Macromolecules **1985**, *18*, 700–708

Temperature Dependence of the Hydrodynamic Radius of Flexible Coils in Solutions. 3. Experimental Evidence for the Crossover between Gaussian and Excluded-Volume Single-Chain Statistics

Petar Vidaković[†] and Francis Rondelez*

Physique de la Matière Condensée,[‡] Collège de France, 75231 Paris Cêdex 05, France.

Received January 31, 1983

ABSTRACT: The temperature variation of the hydrodynamic radius $R_{\mathrm{H}}(T)$ of large polystyrene coils ($M_{\mathrm{w}} = (8.42\text{–}20.6) \times 10^6$) is derived from sedimentation measurements in dilute solutions. The results, obtained in toluene, ethyl acetate, *n*-butyl formate, and cyclopentane, are compared with the predictions of the thermal blob theory[5–7] and with the Padé approximant method of Tanaka.[14] A universal behavior is observed at least for the latter three solvents and possibly for toluene. In particular, the expansion factor $\alpha_{\mathrm{H}} = R_{\mathrm{H}}(T)/R_{\mathrm{H}}(\Theta)$ is observed to vary as $\alpha_{\mathrm{H}} = 0.75(N/N_\tau)^{1/10}$ in the asymptotic regime, where $N/N_\tau = \bar{M}_{\mathrm{w}}\tau^2/n\alpha M_0$ and $\tau = 1 - \Theta/T$. The best fit is obtained by taking the proportionality factor $n\alpha M_0$ to be 1000 ± 50. The crossover between the Gaussian and the excluded-volume behaviors is also observed without ambiguity. We thus confirm the validity of a universal description of polymer solutions, even for hydrodynamic properties.

Introduction

In the first paper of this series,[1] we have started an investigation of the temperature and molecular weight dependences of the hydrodynamic expansion coefficient α_{H} for flexible polymer chains in solutions above their Θ points. $\alpha_{\mathrm{H}}(T)$ is defined by $\alpha_{\mathrm{H}} = R_{\mathrm{H}}(T)/R_{\mathrm{H}}(\Theta)$, where $R_{\mathrm{H}}(T)$ and $R_{\mathrm{H}}(\Theta)$ are the hydrodynamic radii of the coil at temperatures T and Θ, respectively. At the Θ temperature, the coil takes its Gaussian configuration and $R_{\mathrm{H}} \sim N^{1/2}$ where N is the degree of polymerization.[2] At temperatures much larger than Θ, the coil gets progressively swollen and exhibits its excluded-volume behavior, characterized by $R_{\mathrm{H}} \sim N^{3/5}$. Working with several high molecular weight polystyrene fractions in cyclopentane and varying the temperature of the solution in the vicinity of the Θ point, we have been able to follow the onset of the transition between these two behaviors. The results have been compared with the first-order perturbation equation for α_{H} proposed by Stockmayer and Albrecht[3] and also with an empirical extension to hydrodynamics of the mean-field Flory equation for the static expansion factor.[4] Both approaches have been rather deceiving insofar as they only allow for a description of the experimental data over a restricted range of temperature and molecular weight. On the other hand, the comparison with the recent thermal blob theory[5–7] has been more successful, at least qualitatively. In this model, a single chain is viewed as a succession of Gaussian blobs, each made of N_τ monomers, and with excluded-volume interaction between them. N_τ is a function of the reduced temperature $\tau = 1 - \Theta/T$ and varies as $N_\tau \sim \tau^{-2}$. When $N \gg N_\tau$, the chain becomes completely swollen and α_{H} scales as $0.747(N/N_\tau)^{1/10}$. The expansion factor α_{H} is therefore a universal function of N/N_τ, independent of the kind of polymer and solvent condition, and, in that respect, the blob model belongs to the much advocated two-parameter theories' family.[8] Our early experiments were, however, very preliminary and it was not possible at that time to investigate the asymptotic regime in detail. The main reason was that the maximum N/N_τ value attainable 20 °C above the Θ temperature and with the highest molecular weight fraction available (20.6×10^6) was a mere 80, clearly insufficient to deeply enter the asymptotic range.

One approach to get very large N/N_τ values is to work with the so-called good solvents, i.e., polymer–solvent systems which have Θ temperatures much below room temperature. In that case, τ values, and thus N_τ, become of order unity. Consequently, N/N_τ can be easily made large, even with moderately high molecular weight fractions. Since N_τ is practically independent of the actual working temperature (the solvent is athermal), the ratio N/N_τ has now to be varied by changing N. Using such a procedure, Akcasu and Han[6] have compiled literature data for polystyrene in several good solvents such as benzene and tetrahydrofuran and claimed a good agreement with the thermal blob theory. However, definite conclusions have been hampered by the fact that, in none of the systems used, is the Θ temperature accurately known. Therefore N/N_τ can only be estimated to an unspecified proportionality coefficient, different for each polymer–solvent system, and universal curves as a function of N/N_τ cannot be drawn precisely. Another questionable point is that all results have been obtained on relatively low molecular weight samples, $\bar{M}_{\mathrm{w}} < 3.8 \times 10^6$. Under such conditions, it has been shown that the assumption of non-free draining, impenetrable coils, may not be strictly valid.[9] Moreover, our earlier experiments[1] did show an unexpected molecular weight dependence of the hydrodynamic expansion factor when plotted in the reduced N/N_τ variable. Although the effect is weak and does not exceed 10% for the lowest fraction investigated (171 000), it is certainly present and gives evidence for a nonuniversal behavior for nonasymptotically large polymer coils.

In view of this situation, we have tried to complete the existing data for the hydrodynamic expansion coefficient α_{H} by investigating very large molecular weight fractions of polystyrene dissolved in *n*-butyl formate, ethyl acetate, and toluene. The Θ temperature of the first system has been quoted by Schulz and Baumann[10] to be −9 °C, from direct, and therefore reliable, measurements of the temperature dependence of the second virial coefficient. The Θ temperature of the second system has been quoted to be −44 °C by Saeki et al.[11] from measurements of the demixtion temperatures for various molecular weight fractions and concentrations and extrapolation to infinite molecular weight according to the Fox–Flory procedure.[12] The Θ temperature of the third system is not precisely

---

[†] On leave of absence from Odsek za Fizičke i Meteorološke Nauke, Prirodno-Matematički Fakultet, 11001 Belgrade, Yougoslavie.

[‡] Equipe de Recherche Associée au C.N.R.S. (E.R.A. 542).

0024-9297/85/2218-0700$01.50/0

known and cannot in fact be measured directly. Therefore, we had to use an indirect procedure which will be detailed later in the text.

The two polystyrene fractions used are in the 10^7 molecular weight range. The investigated temperature domain is between $\Theta + 17$ °C and $\Theta + 50$ °C for the polystyrene–*n*-butyl formate solutions, between $\Theta + 51$ °C and $\Theta + 83$ °C for polystyrene–ethyl acetate solutions and between 8 and 42 °C for polystyrene–toluene solutions. Therefore the data cover a yet unexplored range of N/N_τ between 30 and 8000. When combined with our earlier results on polystyrene–cyclopentane solutions,[1] and those of Appelt and Meyerhoff on polystyrene–toluene solutions,[13] they allow us to follow the complete transition of polystyrene coils from Gaussian to excluded-volume behavior over four decades of $N/N_\tau(1 - 10^4)$. Comparison is made with the predictions of the thermal blob theory and also with a closed formula based on the Padé approximant method and recently proposed by Tanaka.[14] The experimental setup and the data analysis are only briefly described since this paper is the direct continuation of our previous investigations of hydrodynamic properties of polymer solutions using analytical ultracentrifugation techniques.[1]

Experimental Section

The polystyrene used were two sharp high molecular weight fractions ($\bar{M}_w = 20.6 \times 10^6$ and $\bar{M}_w = 8.42 \times 10^6$) obtained from Toyo Soda Co. Their polydispersity index $\bar{M}_w/\bar{M}_n$ was quoted to be <1.3 and 1.17, respectively. The *n*-butyl formate (analytical grade) was purchased from Merck and redistilled in our laboratory. It was checked by NMR to contain no significant amounts of isobutyl and *tert*-butyl forms. There was also no evidence of water contamination. The ethyl acetate (spectrograde) was purchased from Merck. Since it has been mentioned in the literature[15] that ethyl acetate can contain as much as 8% of water, the solvent used was always freshly distilled and kept on molecular sieves. The toluene (spectrograde) was also purchased from Merck and generally used as received. The demixtion temperatures T_d for polystyrene in these various solvents were measured by the cloud point method to an accuracy of 0.5 °C. In the case of the *n*-butyl formate, the spectrophotometric procedure described in ref 1 was used as a control. The monitoring wavelength was 340 nm, just above the cut-off value for the pure solvent (310 nm). For the 20.6×10^6 molecular weight fraction, T_d was found to be −8.5 and −8.0 °C at concentrations of 1.16×10^{-3} and 4.55×10^{-3} g cm^{-3}, respectively. Under such conditions, T_d is expected to differ from Θ by no more than 0.5 °C.[12] The Θ temperature of our solutions was therefore taken to be −7.5 °C, a very close value from the Schulz and Baumann determination.[10] In ethyl acetate and under similar conditions, T_d was found to be −44 °C and therefore Θ was taken as −43.5 °C, in good agreement with the data of Saeki et al.[11] For toluene, T_d could not be measured directly because the demixtion was not yet observed at the minimum temperature of our cooling unit. We can only say that T_d is lower than −75 °C. We will explain in the discussion part how we have estimated the Θ temperature for polystyrene–toluene solutions to be −154 ± 9 °C.

Table I
Viscosity and Density Data for the Various Solvents Used in the Sedimentation Experiments

solvent	T range, °C	A,[a] 10^{-4} P	B,[a] K	C,[b] 10^{-4} g cm^{-3} °C^{-1}	D,[b] g cm^{-3}
cyclopentane	8–50	1.507	986.39	9.86	0.7651
n-butyl formate	8–50	1.647	1081.62	10.70	0.9168
ethyl acetate	8–50	1.486	997.10	12.27	0.9249
toluene	8–50	1.546	1065.82	9.397	0.8857

[a] A and B are the coefficients describing the temperature dependence of the solvent viscosity $\eta_s = A \exp[B/(T + 273)]$. [b] C and D are the coefficients describing the temperature dependence of the solvent density $\rho = -CT + D$.

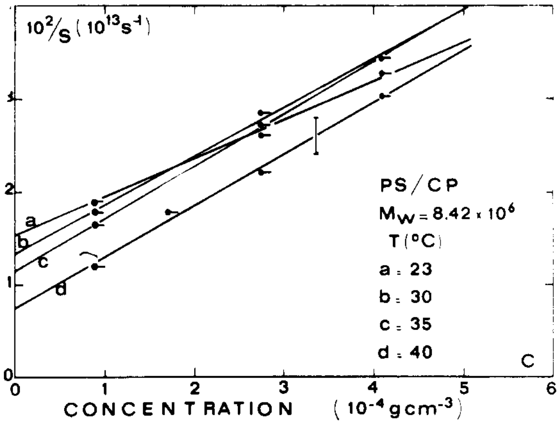

Figure 1. Concentration dependence of the inverse of the sedimentation coefficient for the 8.42×10^6 polystyrene fraction in cyclopentane (Θ = 23 °C) at four different temperatures.

The viscosities of the various solvents were measured separately with an automatic viscometer (Viscomatic MS, Fica, France). The Ubbelohde capillary was first calibrated with triply distilled water at seven temperatures between 10 and 50 °C (i.e., for the actual temperature range of the present sedimentation experiments). In all cases the viscosity was found to closely follow an Arrhenius plot of the form

$$\eta_s(T) = A \exp[B/(T + 273)]$$

where T is expressed in degrees centigrade and η_s in centipoise units. The actual values of A and B for the four solvents investigated are given in Table I. They agree with literature to better than 1% except for *n*-butyl formate. For this latter solvent, the existing data are very scarce and we have found only two values, one at 16.3 °C (η_s = 0.7244 cP) and the other at 20 °C (η_s = 0.704 cP).[15] Both are about 5% higher than our own results. Also given in Table I are the coefficients C and D which describe the temperature dependence of the solvent density according to

$$\rho(T) = -CT + D$$

where T is expressed in degrees centigrade and ρ in g/cm^3. These data were obtained by using a DMA-45 digital density meter (Anton Paar, Graz, Austria).

Results and Discussion

The sedimentation coefficients of two polystyrene fractions have been measured as a function of temperature in extremely dilute solutions ($C = (1\text{–}5) \times 10^{-4}$ g cm^{-3}). The hydrodynamic radii $R_H(T)$ are then derived by using the Svedberg formula

$$S_0 = \bar{M}_w(1 - \bar{v}_2\rho)/6\pi\eta_s R_H \qquad (1)$$

where $\eta_s(T)$ and $\rho(T)$ are the solvent viscosity and density, respectively, $\bar{v}_2$ is the partial specific volume of the polymer in solution, and $S_0(T)$ is the sedimentation coefficient in the limit of infinite dilution where all solute concentration effects can be neglected. Contrary to ref 1, S_0 was not taken as the value of the sedimentation coefficient measured at the lowest concentration experimentally accessible but rather from a true extrapolation. For this purpose, $1/S$ has been plotted as a function of C for four different concentrations and at three temperatures. The results are shown in Figures 1–6 for the three solvents and the two polystyrene fractions. For each temperature, a linear relationship is observed, in agreement with the well-accepted equation $1/S = 1/S_0(1 + k_sC)$. The slope is therefore a direct measure of k_s, the coefficient describing the concentration dependence of the sedimentation coefficient. k_s is both a function of the solution temperature and of the sample molecular weight.[4] Its temperature dependence

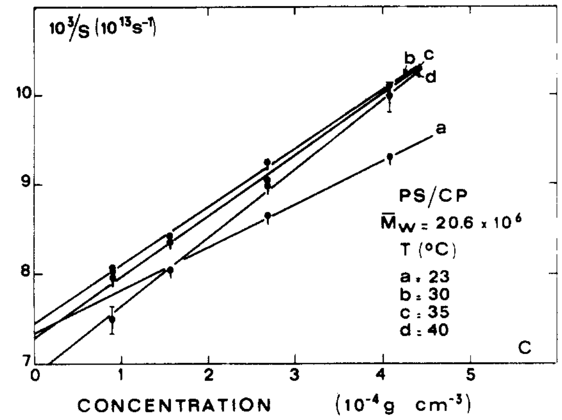

Figure 2. Same as Figure 1 but for the 20.6 × 10^6 polystyrene fraction.

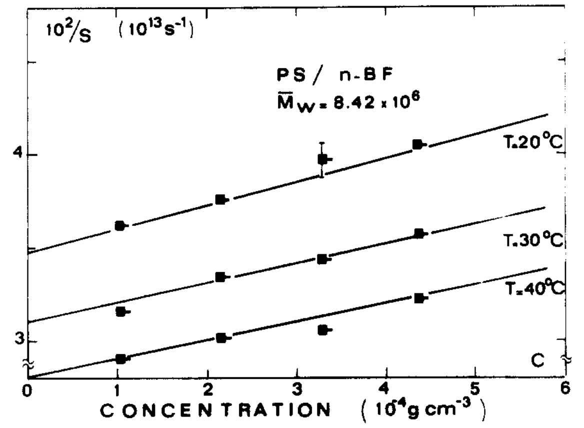

Figure 3. Concentration dependence of the inverse of the sedimentation coefficient for the 8.42 × 10^6 polystyrene fraction in *n*-butyl formate (Θ = −7.5 °C) at three different temperatures.

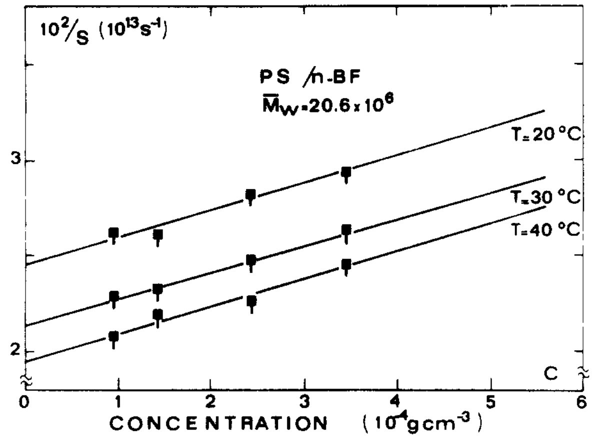

Figure 4. Same as Figure 3 but for the 20.6 × 10^6 polystyrene fraction.

has been plotted in Figures 7–9. The variation is significant for the 20.6 × 10^6 fraction but is practically negligible for the 8.42 × 10^6 fraction. A linear relationship is observed but it should be remarked that the temperature range investigated is extremely limited. Nyström and Roots have reported a similar dependence on the polystyrene–*trans*-decalin system[16] and compared their results with the various theoretical predictions of Puyn-Fixman, Imai, Freed, and Yamakawa.[4] At any rate, the main point is that, k_s being reasonably well-known, it is possible to derive the asymptotic $S_0(T)$ value with a fairly good accuracy, typically 3%. The solvent viscosity $\eta_s(T)$ and density $\rho(T)$ have been measured independently to better than 1%. In first approximation, it can be said that $\bar{v}_2$,

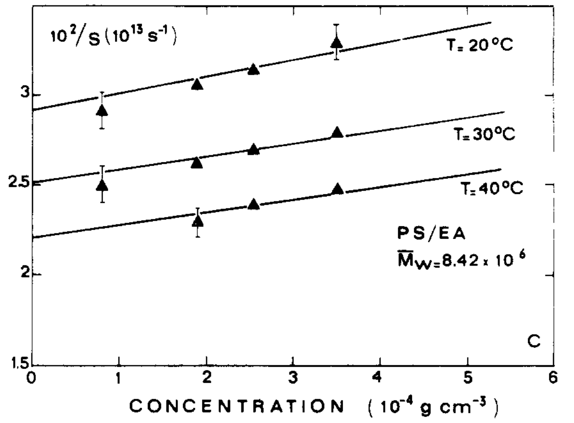

Figure 5. Concentration dependence of the inverse of the sedimentation coefficient for the 8.42 × 10^6 polystyrene fraction in ethyl acetate (Θ = −43.5 °C) at three different temperatures.

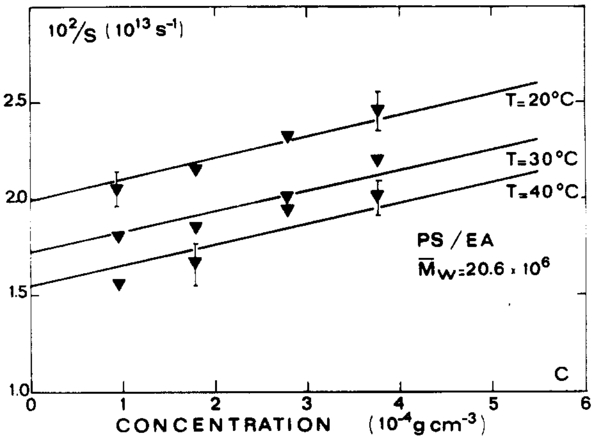

Figure 6. Same as Figure 5 but the 20.6 × 10^6 polystyrene fraction.

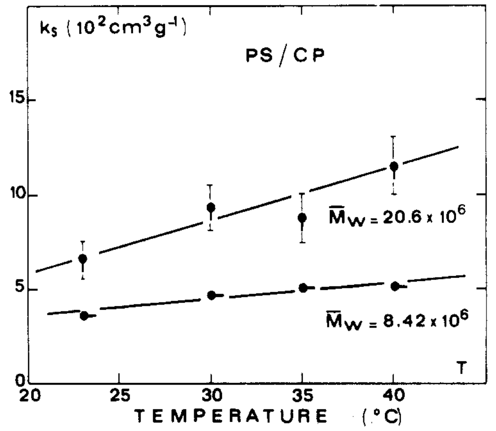

Figure 7. Temperature dependence of k_s, the parameter describing the concentration dependence of the sedimentation coefficient s. $1/s = 1/s_0(1 + k_sC)$. Two different polystyrene fractions—8.42 × 10^6 and 20.6 × 10^6—have been used. Solvent is cyclopentane.

the partial specific volume of the polymer, is little dependent on the nature of the solvent, on the polymer molecular weight, and on the actual temperature, at least above the Θ point. For polystyrene, $\bar{v}_2$ is generally taken to be equal to 0.91–0.93 cm^3/g.[17] However, in order to sustain equivalent accuracy for all the parameters contained in eq 1, a more refined analysis is proper here. The data by Pouyet et al.[18] indicate that, in good solvents, $\bar{v}_2$ decreases with polymer molecular weight above a limiting value of 4 × 10^4. This variation can be fitted empirically by $\bar{v}_2 = -2.78 \times 10^{-3} \log_e \bar{M}_w + 0.944$. This expression was

Table II
Sedimentation Velocity Data for Polystyrene in Various Solvents

$10^{-6}M_w$,	T, °C	$10^{13}S_0$ s	R_H, Å	α_H	N/N_τ[a]
	Cyclopentane (Θ = 23 °C)				
8.42	23.0	86.7	657	1	0
	26.0	88.4	668	1.01	0.8
	27.3	88.6	676	1.02	1.7
	28.3	88.6	684	1.04	2.5
	29.0	89.0	687	1.04	3.3
	30.0	88.2	701	1.06	4.4
	30.4	88.0	706	1.07	5.0
	32.0	90.2	702	1.06	7.3
	35.0	91.2	717	1.09	12.7
	35.0	89.7	730	1.11	12.7
	38.1	91.4	741	1.12	19.8
	40.0	93.1	743	1.13	24.8
	41.0	92.0	760	1.15	27.6
	42.0	93.6	755	1.14	30.6
20.6	23.0	137.2	1026	1	0
	25.2	140.8	1027	1.00	1.1
	26.0	138.5	1053	1.02	2.0
	27.3	141.2	1049	1.02	4.2
	29.0	138.5	1091	1.06	8.1
	30.0	137.3	1113	1.08	10.9
	30.4	141.7	1084	1.05	12.2
	35.0	144.3	1121	1.09	31.2
	36.0	141.2	1158	1.12	36.4
	38.1	142.4	1176	1.14	48.4
	40.0	144.8	1180	1.15	60.7
	41.0	140.7	1228	1.19	67.6
	42.0	142.1	1229	1.19	74.8
	n-Butyl Formate (Θ = −7.5 °C)				
8.42	9.8	24.3	759	1.14	31.4
	15.0	25.7	742	1.11	51.3
	20.0	28.9	814	1.22	74.1
	25.0	29.1	816	1.22	100.0
	30.0	30.3	849	1.27	128.8
	34.5	33.0	834	1.25	156.9
	39.7	34.7	857	1.29	191.6
20.6	9.8	36.7	1246	1.19	77.0
	15.0	37.9	1316	1.26	125.6
	20.0	40.6	1335	1.28	181.2
	25.0	42.7	1375	1.32	244.7
	30.0	43.3	1467	1.41	315.2
	34.5	48.6	1400	1.34	383.9
	37.0	47.2	1496	1.44	424.0
	39.7	49.9	1474	1.41	468.9
	40.0	48.9	1509	1.45	473.9
	42.0	50.4	1508	1.45	508.2
	Ethyl Acetate (Θ = −43.5 °C)				
8.42	8.4	29.1	897	1.35	286.4
	10.0	30.1	891	1.34	300.6
	19.0	34.0	918	1.38	385.3
	20.0	35.5	894	1.34	395.0
	30.0	39.8	932	1.40	494.9
	36.6	42.5	964	1.45	563.0
	36.8	44.1	931	1.40	565.7
	39.4	46.3	921	1.38	592.3
	39.8	45.3	947	1.42	596.5
	40.0	45.2	952	1.43	598.6
	40.0	46.3	928	1.40	598.6
20.6	8.4	41.9	1543	1.48	699.9
	20.0	50.1	1567	1.50	966.5
	30.0	60.3	1529	1.47	1210.9
	30.0	57.9	1585	1.52	1210.9
	32.2	63.7	1551	1.50	1266.1
	36.8	61.7	1632	1.57	1384.0
	39.0	60.8	1673	1.61	1440.4
	39.7	62.0	1672	1.60	1460.9
	40.0	64.5	1651	1.58	1464.6
	Toluene (Θ = −154 ± 9 °C)				
8.42	8.9	20.9	1118	1.68	2808.7
	20.0	24.8	1125	1.69	2966.4
	29.4	27.9	1148	1.72	3093.9
	35.0	30.6	1132	1.70	3167.5
	40.2	31.8	1170	1.76	3234.1
20.6	9.9	31.3	1881	1.81	6907.2
	14.5	33.4	1891	1.82	7068.7
	20.0	36.9	1891	1.82	7257.5
	30.0	41.5	1920	1.84	7589
	33.5	42.9	1956	1.88	7701.7
	41.8	47.5	1980	1.90	7962

[a] The reduced blob parameter N/N_τ is calculated from $\bar{M}_w\tau^2/1000$, as discussed in the text. [b] In toluene, ethyl acetate, and *n*-butyl formate the hydrodynamic expansion factor $\alpha_H = R_H(T)/R_H(\Theta)$ is calculated by taking $R_H(\Theta) = 1039$ Å for the 20.6×10^6 fraction and $R_H(\Theta) = 664$ Å for the 8.42×10^6 fraction.

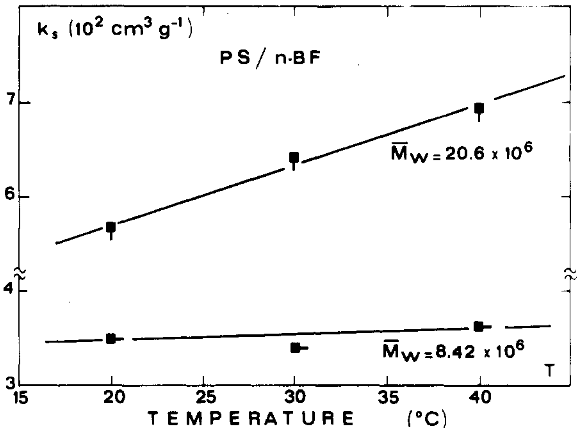

Figure 8. Same as Figure 7 but for polystyrene in *n*-butyl formate.

therefore used to calculate $\bar{v}_2$ for our own samples. At T = 20 °C, we obtain $\bar{v}_2 = 0.8985$ and 0.896 for the 8.42 × 10^6 and 20.6 × 10^6 fractions, respectively. Similarly, in Θ solvents, the same authors[18] indicate that two different expressions have to be used according to the sample molecular weight is higher or lower than approximately 2 × 10^5. Empirical fits yield $\bar{v}_2 = -1.94 \times 10^{-3} \log_e \bar{M}_w + 0.95$ below 2 × 10^5 while $\bar{v}_2 = -4.89 \times 10^{-3} \log_e \bar{M}_w + 0.99$ above. Since all our molecular weights are in the 10^7 range, this last expression was selected to calculate $\bar{v}_2$ for our samples. At $T = \Theta$, $\bar{v}_2$ is found to be 0.910 and 0.905 for the 8.42 and 20.6 × 10^6 molecular fractions, respectively. The two data are very close to each other. However, they differ markedly from the value of 0.934, generally accepted in the literature for polystyrene in cyclohexane[17] and which is only correct at very low molecular weight. The temperature dependence of $\bar{v}_2$ should also be taken into consideration. From the data of Sarazin and François,[17] the temperature coefficient $\alpha = (1/\bar{v}_2)\,(\mathrm{d}\bar{v}_2/\mathrm{d}T)$ can be taken as 2.5 × 10^{-4} for good solvents and 8.8 × 10^{-4} for Θ solvents (at least if we exclude a narrow region corresponding to the onset of the demixtion and where the variations become strongly nonlinear). The changes of $\bar{v}_2$ over a 20 °C temperature interval represent therefore a 2% variation in Θ solvents. For good solvents, it is only a relatively weak effect, 0.5% at the most.

All numerical results have been reported in Table II. The quantity of interest for a check of the various theories is, however, not $R_H(T)$ but rather the ratio $\alpha_H(T) = R_H(T)/R_H(\Theta)$. This requires the knowledge of $R_H(\Theta)$. Unfortunately, it was not possible with our apparatus to directly measure $S_0(\Theta)$, and thus $R_H(\Theta)$, for the *n*-butyl

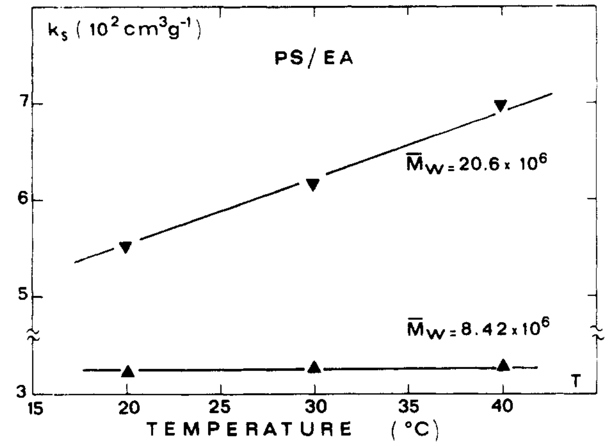

Figure 9. Same as Figure 7 but for polystyrene in ethyl acetate.

formate, ethyl acetate, and toluene solutions. Indeed the lowest temperature accessible with our Spinco model E ultracentrifuge is of the order of 0 °C, which is much higher than the actual Θ temperatures of these three polymer solutions. To solve this difficulty, we have calculated the $R_H(\Theta)$ value of polystyrene in these solvents from the formula $R_H(\Theta) = 0.229\bar{M}_w^{1/2}$ Å proposed by Schmidt and Burchard[19] from a compilation of most of the existing data for the hydrodynamic radius of polystyrene in many Θ solvents. It is generally accepted that coil dimensions in the ideal Θ state are not much dependent on the exact nature of the solvent. This simple rule, however, excludes mixed Θ solvents, for which complex behaviors have been mentioned.[20]

This semiempirical procedure leads to $R_H(\Theta) = 1039$ Å for the 20.6×10^6 fraction and to $R_H(\Theta) = 664$ Å for the 8.42×10^6 fraction. Both values are in good agreement (to better than 1%) with our direct measurement of $R_H(\Theta)$ for polystyrene in cyclopentane (see Table II).

The ratio $\alpha_H(T) = R_H(T)/R_H(\Theta)$ has then been calculated and reported in column 5 of Table II. For each α_H, the corresponding N/N_τ has been derived from the formula $N/N_\tau = \bar{M}_w\tau^2/n\alpha M_0$ proposed by Akcasu and Han[6] for polystyrene in cyclohexane. $n\alpha$ is an adjustable parameter which cannot be derived from first principles. A value $n\alpha = 9.62$ has been assumed here for reasons which will be discussed at length in the following. M_0 is the monomer molecular weight (for polystyrene, $M_0 = 104$). τ is the reduced temperature defined by $\tau = 1 - \Theta/T$.

N/N_τ can be simply related to the well-known z parameter of the two-parameter theories. Indeed N/N_τ is proportional to z^2 since the equation for z is[8]

$$z = 4\pi\left(\frac{\langle R_G^2\rangle_\Theta}{\bar{M}_w}\right)^{-3/2}\left(\frac{\bar{M}_w^{1/2}}{\bar{M}_0^2}\right)v \qquad (2)$$

v is the binary cluster integral and contains the whole temperature dependence of z. A linear relationship with τ is generally assumed and therefore $v = v_\infty\tau$, where v_∞ is a constant.

Although both N/N_τ and z are not directly measurable parameters, z can be calculated, at least in principle, from equilibrium light scattering. The method, first proposed by Miyaki and Fujita,[8] is based on the comparison between the experimental data for the static expansion factor α_G and the Domb asymptotic relation $\alpha_G^2 = 1.53z^{2/5}$ derived from computer data on self-avoiding lattice chains.[21] For polystyrene in cyclohexane, it was proposed that $z = 6.25 \times 10^{-3}(\bar{M}_w\tau^2)^{1/2}$. For polystyrene in benzene, the measurements were performed at a single temperature, $T = 25$ °C, at which $z = 2.60 \times 10^{-3}\bar{M}_w^{1/2}$. For polystyrene in other solvents such as ethyl acetate, n-butyl formate, and cyclopentane, it is probably a good approximation, in the absence of more precise data, to use the same formula as for cyclohexane. The implicit assumption is that $\langle R_G^2\rangle_\Theta/\bar{M}_w$ and v_∞ are independent of the nature of the solvent for a given polymer. Schmidt and Burchard have indeed shown that $\langle R_G^2\rangle_\Theta/\bar{M}_w = 8.8 \times 10^{-2}$ Å^2 mol g^{-1}, to an accuracy of ±2%, over a large range of solvents.[19] Similarly v_∞ is probably not much dependent on the solvent since it basically corresponds to the volume associated with the Kuhn length, a quantity mainly governed by the local chain flexibility and the steric hindrances to bond rotations.

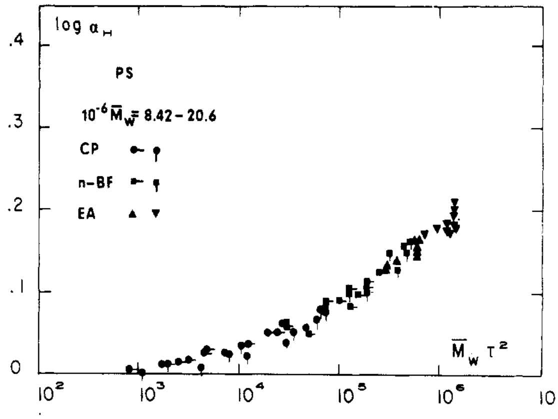

Figure 10. Logarithmic plot of the hydrodynamic expansion factor $\alpha_H(T) = R_H(T)/R_H(\Theta)$ as a function of the parameter $\bar{M}_w\tau^2$ for two polystyrene fractions (8.42×10^6 and 20.6×10^6) in three different solvents. In each case, the data points have been obtained by changing the temperature. Temperature range is 23–42 °C for cyclopentane (Θ = 23 °C), 9–42 °C for n-butyl formate (Θ = −7.5 °C), 8–40 °C for ethyl acetate (Θ = −43.5 °C).

The data for the polystyrene solutions in the three solvents with well-defined Θ temperatures (i.e., ethyl acetate, n-butyl formate, and cyclopentane) have been plotted in Figure 10 as log α_H vs. log $\bar{M}_w\tau^2$. The data points covering the range of $\bar{M}_w\tau^2$ between 3×10^4 and 5×10^5 correspond to the 20.6×10^6 and 8.42×10^6 polystyrene fractions in n-butyl formate (Θ = −7.5 °C) at temperatures between 9.5 and 42 °C. Those covering the range between 3×10^5 and 1.5×10^6 correspond to the same fractions in ethyl acetate (Θ = −43.5 °C) at temperatures between 8 and 40 °C. Those covering the range between 1×10^3 and 8×10^4 correspond to our earlier results of ref 1 for the same two polystyrene fractions in cyclopentane (Θ = 23 °C) and at temperatures between 23 and 43 °C. These later data have, however, been reanalyzed here to account for (i) the concentration dependence (k_s) of the sedimentation coefficient, (ii) the temperature dependences of the solvent density and of the partial specific volume, and (iii) the molecular weight dependence of the partial specific volume.

It is most striking that all the data obtained with the three different solvents superimpose in the regions where the respective $\bar{M}_w\tau^2$ overlap. This is a strong indication of a universal behavior, irrespective of the exact nature of the solvent, for the thermal expansion of the hydrodynamic radius above the Θ conditions. We thus obtain the same behavior, for the hydrodynamic expansion factor, as obtained previously by Miyaki and Fujita for the static expansion factor.[8] Indeed they were able, on a log α_G vs. log $\bar{M}_w$ plot, to bring all the data points for polystyrene in different solvents on a single line by proper horizontal shifting. It should be remarked, however, that here the superposition is achieved directly, since we are using $\bar{M}_w\tau^2$ as the variable instead of $\bar{M}_w$ alone. We have already

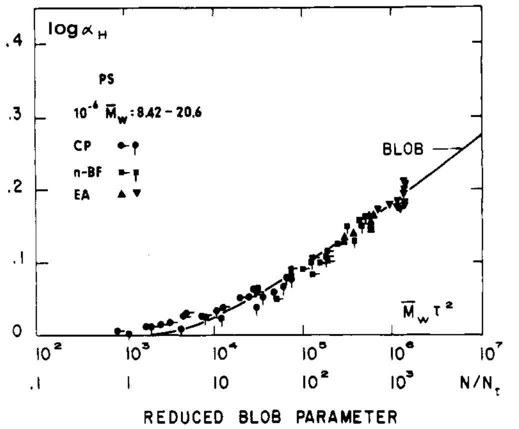

Figure 11. Same as Figure 10 but the solid curve corresponding to the thermal blob theory of Akcasu–Han and Weill–des Cloizeaux[6] has now been added. The best fit was obtained by taking $N/N_\tau = \bar{M}_w\tau^2/n\alpha M_0$ with $n\alpha M_0 = 1000 \pm 50$.

mentioned that $\bar{M}_w\tau^2$ is proportional to the reduced blob parameter N/N_τ. Our results imply that the proportionality factor is a constant for a given polymer, irrespective of the nature of the solvent, at least for the solvents investigated here. Even more important, the fact that α_H is a universal function of N/N_τ (or z^2) confirms the success of the two-parameter theory for molecular properties of linear flexible chains in solution.

Many expressions for $\alpha_H(z)$ have been suggested in the literature. However, for a long while, there was no definite conclusion on a closed expression over a wide range of z for the dynamic expansion factor. The first-order perturbation formula of Stockmayer and Albrecht was only valid at low z values.[3] The α^5 type equation of Flory was based on purely empirical grounds.[4] Our experiments presented in ref 1 have indeed confirmed that both of these approaches were inadequate except over limited ranges of z. In the following we will now compare our data with two different equations which have been recently proposed. The first, due to Weill–des Cloizeaux and Akcasu–Han, is based on the thermal blob description of a polymer chain in the vicinity of a Θ point.[6] The second, due to Tanaka, uses Padé approximants to construct a closed formula which incorporates the first few exact perturbation coefficients for α_H and also rejoins the asymptotic form $\alpha_H \sim z^{1/5}$ at large z.[14]

Let us start with the equation of the thermal blob model. It can be written as[6]

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

where $x^{-1} = N/N_\tau$ and $\nu = {}^3/_5$. The asymptotic behavior for large N/N_τ is

$$\alpha_H(x) = 0.747(N/N_\tau)^{0.1} \qquad (4)$$

We have represented eq 3 as a solid curve on Figure 11. As mentioned previously, N/N_τ is only known to a proportionality factor and therefore, in a log α_H vs. log N/N_τ representation, the whole curve may be shifted horizontally to the left or to the right until the best agreement with experimental data is obtained. The data points of Figure 10 have also been reported here as a function of $\bar{M}_w\tau^2$. It is clearly apparent that a very close fit is obtained when taking $N/N_\tau = \bar{M}_w\tau^2/1000$. The agreement is quite good for N/N_τ between 10 and 10^3 but tends to deteriorate below 10. The coefficient is probably exact to 5%. Returning to the expression $N/N_\tau = \bar{M}_w\tau^2/n\alpha M_0$ proposed originally by Akcasu and Han, we thus obtain $n\alpha = 9.62$. This justifies a posteriori why this particular $n\alpha$ value was chosen in our calculations of N/N_τ in Table II.

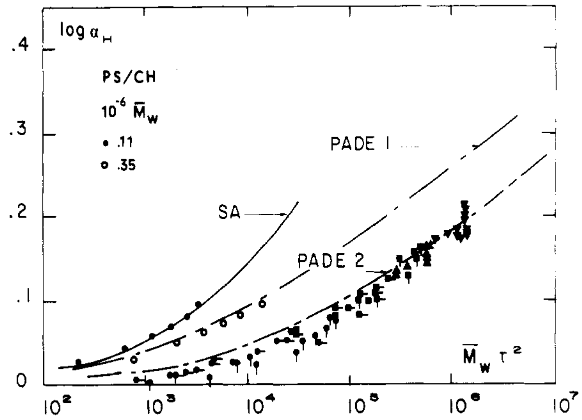

Figure 12. Same as Figure 10 but the curves corresponding to the first-order perturbation theory of Stockmayer–Albrecht (SA, ref 3) and to the Padé approximants of Tanaka (Padé I and Padé II, ref 14) have now been plotted. Two sets of data points obtained by Novotny[26] with low molecular weight polystyrene (110 000 and 355 000) in cyclohexane have also been added.

Our experimental finding that α_H is a universal function of $\bar{M}_w\tau^2$ and is independent of the nature of the solvent, at least for a given polymer, is by no means a straightforward result. It first implies that, in the temperature range investigated, the excluded-volume parameter z is a linear function of $\tau = 1 - \Theta/T$. In principle this should only be true at small τ, that is to say in the vicinity of the Θ point. Here, with ethyl acetate we have worked as far as 83 °C above the Θ temperature and it was not obvious from the beginning that a linear relationship would still be true at such large τ. A critical reading of the literature seems nevertheless to confirm our present observation. Miyaki and Fujita have observed $z \sim \tau$ even 20 °C above Θ for polystyrene in cyclohexane and 40 °C above Θ for polyisobutylene in isoamyl isovalerate.[8] Pritchard and Caroline[22] data on polystyrene in cyclohexane can also be adjusted with $\alpha_H^5 = 1 + B'(\bar{M}_w\tau^2)^{1/2}$ over a range of Θ + 30 °C.

Second, our experimental finding of a universal behavior for α_H also implies that the excluded-volume parameter can be written as $z = K(\bar{M}_w\tau^2)^{1/2}$ with K independent of the nature of the solvent and of temperature. From eq 2 we know that K is related to the product of $\langle R_G^2\rangle_\Theta/\bar{M}_w$ times v_∞. Therefore, we are lead to say from our results that both $\langle R_G^2\rangle_\Theta/\bar{M}_w$ and v_∞ are constants for a given polymer. We have already discussed why this is probably true to a good approximation and have mentioned supporting experimental evidence for polystyrene in a variety of Θ solvents.[19] The temperature dependence is also weak because the hindrance to bond rotation is not affected by temperature changes lower than the corresponding energy barrier.

In comparison with the eq 3 of the thermal blob model, the equation proposed by Tanaka in the framework of Pade approximants[14] is much simpler:

$$\alpha_H^5 = 1 + 3.045z \qquad (5)$$

The prefactor for z has been chosen such that at low z eq 5 yields the perturbation formula of Stockmayer and Albrecht[3] which is exact to first order:

$$\alpha_H = 1 + 0.609z \qquad (6)$$

Equation 5 has been plotted on Figure 12 as a dot–dash line (Padé I). For comparison, eq 6 has also been plotted as a solid curve (SA). The parameter z was taken as $z = 6.25 \times 10^{-3}(\bar{M}_w\tau^2)^{1/2}$ according to Miyaki and Fujita[8] and

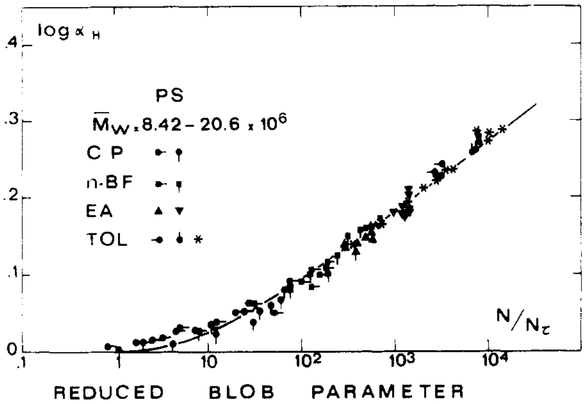

Figure 13. Same as Figure 10 but the data points for polystyrene in toluene have now been added. The Θ-temperature for this system has been taken as −154 °C (see text). The data points for the 8.42 × 10^6 and 20.6 × 10^6 fractions are from this work (−•, ↓). Results by Appelt and Meyerhoff[13] for several fractions between 12.3 × 10^6 and 40.2 × 10^6 have also been plotted (*).

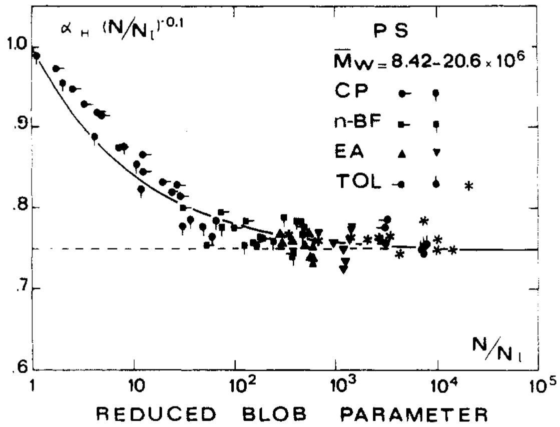

Figure 14. Variation of $\alpha_H(N/N_\tau)^{-0.10}$ as a function of the reduced blob parameter N/N_τ in semilog scales. The data points are the same as in Figure 13. Note that, for $N/N_\tau > 80$, the experimental points fall on a horizontal line, which intercepts the ordinate axis at $\alpha_H(N/N_\tau)^{-0.10} = 0.75 \pm 0.02$. The solid curve corresponds to the thermal blob theory by Akcasu-Han and Weill-des Cloizeaux.[6]

there is therefore no adjustable parameter. We see immediately that the theoretical curve (Padê I) does not provide a good description of our experimental data. In an attempt to improve the quality of the fit, we have floated the front factor in the expression for z. Lowering its value to 1.15 × 10^{-3}, i.e., by more than a factor 5, improves the agreement with the high $\bar{M}_w\tau^2$ data but falls short of describing the low $\bar{M}_w\tau^2$ data (see curve Padê II). Therefore, it seems that a single expression cannot fit the whole range of data.

This being known, we can now return to the thermal blob model and try to discuss the data obtained with the toluene–polystyrene solutions. This is an interesting system to study because it is practically athermal around room temperature. Flory and Fox[12] have quoted its Θ temperature to be −113 °C from an analysis of earlier literature data for intrinsic viscosity. Unfortunately, they had to perform a rather long extrapolation on the temperature scale since all experiments were performed around room temperature. Consequently, the uncertainty on this Θ determination was large, typically 50 °C. Recently, Bianchi and Magnasco,[23] using the same procedure on well-characterized molecular fractions, have quoted a value of Θ = −136 °C. At any rate, since the Θ temperature is very low, τ can be considered as a constant for polystyrene–toluene solutions when varying the temperature between 8 and 42 °C, as in our experiments. If τ is a constant, that means that N_τ is also a fixed parameter, independent of temperature. For our two samples of 8.42 × 10^6 and 20.6 × 10^6, we have forced our experimental points for the hydrodynamic expansion factor of polystyrene coils in toluene to lay on the master curve of the thermal blob theory (see Figure 13). This yields an estimation of N/N_τ around room temperature. We find $N/N_\tau = 3000 \pm 200$ and 7500 ± 500 for the 8.42 × 10^6 and 20.6 × 10^6 polystyrenes, respectively. From this, we calculate that $N_\tau \simeq 27$, i.e., we infer that a single blob contains about 27 monomer units. Using this N_τ value at 20 °C, we can analyze the sedimentation data obtained by Appelt and Meyerhoff[13] for polystyrene in toluene at 20 °C and over an extensive range of molecular weights. We have plotted them together with our own data in Figure 13. This allows us to extend the experimental range of N/N_τ up to an impressive value of 15000. We observe that the agreement with the theoretical curve of the blob model is very good. As a last step, we can therefore try and estimate the Θ temperature of our polystyrene–toluene solutions. Taking N_τ to be of the order of 27 and assuming that the relationship $N/N_\tau = \bar{M}_w\tau^2/1000$ is still obeyed with toluene, we obtain Θ = −154 ± 9 °C. This procedure is obviously very risky since it assumes that N/N_τ is a linear function of τ over an enormous span of temperatures. Nevertheless, there is a surprising close agreement between this Θ value and the literature data quoted above.

Since all the data obtained with polystyrene in cyclopentane, n-butyl formate, ethyl acetate, and possibly toluene can be merged into a unique master curve, it seems reasonable to assume that the temperature and molecular variations of the hydrodynamic expansion factor α_H is a universal function of the reduced parameter N/N_τ. This is in agreement with the thermal blob theory. Moreover, the Θ value derived for toluene solutions using a fit between the experimental data and the theory is close to the best estimate found in the literature for polystyrene–toluene solutions.

As suggested in ref 1, the asymptotic regime is observed to set in for N/N_τ values larger than 80. In Figure 14, we have plotted $\alpha_H(N/N_\tau)^{-1/10}$ as a function of N/N_τ in semilog scales. It is apparent that the points above $N/N_\tau = 80$ fall on a horizontal line parallel to the abscissa axis. The intercept with the ordinate axis corresponds to 0.75 ± 0.02. Therefore all these data can be described with a master curve of the type $\alpha_H = 0.75(N/N_\tau)^{1/10}$. This is in good agreement with the thermal blob theory which states $\alpha_H = 0.747(N/N_\tau)^{1/10}$ for $N \gg N_\tau$.[6] We thus demonstrate that the asymptotic regime can indeed be reached for dynamic variables in polymer solutions. The solid line in Figure 14 corresponds to the complete theoretical curve according to Ackasu-Han and Weill-des Cloizeaux.[6]

It is observed however that the agreement breaks down in the nonasymptotic regime for N/N_τ lower than 30. This comes as no surprise since it cannot be overemphasized that the thermal blob theory is only valid in the large N/N_τ limit. At low N/N_τ values, it does not even converge to the exact first-order perturbation results. As pointed out by several authors, the transition between Gaussian and excluded-volume statistics is indeed much too abrupt. Moreover, the blob model neglects the fact that the statistics between two monomers i and j along the chemical sequence is a function not only of $|i - j|$ but also of the positions of i and j. This has been shown conclusively by several authors using Monte Carlo simulations[24] and also much earlier by Kurata and Yamakawa using perturbation calculations.[25] It remains, however, that the blob theory provides an easy physical picture to the progressive transition of a flexible chain between its ideal, Gaussian, state and its swollen, excluded-volume, state. In view of its crudeness, the model provides a surprisingly good description of the experimental data, probably better than any other theory proposed so far. For some yet unexplained reasons, it appears that for very large chains the onset of the transition is more abrupt than expected from perturbation theories. This should be a subject of further investigation. On the contrary, we have already mentioned in ref 1 that the transition becomes more and more progressive as the sample molecular weight is decreased. This has been confirmed recently by Novotny with polystyrene of M_w = 110 000 and 355 000.[26] The corresponding data point have been plotted on Figure 12. The influence of molecular weight is observed without ambiguity. It has been proposed that the large differences in the α_H values for a given $\bar{M}_w\tau^2$ are related to partial free draining, which is more pronounced with smaller chains. Numerical results by Ullman show that the polymer molecule becomes truly impermeable at extremely high molecular weight ($\sim 10^7$) but is far from the limit in the lower molecular weight range ($<3 \times 10^6$).[27] It may also be due to more subtle effects related to the tricriticality of the Θ point. On the other hand, the fact that the Novotny data for the 110 000 sample falls on the Stockmayer and Albrecht (SA) curve and that those for the 355 000 sample fall on the Tanaka curve (Padê I) is probably accidental.

The present measurements of the dynamic expansion factor α_H allow us to attribute a value of 1000 ± 50 to the $n\alpha M_0$ numerical coefficient in the expression for $N/N_\tau = \bar{M}_w\tau^2/n\alpha M_0$. This determination is at variance with the evaluation $n\alpha M_0 = 416$ first derived by Akcasu and Han[6] and also used in our earlier work.[1] This value was based on a fit between the thermal blob theory and the *static* expansion factor α_G measured in polystyrene–cyclohexane solutions. It is our opinion, however, that the scarcity of data available at that time precluded accurate determinations. In addition, the Θ temperature which could be estimated from the fit was found to be −50 and −41 °C for polystyrene–benzene and polystyrene–toluene solutions, respectively. We have shown in the Experimental Section that at least in the case of toluene this estimation is incorrect. In view of all these difficulties, we have tried to repeat the Ackasu and Han procedure on a wider compilation of experimental α_G values, namely for cyclohexane, *trans*-decalin, and toluene solutions. For the first two solvents, we use the Θ temperatures measured independently in the present paper. For the last one we use our indirect determination Θ = −154 °C. All the data points have been reported on Figure 15. The data in cyclohexane have been taken from Smith and Carpenter[28] and from Slagowski et al.[29] The two points in *trans*-decalin have been measured by Nose and Chu.[30] The data in toluene are from Appelt and Meyerhoff.[13] If we except the data points of Slagowski in cyclohexane which seem too high, all the other points seem to merge into a master curve, when using the variable $\bar{M}_w\tau^2$ (or equivalently N/N_τ). On Figure 15, we have also drawn as a solid line the predictions of the thermal blob theory for the static expansion factor α_G. According to ref 31

$$\alpha_G{}^2(x) = x^2(3 - 2x) + 6x^{1-2\nu}\frac{1 - x^{2\nu+1}}{2\nu + 1} - \frac{1 - x^{2(\nu+1)}}{2(\nu + 1)} \tag{7}$$

where $x = N/N_\tau$ and $\nu = 3/5$. The asymptotic behavior for large N/N_τ is

$$\alpha_G(x) = 0.923(N/N_\tau)^{0.1} \tag{8}$$

To make the plot, the proportionality coefficiency $n\alpha M_0$ between N/N_τ and $\bar{M}_w\tau^2$ has been taken to be 1000, i.e.,

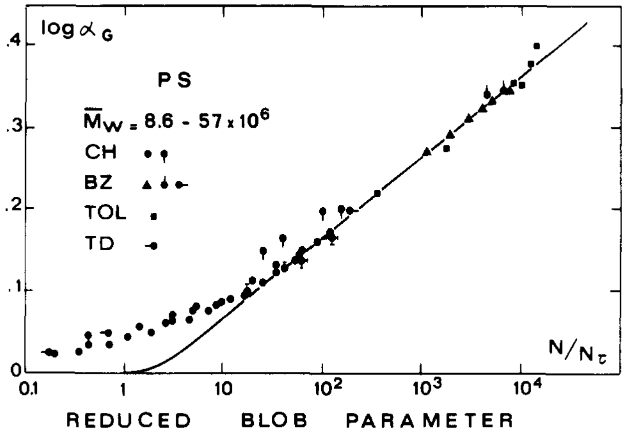

Figure 15. Logarithmic plot of the static expansion factor $\alpha_G(T) = R_G(T)/R_G(\Theta)$ as a function of the reduced blob parameter $N/N_\tau = \bar{M}_w\tau^2/1000$. The data points correspond to a compilation of the literature for very high molecular weight polystyrenes ($\bar{M}_w$ = (8.6–57) × 10^6). Data points for cyclohexane (Θ = 35 °C) are from Slagowski et al.[29] and Miyaki et al.[8] Those in benzene (Θ = −82 °C, see text) are from Miyaki et al.,[8] Slagowski et al.,[29] and Smith et al.[28] Those in toluene (Θ = −154 °C, see text) are from Appelt and Meyerhoff.[13] Those in *trans*-decalin (Θ = 20 °C) are from Nose and Chu.[30]

exactly the value derived from the dynamic case. The agreement with the experimental data is striking, especially in view of the fact that there is no longer any adjustable parameter. To the best of our knowledge this is the first time that such a correspondence between dynamic and static data is achieved and it was certainly not present in Han and Ackasu's work.

In addition, we have plotted on Figure 15 some data points obtained in benzene solutions by Miyaki and Fujita[8] and Smith and Carpenter.[28] Since they were obtained on very high molecular weight samples they fall well into the asymptotic regime and the α_G variation with molecular weight obeys the $N^{0.1}$ power law of eq 6. However, the Θ temperature for benzene–polystyrene solutions, and hence N_τ is unknown. Therefore, we have shifted the points horizontally until they fit with the master curve. This procedure is similar to the one used in the case of the dynamic expansion factor of toluene solutions. From the amount of shift we deduce that Θ should be the order of −80 °C. By comparison, Fox and Flory[12] indicate a value of −160 °C but with a large uncertainty due to the fact that benzene solidifies at +5.5 °C and therefore the Θ temperature can only be obtained from hazardous extrapolations.

It may seem disturbing that the Θ temperatures obtained by our method for the toluene and benzene solutions are so widely different. The common belief is that both solvents behave as equally good solvents for polystyrene chains. However, this is not quite borne out by the most recent data on very large molecular weight chains (which are the ones of interest to us in the present experiments). Miyaki and Fujita indicate that R_G(*z*-average) = 1.21 × $10^{-2}M^{0.595\pm0.05}$ nm for benzene solutions at 25 and 30 °C, based on their data and corroborated by several others.[8] On the other hand, Appelt and Meyerhof indicate that R_G(*z*-average) = 1.27 × $10^{-2}M^{0.605}$ nm for toluene solutions at 20 and 25 °C.[13] There is therefore a 5–15% difference in the molecular sizes for polystyrene chains in these two solvents, toluene appearing to be a slightly better solvent. It cannot be overemphasized that these relatively minute differences can only be detected in very accurate measurements. In that respect, it is satisfying that the Appelt and Meyerhof data for the sedimentation coefficient of polystyrene chains in both toluene and cyclohexane agree with our own data to better than 2% (see eq 11a and 11b of ref 13). Returning to the static expansion factor, it can therefore be said that for a given molecular weight $\bar{M}_w$, α_G will be larger for polystyrene chains in toluene than in benzene. We have assumed here, and this is indeed supported by Schmidt and Burchard,[19] that R_G is identical at the Θ point in both solvents. This difference in α_G, as slight as it might be, has a profound influence on the N_τ value and thus on τ. Indeed, according to eq 6, N/N_τ depends on α_G with a very large power $N/N_\tau = 0.923^{-1}\alpha_G^{10}$. An increase in α_G by 5%, 10%, and 15% from its actual value in benzene solution will shift the Θ temperature from -80 to -100, -135, and -176 °C, respectively. The absolute values quoted here should not be taken too much for granted, and we have already emphasized in the discussion for the case of toluene that rather severe assumptions are involved in our procedure. However, the trend is clear and it seems that the Θ temperature for toluene solutions is lower than that for benzene. It could be interesting to check carefully this point in future work.

In conclusion we can say that, using a combination of data obtained at fixed molecular weight and variable temperatures in Θ solvents and at variable molecular weights and fixed temperature in good solvents, we have been able to explore a large range of the reduced parameter $N/N_\tau(1 - 10^4)$. In the thermal blob theory, N/N_τ describes the number of Gaussian subunits (blobs) contained in a single chain. For N/N_τ around unity, the chain contains essentially a single blob and thus obeys Gaussian statistics. For N/N_τ above 80, the chain contains a sufficient number of blobs to exhibit excluded-volume statistics on a macroscopic scale. For polystyrene coils, the variation of the dynamic expansion coefficient α_H with temperature and molecular weight is found to quantitatively obey the master equation predicted by the blob model. The reduced blob parameter N/N_τ depends on the reduced temperature τ and the molecular weight $\bar{M}_w$ as $\bar{M}_w\tau^2$. The coefficient of proportionality is equal to $(1000 \pm 50)^{-1}$. Analysis of the literature data for the static expansion factor yields results coherent with these findings. This is the first time that a universal curve is shown to correctly describe the dynamic expansion coefficient of polystyrene over a large range of $N/N_\tau(1 - 15\,000)$ and in four different solvents (cyclopentane, *n*-butyl formate, ethyl acetate, and toluene). Miyaki and Fujita in their measurements of the viscosity expansion factor $\alpha_\eta^3 = (\eta)_T/(\eta)_\Theta$ have found[8] that not all their data points obtained for polystyrene in benzene, methyl ethyl ketone, and cyclohexane can be superimposed on a single curve. It is worth pointing out that this important fact was already present in an earlier compilation of data by Han[32] but had been overlooked. Berry had also signaled similar findings as early as 1966.[33] Since we have no reason to suspect the accuracy of the viscosity data, this discrepancy should be a subject of further investigation.

Acknowledgment. We thank J. Malthête for the distillation and characterization of *n*-butyl formate and S. Boileau and P. Hemery for their help in handling extra pure toluene for the demixtion experiment at very low temperatures. We acknowledge the technical assistance of C. Sauterey for the viscosity and density measurements. (P.V.) has benefited from a scholarship of the Joliot-Curie Foundation.

Registry No. PS (homopolymer), 9003-53-6.

References and Notes

(1) Vidakovič, P., Rondelez, F. *Macromolecules* **1983**, *16*, 253.

(2) Flory, P. J. "Principles of Polymer Chemistry"; Cornell University Press: Ithaca, NY, 1971. There are weak logarithmic corrections to ideality which are important theoretically but unobservable in practice. For a recent review see, for example: Duplantier, B., *J. Phys. (Orsay, Fr.)* **1982**, *43*, 991 and references therein.

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

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

(5) Daoud, M.; Jannink, G. *J. Phys. (Orsay, Fr.)* **1976**, *37*, 973.

(6) Akcasu, A. Z.; Han, C. C. *Macromolecules* **1979**, *12*, 276. Weill, G.; des Cloizeaux, J. *J. Phys. (Orsay, Fr.)* **1979**, *41*, 99.

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

(8) See, for example: ref 4 and also Miyaki, Y.; Fujita, H. *Macromolecules* **1981**, *14*, 742.

(9) Debye, P.; Bueche, P. *J. Chem. Phys.* **1948**, *16*, 573.

(10) Schulz, G. V.; Baumann, H. *Makromol. Chem.* **1963**, *60*, 120.

(11) Saeki, S.; Konno, S.; Kuwahara, N.; Nakata, M.; Kaneko, M. *Macromolecules* **1974**, *7*, 521.

(12) Fox, T. G.; Flory, P. J. *J. Am. Chem. Soc.* **1951**, *73*, 1915.

(13) Appelt, B.; Meyerhoff, G. *Macromolecules* **1980**, *13*, 657.

(14) Tanaka, G. *Macromolecules* **1982**, *15*, 1028.

(15) Riddick, J. A.; Bunger, W. B. In "Techniques of Chemistry: Organic Solvents"; Weissberger, A., Ed.; Wiley: New York 1970; Vol. II.

(16) Nyström, B.; Roots, J. *Eur. Polym. J.* **1978**, *14*, 551.

(17) "Polymer Handbook"; Brandrup, J., Immergut, E. H., Eds.; Wiley: New York, 1975. Sarazin, D.; François, J. *Polymer* **1978**, *19*, 699.

(18) Pouyet, G.; Candau, F.; Dayantis, J. *Makromol. Chem.* **1976**, *177*, 2973.

(19) Schmidt, M.; Burchard, W. *Macromolecules* **1981**, *14*, 210.

(20) See, for instance: Munk, P.; Guttierez, B. O. *Macromolecules* **1979**, *12*, 467. Munch, J. P.; Herz, J.; Boileau, S.; Candau, S. *Macromolecules* **1981**, *14*, 1370 and references therein.

(21) Domb, C.; Barrett, A. J.; Lax, M. *J. Phys. A: Math. Gen.* **1973**, *6*, L-82.

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

(23) Bianchi, U.; Magnasco, V. *J. Polym. Sci.* **1959**, *41*, 177.

(24) Wall, F. T.; Erpenbeck, E. J. *J. Chem. Phys.* **1959**, *30*, 634, 637. Alexandrowitz, Z.; Accad, Y. *Macromolecules* **1973**, *6*, 251. Schaeffer, D. W.; Curro, J. G. *Ferroelectrics* **1980**, *30*, 49; *Macromolecules* **1980**, *13*, 1199.

(25) Kurata, M.; Yamakawa, H.; Teramoto, E. *J. Chem. Phys.* **1958**, *28*, 785. Kurata, M.; Yamakawa, H.; Teramoto, E. *J. Chem. Phys.* **1958**, *29*, 311.

(26) Novotny, V. J. *J. Chem. Phys.* **1983**, *78*, 183.

(27) Ullman, R. *Macromolecules* **1981**, *14*, 746.

(28) Smith, T. E.; Carpenter, D. K. *Macromolecules* **1968**, *1*, 204.

(29) Slagowski, E.; Tsai, B.; McIntyre, D. *Macromolecules* **1976**, *9*, 687.

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

(31) Farnoux, B.; et al. *J. Phys. (Orsay, Fr.)* **1978**, *39*, 77.

(32) Han, C. C. *Polymer* **1979**, *20*, 1083.

(33) Berry, G. C. *J. Polym. Sci., Part B* **1966**, *4*, 161.