(4) Mattice, W. L. *Macromolecules* **1981**, *14*, 143.
(5) Mattice, W. L. *Macromolecules* **1982**, *15*, 1633.
(6) Mansfield, M. L.; Stockmayer, W. H. *Macromolecules* **1980**, *13*, 1713.
(7) Fixman, M. *J. Chem. Phys.* **1955**, *23*, 1656.
(8) Mazur, J.; McCrackin, F. *Macromolecules* **1977**, *10*, 326.
(9) Mattice, W. L. *Macromolecules* **1983**, *16*, 1623.
(10) McCrackin, F. L.; Mazur, J. *Macromolecules* **1981**, *14*, 1214.
(11) Abe, A.; Jernigan, R. L.; Flory, P. J. *J. Am. Chem. Soc.* **1966**, *88*, 631.
(12) Mattice, W. L. *Macromolecules* **1975**, *8*, 644.
(13) Mattice, W. L. *Macromolecules* **1981**, *14*, 1485.
(14) Mattice, W. L. *Macromolecules* **1981**, *14*, 1491.
(15) Roovers, J.; Bywater, S. *Macromolecules* **1972**, *5*, 384.
(16) Roovers, J.; Bywater, S. *Macromolecules* **1974**, *7*, 443.
(17) Hadjichristidis, N.; Roovers, J. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 2521.
(18) Roovers, J.; Hadjichristidis, N.; Fetters, L. J. *Macromolecules* **1983**, *16*, 214.
(19) Curro, J. G.; Schaefer, D. W. *Macromolecules* **1980**, *13*, 1199.

# Temperature Dependence of the Hydrodynamic Radius of Flexible Coils in Solutions. 2. Transition from the Θ to the Collapsed State

**Petar Vidaković† and Francis Rondelez***

*Physique de la Matière Condensée,‡ Collège de France, 75231 Paris Cédex 05, France.*
*Received March 18, 1983*

ABSTRACT: The temperature and molecular weight dependence of the hydrodynamic radius $R_H$ of flexible chains below the Θ temperature have been investigated by analytical ultracentrifugation. The measurements have been performed on high molecular weight polystyrenes ($M_w$ = 3.8 × $10^6$, 4.48 × $10^6$, 6.77 × $10^6$, 8.42 × $10^6$, and 20.6 × $10^6$) of narrow polydispersity dissolved in two different solvents, cyclopentane and cyclohexane. All data can be represented on a single master curve if the expansion factor $\alpha_H = R_H(T)/R_H(\Theta)$ is plotted vs. the reduced variable $N/N_\tau = (\bar{M}_w|\tau|^2)/(n\alpha M_0)$. $\tau$ is the reduced temperature $|\tau| = |1 - \Theta/T|$ and $n\alpha M_0$ is an adjustable parameter $\simeq 150 \pm 30$ g mol$^{-1}$. The small $N/N_\tau$ values (<3) correspond to the so-called Θ domain in which the chain is essentially Gaussian and $\alpha_H$ is a constant close to unity. For large $N/N_\tau$ values (>20) the collapse domain is observed in which $\alpha_H$ varies as $\bar{M}_w^{-1/6}|\tau|^{-1/3}$. The molecular weight dependence of $\alpha_H$ demonstrates directly for the first time that the collapse domain is characterized by $R_H \sim \bar{M}_w^{1/3}$. The crossover between these two regimes is smooth and continuous. Our results are in agreement with the theoretical predictions advocating a continuous contraction for flexible chains in the temperature range between the Θ point and the coexistence curve. We have also observed a small residual molecular weight dependence in our scaled representation of $\alpha_H$. This, the slight apparent dependence of $n\alpha M_0$ with the nature of the solvent and the difference between the $n\alpha M_0$ values above and below the Θ temperature, respectively, is yet to be explained.

## Introduction

In the course of our general study on the temperature dependence of the hydrodynamic radius of flexible chains in solutions,[1,2] we have investigated the temperature range delimited by the Θ point on one side, and by the coexistence curve where phase separation will take place, on the other. As the temperature is lowered, the hydrodynamic radius $R_H$ is expected to decrease sharply from its Θ value $R_H(\Theta) \sim N^{1/2}$ to its collapse value $R_H(T \ll \Theta) \sim N^{1/3}$ because of the increased attractive interaction between the monomer segments ($N$ is the polymerization index). This latter relationship can be easily derived from the argument that in this asymptotic regime the internal globule concentration $c_i \simeq N/R_H^3$ is solely controlled by the steric repulsions between the individual segments and is no longer dependent on chain length. According to both classical mean-field theories and renormalization group approaches, $R_H$ should vary as $N^{1/3}|\tau|^{-1/3}$ in the temperature domain where the chain contraction is taking place. On the other hand, the nature of the transition between the Gaussian and the collapsing behavior is still a matter of controversy between theoreticians. For sufficiently flexible and/or large chains, it is generally agreed that the transition should be smooth and continuous rather than discrete. A comprehensive review of the field has been recently published by Williams, Brochard and Frisch.[3] These authors also discuss the many experimental attempts to observe this coil–globule transition. In view of the vast arsenal of techniques put to use—small-angle neutron scattering,[4] viscosity,[5] and elastic and quasi-elastic light scattering[6-11]—the results have been rather disappointing. With one notable exception,[9,10] no group has reported evidence for a complete transition between the Θ state and the asymptotic collapse regime. Even in that case only the temperature variation of the chain radius has been investigated but not the molecular weight dependence, which would have given decisive proof that the chain was contracting to a globular state. It is true that the conditions necessary for the experiments are extremely stringent. Highly dilute solutions only must be used if single-chain contraction is to be observed rather than a spurious interchain penetration leading to aggregation and coalescence. An indirect advantage of dilution is that it widens the range of temperatures accessible between the Θ point and the demixion curve. Sharp molecular weight fractions are also a prerequisite to minimize fractional separation and avoid shifting the molecular weight distribution to smaller $N$ as the temperature is lowered. Last, a meaningful comparison with theory requires extremely large molecular fractions ($N \simeq 10^5$). Unfortunately this requirement is somewhat contradictory with the other two.

† Permanent address: Odsek za Fizičke i Meteorološke Nauke Prirodno—Matematički fakultet, 11001 Beograd, P.O.B. 550, Yugoslavia.
‡ Equipe de Recherche Associée au C.N.R.S. (E.R.A. 542).

0024-9297/84/2217-0418$01.50/0 

It is therefore to the merit of Sun et al.[9,10] to have overcome all of these difficulties. Using light beating spectroscopy and photon counting, they have worked with a single polystyrene sample of molecular weight $\bar{M}_w = 26 \times 10^6$, polydispersity $\bar{M}_w/\bar{M}_n \simeq 1.3$, at concentrations between $9 \times 10^{-8}$ and $9 \times 10^{-5}$ g cm$^{-3}$ in cyclohexane. They have observed a 60% decrease in the hydrodynamic radius during the chain contraction process and an even larger decrease, ~80%, for the radius of gyration.

In the present work, we report on the coil–globule transition for five narrow molecular weight fractions of polystyrene in two different solvents. We observe for the first time that, in the collapsing regime, the molecular weight dependence of the hydrodynamic radius varies as $R_H \sim N^{1/3}$, in agreement with the theoretical predictions. The expansion factor $\alpha_H$ is shown to follow a universal behavior if the scaled variable $\bar{M}_w|\tau|^2$ is used. Comparison is made with the results of previous workers, which reveals a numerical discrepancy in the Sun et al. data.

## Theoretical Models

As mentioned above, both mean field and renormalization group theories have been applied to the description of the collapsed state. The mean field approximation is based on the well-known Flory-type equation for the free energy of mixing of a polymer with a solvent, suitably extended to cover collapsed situations. The main point is that not only binary but also ternary monomer interactions are important. In the form proposed by Ptitsyn[12] and refined by de Gennes,[13] the equation for the expansion factor $\alpha = R(T)/R(\Theta)$ is

$$\alpha^5 - \alpha^3 - (y/\alpha^3) \cong N^{1/2}(v/a^3) \qquad (1)$$

$R$ is a typical chain dimension and, depending on experiment, can be either the hydrodynamic radius $R_H$ or the radius of gyration $R_G$. $y$ is the second virial coefficient, also called the binary cluster integral. In the vicinity of the Θ point, it varies linearly with temperature as $v = v_\infty\tau$, where $v_\infty$ is a constant $\sim a^3$, $a$ being the monomer length. $y$ is a dimensionless parameter proportional to the third virial coefficient $w$, $y = w/a^6$. In the temperature range of interest, it is positive and temperature independent. Its value is related to the chain flexibility, being of order 1 for flexible chains and going to 0 for rigid ones.

When applied to hydrodynamic variables, the mean-field equation yields for poor solvents $[(N^{1/2}v/a^3 \ll 0)]$

$$R_H(T) = \alpha_H R_H(\Theta) \sim N^{1/3}|\tau|^{-1/3}$$

On the other hand eq 1 is clearly invalid in the immediate vicinity of the Θ point. Sanchez has proposed an explicit formula for the temperature dependence of the radius of gyration which does not have this difficulty.[14] Its construction has been recently slightly improved by Sun et al.[10]

Following the recognition by de Gennes[13] that the Θ point is in fact a tricritical point, Daoud and Jannink[15] have determined the complete phase diagram of polymer solutions and constructed the scaling laws in the different regimes. Below the Θ point, the chain stays quasi-ideal over a temperature range $|T^* - \Theta| \sim N^{-1/2}$. At lower temperatures it enters the collapsed state where $R \sim |\tau|^{-1} \cdot f(N^{-1}\tau^{-2})$. $f$ can be written as a power law $f = (N\tau^2)^k$, with $k = 1/3$ to ensure that the internal coil density is molecular weight independent. This yields $R \sim N^{1/3}|\tau|^{-1/3}$ in the collapsing regime.

A physical picture of the collapse transition based on the renormalization group calculations was later proposed by de Gennes.[16] Below the Θ point, the chain of $N$ monomers is viewed as a succession of blobs each containing $N_\tau$ monomers. Inside each blob the Θ conditions still hold and Gaussian statistics are obeyed. However, the necklace of blobs is a collapsed structure. In the Θ region, the number $N/N_\tau$ of blobs is equal to unity and the whole chain is therefore quasi-ideal. In the collapse region, $N/N_\tau$ increases continuously as the temperature is lowered and when each blob is reduced down to the monomer size, the chain is fully condensed. Following this description, the complete calculations of the crossover behavior between the Θ and the extended state proposed by Weill and des Cloizeaux[17] and Ackasu and Han[18] can be directly applied to the collapse case by replacing the exponent $\nu = {}^3/_5$ by $\nu = {}^1/_3$ in their equations for $\alpha_H$ and $\alpha_G$. For hydrodynamic variables we obtain

$$\alpha_H = \frac{4}{x^{1/2}}\left[2(3-x) + 9\left(\frac{x^{-2/3}-1}{2} - \frac{x^{-2/3}-x}{5}\right)\right]^{-1} \qquad (2)$$

where $x = (N/N_\tau)^{-1}$, $N/N_\tau = (\bar{M}_w\tau^2)/(n\alpha M_0)$ is called the reduced blob parameter, $M_0$ is the molecular weight per monomer, $n$ is the number of monomer units in a statistical length, and $\alpha$ is an unknown coefficient to be adjusted experimentally. In the asymptotic limit where the number of blobs is very large, i.e., $N/N_\tau \gg 1$, one reaches the simple expression

$$\alpha_H \to 1.48(N/N_\tau)^{-1/6} \qquad (3)$$

This equation has the merit of showing that meaningful asymptotic exponents are only obtained at large $N/N_\tau$. It also stresses the importance of working with large chains since, at a given temperature, $N/N_\tau$ is directly proportional to $\bar{M}_w$.

It is noteworthy that both theoretical approaches lead to the same result $R_H \sim |\tau|^{-1/3}N^{1/3}$ for a collapsing chain and also show that the $\alpha$–$T$ curve has a universal form when the reduced variable $\bar{M}_w\tau^2$ (or equivalently $N/N_\tau$) is used.

There are however several differences which must be pointed out. (1) Rigorously speaking, mean field is correct in three dimensions but breaks down at lower dimensionalities.[13] (2) Only the mean field approach incorporates the notion of chain flexibility through the parameter $y$. Several authors[19] have emphasized that the transition to the collapsing region may not be continuous if $y$ falls below a minimum value. The transition should then become discontinuous (first order in the Landau sense). This detailed description is completely lost in the scaling arguments. de Gennes[13] has pointed out, however, that, in the limit of infinite chains, the transition is smooth whatever the flexibility may be. This conclusion was also reached by Moore[20] in a self-consistent field approach and by Sanchez[14] in a mean field calculation accounting approximately for all terms in the virial expansion of the intersegment interaction energy.

## Experimental Section

Five sharp molecular fractions of polystyrene were purchased from Toyo Soda Co. (Japan) and used as received. Their nominal molecular weights and polydispersities were $3.84 \times 10^6$ ($\bar{M}_w/\bar{M}_n < 1.05$), $4.48 \times 10^6$ ($\bar{M}_w/\bar{M}_n < 1.14$), $6.77 \times 10^6$ ($\bar{M}_w/\bar{M}_n < 1.14$), $8.42 \times 10^6$ ($\bar{M}_w/\bar{M}_n < 1.17$), and $20.6 \times 10^6$ ($\bar{M}_w/\bar{M}_n$ not given). These fractions were dissolved at low concentrations ($c \simeq 10^{-4}$–$10^{-6}$ g cm$^{-3}$) in cyclopentane and cyclohexane of spectrophotometric quality (Merck, Darmstadt, Germany). These solvents form ideal solutions with polystyrene around room temperature. Their Θ temperatures have been measured to be 23 and 35.4 °C, respectively, in our preceding papers[1,21] and were not remeasured here. Solutions were introduced into the sedimentation cells at high temperatures (40 °C) and were then allowed to slowly equilibrate down to the desired temperature of experiment. The

lowest temperature attainable for each molecular weight sample was limited by the onset of phase demixtion. Its actual value depends on solute concentration and decreases with decreasing concentrations. In all our experiments, the temperature was kept at least 0.5 °C above the temperature at which phase separation could be observed visually through the sudden disappearance of the solvent–solute boundary in the sedimentation cell. Above this temperature, no evidence of phase separation or even aggregation could ever be detected under our experimental conditions. The centrifugation runs were performed at 26 000 rpm in a Spinco Model E analytical ultracentrifuge. The displacement of the boundary between pure solvent and solution was recorded as a function of elapsed time and later analyzed with a profile projector. Two different optical methods were used for detection: (1) the classical Schlieren technique, valid for concentrations larger than about $2 \times 10^{-5}$ g cm$^{-3}$, and which reveals the position of the maximum of the refractive index increment in the solution; (2) the ultraviolet method, valid to lower concentrations, $\gtrsim 4 \times 10^{-6}$ g cm$^{-3}$, in which the boundary is detected by the associated abrupt change in the sample optical density. In this case, a collimated beam of monochromatic light is passed through the cell and the transmitted light intensity is measured as a function of the position in the cell by a traveling photomultiplier equipped with a narrow slit (0.1 mm). With differential measuring schemes, optical density changes as low as $10^{-2}$ are detectable. For polystyrene in cyclopentane at 264 nm, this corresponds to a concentration of $4 \times 10^{-6}$ g cm$^3$ if 30 mm optical path length cells are used. The aluminum cells were 4° single sector, 15 mm long. The sedimentation coefficients were calculated from the positions of the boundary by a least-square fitting procedure with a quadratic function of the elapsed time. As discussed in ref 21, this allows to correct for the unavoidable hydrostatic pressure and dilution effects which occur during the sedimentation process. Typical accuracy of sedimentation coefficient data is better than 4%.

## Results

The hydrodynamic radius $R_H$ is readily derived from the sedimentation coefficient $S$ by the Svedberg formula

$$S_0 = \frac{M_w(1 - \bar{v}_2\rho)}{6\pi\eta_s R_H} \tag{4}$$

$\bar{v}_2$ is the partial specific volume of the polymer and $\rho$ and $\eta_s$ are the solvent density and viscosity, respectively. $S_0(T)$ is the sedimentation coefficient in the limit of infinite dilution where all solute concentration effects can be neglected. Rigorously speaking, it is necessary to measure $S$ at various concentrations $C$ and extrapolate to zero concentration to obtain $S_0$. However the concentrations used here are small enough to make this correction necessary. It is generally assumed that $S^{-1} = S_0^{-1}(1 + k_sC)$. $k_s$ is a coefficient that depends on molecular weight. At the Θ point $k_s$ has been measured to be $(0.052 \pm 0.010)M_w^{1/2}$ cm$^3$ g$^{-1}$ for polystyrene in cyclohexane[21] and $(0.13 \pm 0.01)M_w^{1/2}$ cm$^3$ g$^{-1}$ for polystyrene in cyclopentane.[2] For the $20.6 \times 10^6$ molecular fraction and at the largest concentration of $2 \times 10^{-5}$ g cm$^3$, the $k_sC$ term does not then exceed 1%. Below the Θ point the correction term is even lower since $k_s$ decreases with temperature. Nyström, Roots, and Bergman[22] have reported a vanishingly small $k_s$ value in the vicinity of the upper consolute temperature of polystyrene in cyclopentane. The temperature variations of $\rho$ and $\eta_s$ have been measured previously for both cyclopentane[2] and cyclohexane.[23] $\rho$ varies linearly with temperature as $\rho(T) = -CT + D$, with $C = 9.86 \times 10^{-4}$ and $9.32 \times 10^{-4}$ g cm$^{-3}$ °C$^{-1}$ and $D = 0.76$ and 0.79 g cm$^{-3}$, respectively. $\eta_s$ follows an Arrhenius law $\eta_s = A \exp[B/(T + 273)]$, with $A = 1.5 \times 10^{-4}$ and $0.6 \times 10^{-4}$ and $B = 986$ and 1481 K, respectively. $\bar{v}_2$ for polystyrene in Θ solvents has been measured as a function of molecular weight by Pouyet, Candau, and Dayantis[24] and as a function of temperature by Sarazin and François.[25] Here we use $\bar{v}_2 = -4.89 \times 10^{-3} \ln \bar{M}_w + 0.99$, which is valid for molecular

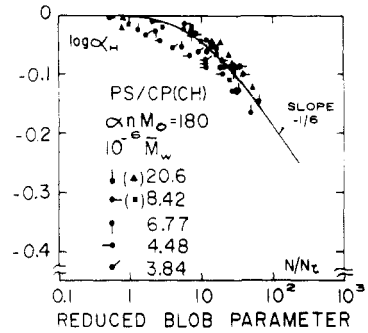


**Figure 1.** Logarithmic plot of the hydrodynamic expansion factor $\alpha_H(T) = R_H(T)/R_H(\Theta)$ as a function of the reduced blob parameter $N/N_\tau$ for five polystyrene fractions: $10^{-6}\bar{M}_w = 3.84$, 4.48, 6.77, 8.42, and 20.6 (corresponding symbols shown in figure), in two different solvents. In each case the data points have been obtained by changing the temperature from the Θ temperature down to the corresponding coexistence curve. Lowest temperature is 28.3 °C in the case of cyclohexane (Θ = 35.4 °C) and 13.0 °C in the case of cyclopentane (Θ = 23 °C). The values of $N/N_\tau$ have been calculated from $\bar{M}_w\tau^2/180$, where $\tau = |1 - \Theta/T|$, as explained in the text. The solid curve corresponds to the thermal blob theory.

fractions above $2 \times 10^5$. This yields $\bar{v}_2 = 0.910$ and 0.905 cm$^3$ g$^{-1}$ for $\bar{M}_w = 8.42 \times 10^6$ and $20.6 \times 10^6$, respectively. The temperature coefficient of $\bar{v}_2$ is $\alpha = (1/\bar{v}_2)(d\bar{v}_2/dT) = 8.8 \times 10^{-4}$, which gives a negligible $10^{-3}$ correction term over the 10 °C temperature interval investigated here.

The calculated $R_H$ values for the five polystyrene fractions in the two different solvents have been reported in Table I, at various temperatures. The corresponding expansion factor $\alpha_H = R_H(T)/R_H(\Theta)$ is also given. For $R_H(\Theta)$ we use the values determined experimentally. They are in perfect agreement with the general expression $R_H(\Theta) = 0.229\bar{M}_w^{1/2}$ (±2%) proposed by Schmidt and Burchard[26] from a vast compilation of literature data. The reduced variable $\bar{M}_w\tau^2$ has been calculated for each temperature and appears in the last column of Table I. Let us recall that the reduced parameter $N/N_\tau$ of the thermal blob theory is directly related to $\bar{M}_w\tau^2$ by $N/N_\tau = (\bar{M}_w\tau^2)/(n\alpha M_0)$.

It has been, however, emphasized by Ackasu and Han,[18] that the prefactor $(n\alpha M_0)^{-1}$ cannot be obtained from first principles and has to be determined empirically from a fit adjustment with the experimental data. This is why we have not indicated the $N/N_\tau$ values in Table I.

In Figure 1 we have collected all our expansion factor data as a function of $N/N_\tau$ in logarithmic scales. It is striking that, in this representation, the data obtained on several fractions and in two solvents tend to obey a law of superposition. As explained above, the absolute values of $N/N_\tau$ are still unknown at this stage and the data points can therefore all be shifted simultaneously, to the right or to the left, by an amount equal to the proportionality coefficient between $\bar{M}_w\tau^2$ and $N/N_\tau$. We have adjusted the proportionality coefficient so the experimental points superimpose on the theoretical curve of the thermal blob model, which has been drawn as a solid line (see eq 2). We readily observe that the agreement is quite good when taking $n\alpha M_0 = 180$ g mol$^{-1}$, especially for the larger molecular weight fractions. This is even more obvious when the expansion factor data for the two or three higher fractions are plotted on separate graphs for cyclopentane and cyclohexane (see Figures 2 and 3). To within the experimental accuracy, the points for the different fractions are superimposed. Moreover the variation with $N/N_\tau$ follows very closely that predicted by the blob model. Here the proportionality coefficient $n\alpha M_0$ has been taken as 126 in cyclopentane and 166 in cyclohexane, following a dif-

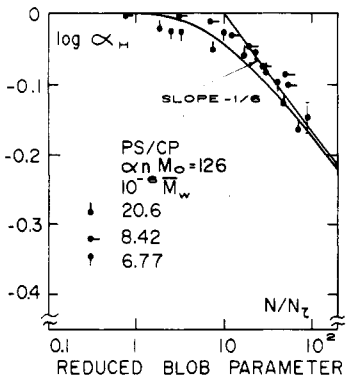


**Figure 2.** Logarithmic plot of the hydrodynamic expansion factor $\alpha_H$ as a function of the reduced blob parameter $N/N_\tau$ for the three highest polystyrene fractions in cyclopentane: $10^{-6}\bar{M}_w$ = 6.77, 8.42, and 20.6 (corresponding symbols shown in figure). The solid curve corresponds to the thermal blob model. $N/N_\tau$ is taken as $\bar{M}_w\tau^2/126$.

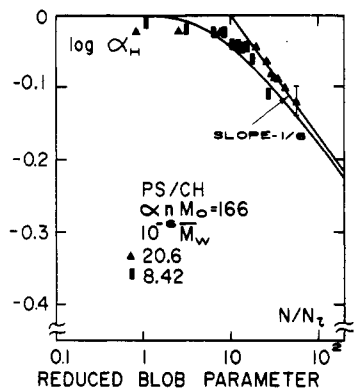


**Figure 3.** Same as Figure 2 but for the two highest polystyrene fractions in cyclohexane: $10^{-6}\bar{M}_w$ = 8.42 (■) and 20.6 (▲). $N/N_\tau$ is taken as $\bar{M}_w\tau^2/166$.

ferent procedure of adjustment which will be discussed later in the text. As observed in both Figures 2 and 3, the expansion coefficient first stays very close to unity as $N/N_\tau$ is increased. For $N/N_\tau$ between 1 and 3, the total variation does not exceed 3%, which is comparable, if not less, to the experimental error. We believe that this region corresponds to the so-called Θ domain of Daoud and Jannink,[15] in which the chain obeys Gaussian statistics and is close to ideality. The width of this domain is predicted to be $\tau^* \sim N^{-1/2}$. It can be said equivalently that $N/N_{\tau^*}$ should be a constant. Here we find that $N/N_{\tau^*} \simeq 3$, which yields $\tau^* \simeq 23\bar{M}_w^{-1/2}$. At large $N/N_\tau$, typically above 20, the variation of the expansion coefficient becomes much steeper. Although the data in this region cover less than one decade in $N/N_\tau$, it appears that $\alpha_H \sim (N/N_\tau)^{-1/8}$ to a fairly good accuracy. This power law is in excellent agreement with the predictions for the collapsing region. It implies that the chain hydrodynamic radius scales with temperature and molecular weight as $R_H \sim N^{1/3}|\tau|^{-1/3}$. The most critical check that the chain has indeed started to collapse is to investigate the molecular weight dependence of $\alpha_H$ at several discrete temperatures. This is done in Figure 4, where $\alpha_H$ is plotted as a function of $\bar{M}_w$, in logarithmic scales, for three temperatures 21, 19, and 17 °C in cyclopentane solutions. Very close to the Θ temperature, $\alpha_H$ is almost independent of molecular weight. This implies that $R_H(T = 21\ °C) \cong R_H(\Theta) \sim \bar{M}_w^{1/2}$. On the contrary, $\alpha_H$ decreases sharply with molecular weight at the two lowest temperatures. At $T$ = 17 °C, it scales as $\bar{M}_w^{-0.15\pm0.02}$. This implies that $R_H \sim \bar{M}_w^{1/3}$, which is in good agreement with the predictions for a collapse chain. For $T$ = 19 °C, a slightly higher value of the exponent is found

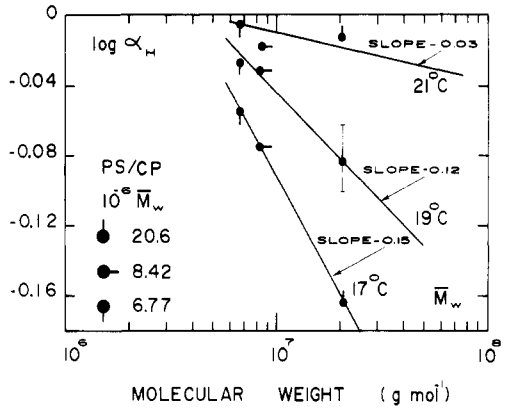


**Figure 4.** Logarithmic plot of the hydrodynamic expansion factor as a function of sample molecular weight $\bar{M}_w$ at three different temperatures. Solution is polystyrene in cyclopentane.

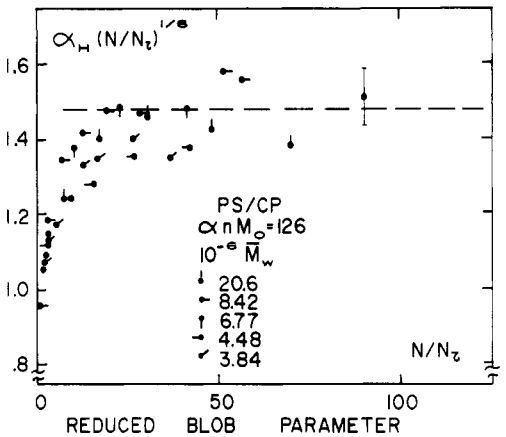


**Figure 5.** Variation of $\alpha_H(N/N_\tau)^{1/6}$ as a function of the reduced blob parameter $N/N_\tau$. The data points correspond to five molecular fractions: $10^{-6}\bar{M}_w$ = 3.84, 4.48, 6.77, 8.42, and 20.6 dissolved in cyclopentane (corresponding symbols shown in figure). $N/N_\tau$ has been calculated from $N/N_\tau = \bar{M}_w\tau^2/126$. Note than for $N/N_\tau \gtrsim 20$, the experimental points fall on a horizontal line. Its intercept with the ordinate axis is 1.48 (see text for details).

since $\alpha_H \sim \bar{M}_w^{-0.12}$. This power law is however questionable since all data points are located at the extreme lower limit of the collapsing domain with calculated $N/N_\tau$ values below 30. Our data points at 15 °C shown in Table I are unfortunately not exploitable to confirm that the asymptotic region has indeed been reached. They correspond to a molecular weight range which is both too low and too narrow ($4.48 \times 10^6$–$8.42 \times 10^6$) to obtain meaningful power law exponents. Last, it is interesting to note the large differences in the $\alpha_H$ values for a given molecular weight, between 19, 17, and 15 °C. This means that the fully globular state, with $R_H \sim N^{1/3}$, independent of temperature, has not yet been reached. This would require to work at even lower temperatures which are inaccessible in the present experiments without inducing the demixtion of the solution at the same time.

Another representation of the collapsing region is given in Figures 5 and 6 where $\alpha_H(N/N_\tau)^{1/6}$ has been plotted as a function of $N/N_\tau$. According to the blob theory (see eq 3), the collapsing region is characterized by $\alpha_H(N/N_\tau)^{1/6} = A$, the value of the constant $A$ being 1.48. Therefore, the data points are expected to increase smoothly at low $N/N_\tau$ and then to saturate. Such a behavior can be observed in Figure 5 for the cyclopentane data and in Figure 6 for the cyclohexane data. The experimental points fall on a horizontal line above a limiting value of $N/N_\tau \simeq 20$. The intercept of this line with the ordinate axis yields the value of the constant. Here we have chosen to adjust the

Table I
Sedimentation Velocity for Polystyrene in Cyclopentane and Cyclohexane below the Θ Temperature

| $10^{-6}\bar{M}_w$, g mol$^{-1}$ | $10^6C$, g cm$^{-3}$ | $T$, °C | $10^{13}S$, s | $R_H$, Å | $\alpha_H$ | $10^{-3}\bar{M}_w\tau^2$, g mol$^{-1}$ |
|---|---|---|---|---|---|---|
| | | | Cyclohexane (Θ = 35.4 °C) | | | |
| 20.6 | 55.0 | 35.4 | 68.1 | 1089.0 | 1 | 0 |
| | | 34.6 | 70.6 | 1036.9 | 0.952 | 0.139 |
| | | 34.0 | 70.0 | 1035.7 | 0.951 | 0.428 |
| | | 33.0 | 69.57 | 1025.3 | 0.942 | 1.266 |
| | | 32.0 | 71.46 | 981.9 | 0.902 | 2.557 |
| | 21.0 | 31.5 | 70.61 | 985.2 | 0.905 | 3.376 |
| | | 31.0 | 73.92 | 933.7 | 0.857 | 4.311 |
| | | 30.5 | 76.85 | 890.7 | 0.818 | 5.364 |
| | | 30.1 | 76.38 | 890.3 | 0.818 | 6.292 |
| | | 29.8 | 78.48 | 862.1 | 0.792 | 7.039 |
| | | 28.8 | 80.61 | 825.6 | 0.758 | 9.360 |
| 8.42 | 56.0 | 35.4 | 43.6 | 688.8 | 1 | 0 |
| | | 34.0 | 43.79 | 669.4 | 0.977 | 0.175 |
| | | 33.0 | 43.85 | 657.6 | 0.955 | 0.517 |
| | | 32.0 | 43.46 | 652.7 | 0.948 | 1.045 |
| | | 31.5 | 42.90 | 655.8 | 0.952 | 1.380 |
| | 22.0 | 31.0 | 44.68 | 624.5 | 0.907 | 1.762 |
| | | 30.7 | 44.32 | 626.5 | 0.910 | 2.015 |
| | | 30.5 | 44.81 | 617.6 | 0.897 | 2.193 |
| | | 30.1 | 44.05 | 624.05 | 0.906 | 2.572 |
| | | 29.8 | 45.69 | 598.6 | 0.860 | 2.877 |
| | | 28.3 | 56.68 | 533.9 | 0.775 | 4.500 |
| | | | Cyclopentane (Θ = 23 °C) | | | |
| 20.6 | 50.0 | 23.0 | 137.26 | 1026.3 | 1 | 0 |
| | | 22.0 | 140.69 | 989.3 | 0.964 | 0.236 |
| | | 21.0 | 149.09 | 922.4 | 0.899 | 0.952 |
| | | 20.0 | 149.85 | 906.5 | 0.883 | 2.157 |
| | | 19.0 | 156.39 | 858.1 | 0.836 | 3.862 |
| | 20.0 | 18.0 | 170.65 | 776.8 | 0.757 | 6.075 |
| | | 17.0 | 184.9 | 708.1 | 0.689 | 8.809 |
| | 4.6 | 16.2 | 174.55 | 742.6 | 0.724 | 11.377 |
| 8.42 | 55.0 | 23.0 | 86.71 | 657.5 | 1 | 0 |
| | | 22.0 | 84.34 | 667.8 | 1.015 | 0.097 |
| | | 21.0 | 85.28 | 652.5 | 0.992 | 0.389 |
| | | 20.0 | 84.97 | 647.0 | 0.984 | 0.882 |
| | | 19.0 | 87.78 | 618.7 | 0.941 | 1.578 |
| | | 18.0 | 89.91 | 596.6 | 0.907 | 2.483 |
| | 20.0 | 17.0 | 94.70 | 559.4 | 0.851 | 3.601 |
| | | 15.0 | 94.85 | 544.7 | 0.828 | 6.490 |
| | 4.6 | 14.6 | 97.30 | 527.7 | 0.802 | 7.175 |
| 6.77 | 55.0 | 23.0 | 76.3 | 600.0 | 1 | 0 |
| | | 21.0 | 79.45 | 561.9 | 0.937 | 0.313 |
| | | 20.7 | 80.00 | 558.7 | 0.931 | 0.415 |
| | | 19.0 | 77.85 | 559.5 | 0.933 | 1.269 |
| | | 17.0 | 80.75 | 526.2 | 0.877 | 2.895 |
| | | 15.0 | 87.19 | 475.3 | 0.792 | 5.218 |
| 4.48 | 55.0 | 23.0 | 64.06 | 470.0 | 1 | 0 |
| | | 20.0 | 66.84 | 437.6 | 0.931 | 0.469 |
| | | 18.2 | 68.70 | 413.5 | 0.879 | 1.216 |
| | | 16.8 | 71.43 | 390.83 | 0.832 | 2.048 |
| | | 15.0 | 72.20 | 378.02 | 0.804 | 3.453 |
| | | 13.1 | 74.66 | 356.9 | 0.759 | 5.359 |
| 3.84 | 55.0 | 23.0 | 58.21 | 442.3 | 1 | 0 |
| | | 20.4 | 59.86 | 417.1 | 0.943 | 0.301 |
| | | 20.0 | 59.13 | 420.3 | 0.950 | 0.402 |
| | | 19.0 | 62.34 | 393.4 | 0.889 | 0.720 |
| | | 17.0 | 61.48 | 389.5 | 0.881 | 1.642 |
| | | 16.2 | 62.64 | 378.4 | 0.855 | 2.121 |
| | | 14.5 | 63.12 | 367.6 | 0.831 | 3.353 |
| | | 13.0 | 68.58 | 332.0 | 0.751 | 4.690 |

absolute $N/N_\tau$ values (by multiplying them by a numerical coefficient) so the intercept of the asymptotic horizontal line takes the theoretical value of 1.48. Using this procedure we obtain the correspondence between the measured $\bar{M}_w\tau^2$ and the calculated $N/N_\tau$ values. $N/N_\tau = (\bar{M}_w\tau^2)/(n\alpha M_0)$, with $n\alpha M_0$ = 126 and 166 g mol$^{-1}$ for cyclopentane and cyclohexane, respectively. The uncertainty of the determination is estimated to be ±30 g mol$^{-1}$. Our experience with dynamic expansion coefficients above the Θ temperature (i.e., for expanding chains) is that $n\alpha M_0$ is little, if any, dependent on the nature of the solvent for a particular polymer.[2] The present results are not in contradiction with this finding, and we can assume that below Θ temperatures $n\alpha M_0$ is equal to 150 ± 30 g mol$^{-1}$. Only more refined experiments will be able to tell if the difference between $n\alpha M_0$ = 126 g mol$^{-1}$ for cyclopentane solution and $n\alpha M_0$ = 166 g mol$^{-1}$ for cyclohexane solution is significative or is an artifact due to our limited experimental accuracy for both cyclopentane and cyclohexane solvents. A more puzzling point however is that these

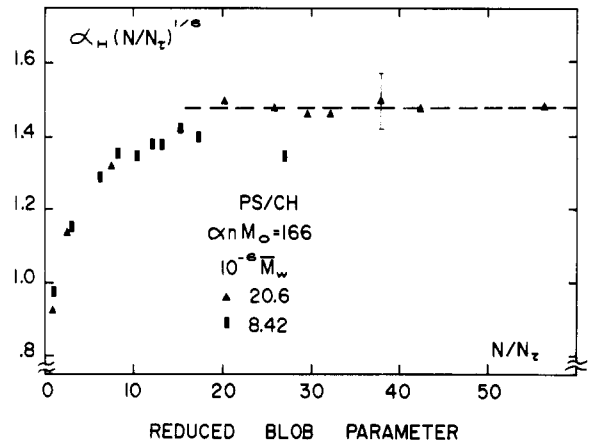


**Figure 6.** Same as Figure 5 but for two fractions in cyclohexane. $10^{-6}\bar{M}_w$ = 8.42 (■) and 20.6 (▲). $N/N_\tau$ has been calculated from $N/N_\tau = \bar{M}_w\tau^2/166$ (see text for details).

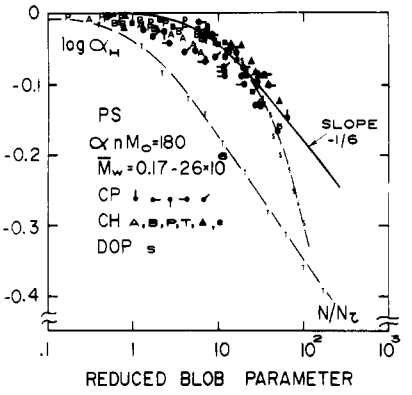


**Figure 7.** Compilation of literature results on the hydrodynamic expansion factor $\alpha_H$ as a function of $N/N_\tau$ *below* the Θ temperature of the solutions. Our results of Figure 1 for polystyrene in cyclohexane and cyclopentane have also been reported. The data indicated by a B, A, P, or T are from Bauer and Ullman,[8] Perzynski, Adam, and Delsanti,[5] Pritchard and Caroline,[7] or Sun, Nishio, Swislow, and Tanaka,[10] respectively. They are all for polystyrene in cyclohexane. The data indicated by an S are from Štěpánek, Koňák, and Sedláček[11] for polystyrene in dioctyl phthalate. The solid curve corresponds to the thermal blob model with $N/N_\tau = \bar{M}_w\tau^2/180$. The dashed lines are just a guide for the eye.

$n\alpha M_0$ values do not seem to be identical with the value of $n\alpha M_0 = 1000 \pm 50$ g mol$^{-1}$ found above the Θ temperature.[2] The difference is very large and clearly outside experimental error. In the thermal blob theory, Ackasu and Han[18] have shown that $n\alpha M_0$ is related to the binary cluster integral $\delta = v_\infty\tau$. More precisely, $n\alpha \sim (l^3/v_\infty)^2$, where $l$ is the statistical length and contains $n$ monomer units. To say that $n\alpha M_0$ is different below and above the Θ point is therefore equivalent to say that $v_\infty$ does not have the same values in these two temperature ranges. $v_\infty$ is apparently larger in the collapsing regime. This may be due to the stronger influence of higher than binary interactions as the internal chain density increases. More experiments are necessary to check this point further. The effect seems large enough to also justify a theoretical effort which could give new insight on the detailed mechanism of the coil collapse.

Returning to Figure 1, we can now examine the influence of molecular weight on the data. Although we have said earlier that the data follow a universal curve, this is only true in first approximation. A closer examination shows a slight systematic variation in the $a_H$ values measured for a given $N/N_\tau$, especially in the lower range of $N/N_\tau$. The sign of the effect is such that the transition to the collapsing region becomes less abrupt and noticeable for the lowest molecular fractions. For instance, the $a_H$ variation for the $3.84 \times 10^6$ sample is very smooth. The absolute $a_H$ values are also a few percent smaller on the average than for the $20.6 \times 10^6$ sample. Such a residual molecular weight dependence may not be too surprising. It was already present in our previous experiments on the dynamic expansion factor above the Θ temperatures.[2] It may come from the logarithmic corrections related to the fact that the Θ point is a tricritical point. It is also possible that, for hydrodynamic properties, the assumption of totally nonfree draining is too crude, especially at low molecular weight, and should be refined.

It is now interesting to compare our data with the earlier results of the literature in the same polystyrene–cyclohexane system. In Figure 7, we have compiled the various measurements of the dynamic expansion factor. Bauer and Ullman[8] have used fractions with $\bar{M}_w = 5.4 \times 10^4$–$44 \times 10^6$, Pritchard and Caroline $\bar{M}_w = 1.7 \times 10^5$–$5.35 \times 10^6$,[7] Perzynski, Adam, and Delsanti $\bar{M}_w = 1.7 \times 10^5$, $4.1 \times 10^5$, and $12.6 \times 10^5$,[5] Sun, Nishio, Swislow, and Tanaka $\bar{M}_w = 26 \times 10^6$.[9,10] We have also added the recent data of Šteěpánek, Koňáck, and Sedláček on polystyrene with $\bar{M}_w = 2 \times 10^6$ in dioctyl phthalate.[11] It is immediately apparent from the figure that these results can be gathered in two categories: on one hand, those of Sun et al. and Štěpánek et al., which cover an extended range of $N/N_\tau$ (1–170) and over which $\alpha_H$ decreases by an impressive 60%; on the other hand, all the remaining data, which cover a much more limited range, typically between 0.1 and 13, and over which $\alpha_H$ decreases by a modest 15%. By comparison, our own results correspond to an intermediate range of $N/N_\tau$, between 0.5 and 70, with an $\alpha_H$ variation of 32%. The first remark is that the results of Bauer et al., Perzynski et al., and Pritchard et al. are fully consistent with ours. This is especially true in view of the inevitable data scattering due to the use of different molecular fractions. However, these authors never reach the collapsing regime characterized by a power law of exponent $-1/6$. On the contrary, Sun et al. and Štěpánek et al. do reach an asymptotic regime. Nevertheless some difficulties are obvious. In Štěpánek's data the slope seems much too large to correspond to the collapsing regime. In Sun's data, the collapsing regime is observed to set in for $N/N_\tau$ values which seems much too low ($N/N_\tau \geq 3$) compared to all other experiments.

In view of these striking discrepancies we have undertaken a critical examination of these last two sets of results. We start first with those of the MIT group.[9,10] For their nominal $26 \times 10^6$ molecular weight sample (quoted polydispersity is 1.3), they find a hydrodynamic radius of 1367 ± 50 Å at the Θ point and a radius of gyration of 1835 Å. Both of these values seem too large when compared with the values calculated from the Schmidt and Burchard formula,[26] which yields 1167 and 1478 Å, respectively. The difference is more than 17% and largely exceeds the experimental uncertainty of ~4%.

The most obvious way to resolve this discrepancy is to assume that the actual sample molecular weight has been underestimated. The radii data seem to indicate a molecular weight of $35 \times 10^6$ rather than $26 \times 10^6$. Such a readjustment would have the beneficial effect to shift to the right the experimental points in Figure 7. Unfortunately the shifting factor of 35/26 = 1.35 is still not sufficient to bring the results in superposition on the other data. A factor on the order of 10 would be required, and this supposes unrealistically large molecular weight values. It is the general experience that polystyrene samples above

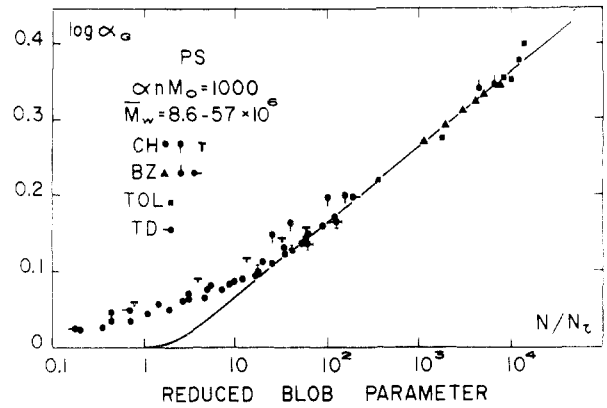


**Figure 8.** Logarithmic plot of the static expansion $\alpha_G(T) = R_G(T)/R_G(\Theta)$ as a function of the reduced blob parameter $N/N_\tau = \bar{M}_w\tau^2/1000$ in the temperature range *above* the Θ temperature of the solutions. The data points are a compilation of the literature results for very high molecular weight polystyrenes $\bar{M}_w = (8.6\text{–}5.7) \times 10^6$. Various solvents have been used. CH is for cyclohexane, BZ for benzene, TOL for toluene, TD for *trans*-decalin. The points indicated by a T are from Sun, Nishio, Swislow, and Tanaka.[10] Note that they are slightly shifted to the left compared to most of the others. This is also the case for the points indicated by a ●, which are from Slagowski, Tsai, and McIntyre.[6] The solid curve corresponds to the thermal blob model.

$10^7$ are easily degraded into lower molecular fractions but not that they contain a significant amount of still higher molecular weight material. We have also examined the MIT results above the Θ temperature. Figure 8 shows their measurements of the static expansion factor $\alpha_G = R_G(T)/R_G(\Theta)$ as a function of $N/N_\tau$, compared with a compilation of literature data. Again a shift to the right would be required to bring all data in superposition. This time a factor of 2 only would be necessary, which is more in the range of the 1.35 factor. A similar comparison for the dynamic expansion factor $\alpha_H$ has not been possible because of the large scattering in the original data. This imprecision is due, according to the authors, to the interference of the internal chain modes with the translational diffusion processes.[10]

The other way to try and resolve the discrepancy between the experimental $R_H(\Theta)$ value and the nominal molecular weight is to assume that the Θ temperature has been overestimated. This would suppose in practice to lower the actual Θ temperature of their solutions from 35.4 to 34.2 °C. This assumption is not too unrealistic since quite a range of Θ values between 34 and 35 °C has been mentioned in the literature. Let us therefore examine the consequences of this renormalization on the data plots in Figures 7 and 8. In the swelling regime, the data will be shifted to the right since $N/N_\tau = (\bar{M}_w\tau^2)/(n\alpha M_0)$ is now larger than originally estimated ($\tau$ being larger). This is the correct trend. However, we have to apply at the same time an upward shift to account for the concomitant increase in $\alpha_H$ (the true $R_H(\Theta)$ being now smaller). On the whole the discrepancy with the literature data remains uncorrected. The same conclusion holds for the collapsing regime. There will be a shift to the left due to the decrease in $\tau$, coupled with an upward shift to account for the increase in $\alpha_H$. In brief, the modification of the Θ temperature does not help to clarify the MIT data. It is our opinion that they are plagued by an artifact which affects the absolute values of both $R_H$ and $R_G$ but does not seem to perturb their variations with temperature. It is striking that the experimental ratio of $R_G$ over $R_H$ at large $N/N_\tau$ values is in perfect agreement with the expectation for a compact form. Indeed the measured $R_G/R_H$ is 0.74 ± 0.04, while $R_G/R_H$ is calculated to be $(3/5)^{1/2} \simeq 0.77$ for a solid sphere. This, coupled with the observation of the correct $-1/6$ slope, leaves little doubt that the collapsing regime has been correctly reached in their experiments and that the discrepancy is only qualitative.

In comparison, the data of the Prague group[11] pose a much more serious problem. The most embarrassing fact is that their $\alpha_H$ variation, in the large $N/N_\tau$ region, is much too rapid. The slope is close to −1/2.3, i.e., nearly a factor of 3 lower than expected for the collapsing regime. The ratio $R_G/R_H$ is also not in agreement with the model of a solid, compact sphere. Observation of Figure 2 of ref 11 shows that, below the Θ point, $R_H$ and $R_G$ are practically identical in the whole temperature range, contrary to the Sun et al. data[10] where the ratio $R_G/R_H$ changes continuously from a value higher than 1 to less than 1. These two difficulties may come from the fact that the experiment has not been performed at thermodynamic equilibrium. Rather, the authors have tried to take advantage of the high viscosity of their particular solvent, dioctyl phthalate, to be able to cross the static coexistence curve without inducing phase separation. In principle this dynamic method enables them to work at lower temperatures than normally possible and therefore to extend their range of measurement in the collapsing region. However, the procedure contains also a significant danger of inducing fractional separation according to molecular weight. As the temperature is lowered, the largest chains will tend to precipitate first and the molecular weight distribution will be shifted toward lower values. Such an effect would certainly explain why $\alpha_H$ is observed to vary too quickly. $R_H(T)$ is decreasing not only because of the chain collapsing but also because of the spurious decrease in the $\bar{M}_w$ of the sample. This interpretation is particularly reasonable in view of the large polydispersity, ≃1.3, of the sample used by these authors. For this very same reason, the detailed study of the upper consolute temperature as a critical point with diverging quantities and characteristic critical exponents has long evaded the skill of the experimenters.[27] It should be interesting to repeat the experiment while changing the polydispersity index. Values less than 1.05 are common with molecular weights in the $10^6$ range. It must be noted also that the concentrations used, $(1\text{–}8) \times 10^{-4}$ g cm$^{-3}$, were quite high, and the possibility of interpenetration between different chains cannot be totally neglected.

## Conclusion

To conclude, the present measurements of the hydrodynamic radius of polystyrenes below the Θ temperature have allowed us to investigate several important features of the collapse behavior of flexible polymer chains in solutions. First, we show that the data obtained on five high molecular weight fractions in two different solvents obey a law of superposition when plotted as a function of the reduced variable $\bar{M}_w\tau^2$ or equivalently $N/N_\tau = (\bar{M}_w\tau^2)/(n\alpha M_0)$. Second, two different regimes are easily distinguishable. For low values of $N/N_\tau$ ($N/N_\tau < 3$), i.e., close to the Θ temperature and/or for low molecular weights, the chains are nearly ideal coils with Gaussian statistics. This is the so-called Θ domain of Daoud and Jannink in which the chains are characterized by $R_H \sim N^{1/2}$, independent of temperature. For higher values of $N/N_\tau$ ($N/N_\tau > 20$), the chains undergo a coil to globule transition. The transition is smooth and continuous. The hydrodynamic radius gradually decreases with a temperature dependence $|\tau|^{-1/3}$. In that collapsing regime, the molecular weight dependence of the chains is characterized by $R_H \sim N^{1/3}$. This later dependence demonstrates unambiguously for the first time that the coil has indeed entered its collapsed

state. The internal monomer concentration is then independent of molecular weight and depends solely on the balance between steric repulsions and van der Waals attractions. The transition can be described with reasonable accuracy by the thermal blob model.

It must be pointed out, however, that several difficulties remain to be solved: (1) The need to use slightly different $n\alpha M_0$ values for polystyrene in cyclopentane and cyclohexane is not in agreement with a universal behavior. It is not clear yet if this discrepancy arises from our limited experimental accuracy or is more fundamental. (2) The average $n\alpha M_0$ value of 150 ± 30 g mol$^{-1}$ in the collapsed state is much lower than the measured corresponding value of 1000 ± 50 g mol$^{-1}$ previously found in the extended state. This difference may reflect the influence of the higher than binary interactions in the collapsed state. (3) The slight residual molecular weight dependence in our universal plots is not accounted for by the theory. (4) So far, the molecular weight dependence of the hydrodynamic radius characteristic of the collapsing regime has been proved only at a single temperature. This should be repeated at several different temperatures.

When applicable, the comparison of the present data with the literature shows a good agreement in general. There are however two notable exceptions that both correspond to attempts to reach the totally collapsed regime in which the hydrodynamic radius of the globular chain saturates to its minimum value. The disagreement is very serious for the Prague group while it is probably only qualitative for the MIT group. These experiments should be repeated especially in view of the fact that the light scattering technique allows use of lower concentrations than the present sedimentation experiments. The accessible temperature range is then sufficiently large to cover the entire coil–globule transition. Last, to test the eventual superiority of the mean-field theory over the blob model, it would be very interesting to work on polymers of various flexibility since only the former approach includes this important parameter.

**Registry No.** Polystyrene, 9003-53-6.

## References and Notes


(1) P. Vidakovic and F. Rondelez, *Macromolecules*, **16**, 253 (1983).
(2) P. Vidakovic and F. Rondelez, *Macromolecules*, submitted for publication.
(3) C. Williams, F. Brochard, and H. Frisch, *Ann. Rev. Phys. Chem.*, **32**, 433 (1981).
(4) M. Nierlich, J. P. Cotton, and B. Farnoux, *J. Chem. Phys.*, **69**, 1379 (1978).
(5) R. Perzynski, M. Adam, and M. Delsanti, *J. Phys. (Orsay, Fr.)*, **43**, 129 (1982).
(6) E. L. Slagowski, B. Tsai, and D. McIntyre, *Macromolecules*, **9**, 687 (1976).
(7) M. J. Pritchard and R. D. Caroline, *Macromolecules*, *13*, 957 (1980).
(8) D. R. Bauer and R. Ullman, *Macromolecules*, **13**, 392 (1980).
(9) G. Swislow, S. T. Sun, I. Nishio, and T. Tanaka, *Phys. Rev. Lett.*, **44**, 796 (1980).
(10) S. T. Sun, I. Nishio, G. Swislow, and T. Tanaka, *J. Chem. Phys.*, **73**, 5971 (1980).
(11) P. Štěpánek, C. Koňák, and B. Sedláček, *Macromolecules*, **15**, 1214 (1982).
(12) O. B. Ptitsyn, A. K. Kron, and Y. Y. Eizner, *J. Polym. Sci., Part C*, **16**, 3509 (1968).
(13) P. G. de Gennes, *J. Phys., Lett. (Orsay, Fr.)*, **36**, L-55 (1975).
(14) I. C. Sanchez, *Macromolecules*, **12**, 980 (1979).
(15) M. Daoud and J. Jannink, *J. Phys. (Orsay, Fr.)*, **37**, 973 (1976).
(16) P. G. de Gennes, *J. Phys., Lett. (Orsay, Fr.)* **39**, L-299 (1978).
(17) G. Weill and J. des Cloizeaux, *J. Phys. (Orsay, Fr.)*, **40**, 99 (1979).
(18) A. Z. Ackasu and C. C. Han, *Macromolecules*, **12**, 276 (1979).
(19) See for example: C. Post and B. Zimm, *Biopolymers*, **18**, 1487 (1979), and also ref (13).
(20) M. A. Moore, *J. Phys. A*, **10**, 305 (1977).
(21) P. Vidakovic, C. Allain, and F. Rondelez, *Macromolecules*, **15**, 1571 (1982).
(22) B. Nyström, J. Roots, and R. Bergman, *Polymers*, **20**, 157 (1979).
(23) M. Adam and M. Delsanti, *J. Phys. (Orsay, Fr.)*, **41**, 713 (1980).
(24) G. Pouyet, F. Candau, and J. Dayantis, *Makromol. Chem.*, **177**, 2973 (1976).
(25) D. Sarazin and J. François, *Polymers*, **19**, 699 (1978).
(26) M. Schmidt and W. Burchard, *Macromolecules*, **14**, 210 (1981).
(27) M. Adam, private communication. See also: N. Kuwahara, M. Tachikawa, K. Hamano, and Y. Kenmochi, *Phys. Rev.*, **A25**, 3449 (1982).


# Dynamic Light Scattering Studies of Polymer Solutions. 3. Translational Diffusion and Internal Motion of High Molecular Weight Polystyrenes in Benzene at Infinite Dilution


**Norio Nemoto, Yutaka Makita, Yoshisuke Tsunashima, and Michio Kurata***

*Institute for Chemical Research, Kyoto University, Uji, Kyoto-fu 611, Japan.*

*Received February 24, 1983*


ABSTRACT: Dynamic light scattering studies have been made on dilute solutions of narrow-distribution polystyrenes in benzene at 30 °C over a wide range of $qR_G$ ($\equiv X^{1/2}$). The intensity autocorrelation function has been analyzed with the histogram method. The analysis made it possible to estimate the translational diffusion coefficient $D$, the effective decay rate $\Gamma_e$, and the intensity of the translational diffusion motion relative to the total intensity $P_0/P$ at finite polymer concentration. Those quantities have been linearly extrapolated to infinite dilution to obtain values characteristic of a single swollen coil. It has been found that the hydrodynamic radius $R_H$ calculated from $D_0$ increases in proportion to $M_w^{0.55}$ and expansion factors $\alpha_H$ and $\alpha_s$ have different functional dependences on the excluded volume parameter $z$. It has also been found that, for $X^{1/2} \gg 1$, the quantity $(\Gamma_e)_{c\to 0}/(q^3 k_B T/\eta_0)$ approaches a constant value which is less than the theoretical value by 25%. The $X$ dependence of $(P_0/P)_{c\to 0}$ suggests that the internal motion is suppressed in a single swollen coil to some extent in comparison with that in a Gaussian coil. The concentration dependence of $D$ is also briefly discussed.


## Introduction

In a previous report,[1] we have investigated dynamics of dilute solutions of narrow-distribution polystyrenes (PS) in *trans*-decalin at the Θ temperature over a wide range of $qR_G \equiv X^{1/2}$ by means of homodyne photon correlation spectroscopy. Here $q$ is the scattering vector and $R_G$ is the radius of gyration. We have found that the dynamical behavior of an isolated unperturbed chain is quantitatively

0024-9297/84/2217-0425$01.50/0 