs. N/N_τ given in the theoretical section, eq 3. The data points are all slightly above (by a few percent) the theoretical curve, which thus predicts too rapid a transition toward the Gaussian chain behavior when N/N_τ is decreased. It has already been mentioned many times that the blob theory does not interpolate very well between the excluded volume and the Gaussian statistics because it is based on a step change of behavior. This change is certainly more gradual in reality. These may also be logarithmic corrections that have been overlooked in the theory. The fact that the agreement between experiment and theory becomes gradually better as the sample molecular weight is increased may, however, provide alternative explanations. It is possible that even at relatively large molecular weight values, the coil should not be considered as impenetrable to the solvent. This partial free drainage would lead to an extra friction within the polymer chain and will therefore induce an increase in its effective hydrodynamic radius. A specific hydrodynamic interaction between the polymer and the solvent can also not be ruled out. Such effects have been reported for polystyrene in butanone[34] and for poly(dimethylsiloxane) in bromocyclohexane.[35] This explains why the hydrodynamic radius of a chain dissolved in a Θ solvent can sometimes be larger than in thermodynamically better solvents. Both of these factors will preclude the description of α_H in terms of a simple universal function of $N/N_\tau = B\tau^2$, with B independent of molecular weight.

Last, it is appropriate to compare our results with the predictions of the so-called modified blob theories that have been recently proposed independently by Ackasu, Benmouna, and Alkhafaji (A–B–A for short)[17] and François, Schwartz, and Weill (F–S–W for short).[12] Both groups have tried to substitute a more progressive transition to the step change in statistics between portions of the chain below and above N_τ. Ackasu et al.[17] have used a generalization of the Flory formula to all n (n is the chemical distance between two monomers) while retaining the fundamental idea that the smaller sections of the chain swell less than the longer ones.

$$\alpha^5(n) - \alpha^3(n) = bz(n) = (n/N_\tau)^{1/2}$$

François et al.[12] have introduced a continuous function for the exponent ν describing the local swelling of the chain. Two arbitrary forms with two adjustable parameters have been considered in order to fit their data in their particular polyacrylamide–water system.

The numerical calculations of these two theories have been reported in Figures 7 and 8.[36] Contrary to what could have been hoped, no significant improvement of the data description is observed, even in the intermediate N/N_τ range, where these modified theories should be fully applicable. The F–S–W version seems to provide a small improvement at large N/N_τ (higher than 80). However, it fails to explain the low N/N_τ behavior, contrary to its primary goal. The A–B–A version does not appear to be much better. On the other hand, it should be realized that the representation shown in Figure 7 uses the numerical value of 416 for the proportionality coefficient between N/N_τ and $\bar{M}_w\tau^2$. Such a value has been established by fitting the high molecular weight data points to the original blob theory. Therefore it is not strictly correct to transfer it directly to the modified blob theory. In that latter case a different value may well be required.[37] This can be easily accounted for by multiplying the N/N_τ values of Figure 7 by an adjustable coefficient (or equivalently, by shifting horizontally the whole A–B–A curve in the logarithmic representation). The results are unfortunately rather disappointing. Using a multiplication factor of 40 allows one to describe the intermediate N/N_τ region quite correctly but then the calculated curve falls too low for the large N/N_τ data points. On the other hand, using a lower multiplication factor of 10 allows one to describe the asymptotic region more satisfactorily but then the theoretical curve passes too high in the intermediate region.

We believe that the main flaw of this modified thermal blob model is that it predicts too gradual a transition to the asymptotic regime. Experimentally, we observe the asymptotic behavior $\alpha_H \propto (N/N_\tau)^{0.1}$ to set in over a relatively short range of N/N_τ values. As a consequence, when one tries to fit the theoretical curve to the large N/N_τ data points, the intermediate region is systematically ill-described.

We can therefore conclude that, based on our experiments, neither of these modified blob theories seems to significantly improve our understanding of the temperature dependence of the hydrodynamic expansion factor α_H.

Conclusion

We have presented here extensive data on the hydrodynamic expansion factor α_H for polystyrene chains in two different solvents, cyclopentane and cyclohexane, in a temperature range from 0 to 20 °C above their Θ points. The measurements have been performed on the highest monodisperse fractions currently commercially available. Therefore they cover an unusually broad range of N/N_τ between 0.2 and 180. It is shown that the asymptotic law predicted by the thermal blob theory $\alpha_H \rightarrow 0.747(N/N_\tau)^{1/10}$ is probably reached for values of N/N_τ larger than 70. In the intermediate range $70 > N/N_\tau > 1$, the complete analytical expression for α_H as derived from the blob theory does not provide a perfect fit to the experimental data. There is a systematic underestimation, which should not be considered as dramatic since it never exceeds 4% for $N/N_\tau < 20$. Moreover, a variation of roughly the same amplitude is observed in the experimental points when the sample molecular weight is increased from 1.25×10^6 to 20.6×10^6. It is therefore probable that the agreement with the thermal blob theory would improve, were it possible to further increase the sample molecular weights. In the absence of any better theory, an equation of the Flory type with $\alpha_H^5 - \alpha_H^3 = bz = b'(N/N_\tau)^{1/2}$ can also be used, with

b between 0.49 and 0.60 ($b' = 0.062$–0.076). Last, in the very low range of N/N_τ, i.e., $N/N_\tau < 0.4$, our data are well described by the Stockmayer–Albrecht linear relationship, $\alpha_{\rm H} = 1 + 0.609z$. We have simply confirmed here a well-established result.

We are presently trying to extend our measurements toward larger N/N_τ values by working on systems with relatively low Θ temperatures and by using even higher molecular weight fractions. We thus hope to better approach the stringent validity conditions of the thermal blob theory for hydrodynamic variables.

Acknowledgment. One of us (P.V.) wants to thank the C.I.E.S. and the Joliot Curie Foundation for the attribution of two scholarships during his doctoral stay at the Collège de France. We acknowledge helpful discussions with P.-G. de Gennes, M. Adam and M. Delsanti.

Registry No. Polystyrene, 9003-53-6.

References and Notes

(1) de Gennes, P.-G. "Scaling Concepts in Polymer Physics"; Cornell University Press: Ithaca, NY, 1979.

(2) Daoud, M.; Jannink, G. *J. Phys. (Paris)* **1976**, *37*, 973.

(3) Flory, P. J. "Principles of Polymer Chemistry"; Cornell University Press; Ithaca: NY, 1966.

(4) Yamakawa, H. "Modern Theory of Polymer Solutions", Harper and Row: New York, 1971.

(5) Farnoux, B.; Boué, F.; Cotton, J. P.; Daoud, M.; Jannink, G.; Nierlich, M.; de Gennes, P.-G. *J. Phys. (Paris)* **1978**, *39*, 77.

(6) Ackasu, A. Z.; Han, C. C. *Macromolecules* **1979**, *12*, 276.

(7) Weill, G.; des Cloizeaux, J. *J. Phys. (Paris)* **1979**, *40*, 99.

(8) Stockmayer, W. H.; Albrecht, A. C. *J. Polym. Sci.* **1958**, *32*, 215.

(9) Miyaki, Y.; Fujita, H. *Macromolecules* **1981**, *14*, 742.

(10) Noda, I.; Mizutani, K.; Kato, T. *Macromolecules* **1977**, *10*, 618.

(11) Mulderije, J. J. H. *Macromolecules* **1980**, *13*, 1207.

(12) François, J.; Schwartz, T.; Weill, G. *Macromolecules* **1980**, *13*, 564.

(13) Nose, T.; Chu, B. *Macromolecules* **1979**, *12*, 1122.

(14) Adam, M.; Delsanti, M. J. Phys. *(Paris)* **1980**, *41*, 713.

(15) Pritchard, M. J.; Caroline, D. *Macromolecules* **1980**, *13*, 957; **1981**, *14*, 424.

(16) Nyström, B.; Roots, J.; Bergman, R. *Polymer* **1979**, *20*, 157.

(17) Ackasu, A. Z.; Benmouna, M.; Alkahafaji, S. *Macromolecules* **1981**, *14*, 147.

(18) Fujita, H.; Norisuye, T. *Macromolecules* **1981**, *14*, 1130.

(19) (a) Vidakovic, P.; Allain, C.; Rondelez, F. *J. Phys. (Paris) Lett.* **1981**, *42*, 323. (b) *Macromolecules* **1982**, *15*, 1571.

(20) Slagowski, E.; Tsai, B.; Mc'Intyre, D. *Macromolecules* **1976**, *9*, 687.

(21) Bauer, D. R.; Ullman, R. *Macromolecules* **1980**, *13*, 392.

(22) Sun, S. T.; Nishio, I.; Swislow, G.; Tanaka, T. *J. Chem. Phys.* **1980**, *73*, 5971.

(23) Miyaki, Y.; Einaga, Y.; Fujita, H. *Macromolecules* **1978**, *11*, 1180.

(24) Strazielle, C.; Benoit, H. *Macromolecules* **1975**, *8*, 203.

(25) Wolf, B. A.; Geerissen, H. *Colloid Polym. Sci.* **1981**, *259*, 1214.

(26) Timmermans, J. "Physico-Chemical Constants of Pure Organic Compounds"; Elsevier: New York, 1950. Dean, J. A., Ed. "Lange's Handbook of Chemistry"; McGraw-Hill: New York, 1973. "Handbook of Chemistry and Physics", 51st ed.; Chemical Rubber Co.: Cleveland, 1971. Brandup, J., Immergut, E. H., Eds. "Polymer Handbook", Wiley: New York, 1975.

(27) (a) Sarazin, D.; François, J. *Polymer* **1978**, *19*, 699. (b) Nyström, B.; Roots, J. *Polymer* **1977**, *18* 1289. It is assumed that the partial specific volume of polystyrene will be the same in *trans*-Decalin and cyclopentane, which are two Θ solvents at nearly identical temperatures.

(28) Kirkwood, J. G.; Riseman, J. *J. Chem. Phys.* **1948**, *16*, 565.

(29) Stockmayer, W. H.; Fixman, M. *J. Polym. Sci., Part C* **1963**, *1*, 137.

(30) Berry, G. C. *J. Polym. Sci.* **1966**, *4*, 161.

(31) Miyaki, Y.; Einaga, Y.; Fujita, H.; Fukuda, M. *Macromolecules* **1980**, *13*, 588.

(32) Kato, T.; Miyaso, K.; Noda, I.; Fujimoto, T.; Nagasawa, M. *Macromolecules* **1970**, *3*, 777.

(33) Domb, C.; Barrett, A. *Polymer* **1976**, *17*, 179.

(34) King, T. A.; Knox, A.; Lee, W. I.; McAdam, J. D. G. *Polymer* **1973**, *14*, 151, 273.

(35) For a recent discussion, see: Munch, J. P.; Herz, J.; Boileau, S.; Candau, S. *Macromolecules* **1981**, *14*, 1370.

(36) Note that the eq 20 in ref 17 is incorrect. Using the same notations, it should be written as

$$\alpha_{\rm H}^{-1} = \frac{3}{2Z}\left\{\left(\frac{5}{4}\alpha_R^{4} - \frac{3}{2}\alpha_R^{2} + \frac{1}{4}\right) - \frac{1}{Z^2}\left(\frac{5}{14}\alpha_R^{14} - \frac{13}{12}\alpha_R^{12} + \frac{11}{10}\alpha_R^{10} - \frac{3}{8}\alpha_R^{8} + \frac{1}{840}\right)\right\}$$

where $Z = (N/N_\tau)^{1/2}$. For large Z, $\alpha_{\rm H} \rightarrow 0.747Z^{1/5}$. For small Z, $\alpha_{\rm H} \rightarrow 1 + {}^{1}/_{4}Z$. On the other hand, the plot of $\alpha_{\rm H}$ for the modified blob theory (Figure 3 of the same paper) seems to be correct.

(37) We thank one of the referees for bringing this point to our attention.

Concentration Dependence of Polymer Self-Diffusion Coefficients

J. S. Vrentas,* J. L. Duda, and L.-W. Ni

Department of Chemical Engineering, The Pennsylvania State University,
University Park, Pennsylvania 16802. Received April 12, 1982

ABSTRACT: An approach is presented for analyzing the concentration dependence of polymer self-diffusion coefficients for concentrated polymer solutions. The random motion of expanded polymer chains is treated by using the free-volume theory of transport. The effect of polymer molecular weight on the concentration dependence of the polymer self-diffusion coefficient is studied. In addition, the effect of the free-volume characteristics of the polymer and solvent on the concentration behavior of both polymer and solvent self-diffusion coefficients is investigated. Calculations are carried out on two model polymer–solvent systems, and the computed concentration trends are compared with experimental data.

Useful information about molecular mobility can be obtained from diffusion studies in the absence of any concentration gradients. Both polymer and solvent self-diffusion coefficients in polymer–solvent mixtures have been measured by using radioactive tracer[1,2] and NMR techniques.[3,4] For the solvent self-diffusion coefficient, D_1, experiments[2,3] reveal the following type of concentration dependence:

$$\partial \ln D_1/\partial\omega_1 > 0 \qquad (1)$$

$$\partial^2 \ln D_1/\partial\omega_1^2 < 0 \qquad (2)$$

where ω_1 is the solvent mass fraction. Here, and in the remainder of this paper, we suppose that the concentration dependence of the solution density is sufficiently small so that, for example, $\partial^2 \ln D_1/\partial\omega_1^2$ has the same sign as ∂^2 ln

0024-9297/83/2216-0261$01.50/0