

the application of electrical voltage and manifested by the light and dark alternations known as Williams Domains.^{12,23}

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Molecular Weight and Temperature Dependence of Polymer Dimensions in Solution

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ABSTRACT: The molecular weight (M_w) and temperature (T) dependence of the radius of gyration (R_G) and hydrodynamic radius (R_H) of a polymer in a dilute solution are investigated. The theoretical predictions are compared with experimental results on polystyrene in various solvents as functions of M_w and T . It is found that the existing data fall in a region of values where R_H cannot be represented by a simple power law $R_H \sim N^{\nu'}$, whereas most of the data on R_G satisfy $R_G \sim N^{\nu}$. It is concluded that a power law fit to data would yield a $\nu' < \nu$ in this region, even though the theory predicts $\nu' = \nu$ in the asymptotic region. The quantitative aspects of the blob theory are also discussed and compared in some cases to the modified Flory theory.

This paper investigates the molecular weight and temperature dependence of polymer dimensions in solution under actual experimental conditions and presents a quantitative comparison of the existing data on polystyrene in various solvents, with the theoretical predictions.

In equilibrium, the mean size of a polymer molecule is characterized by its radius of gyration R_G , which is a static property of the polymer measured in static experiments, e.g., by observing the static structure factor $S(q)$ as a function of momentum transfer q .

In the interpretation of dynamic experiments the hydrodynamic radius R_H of the polymer is defined by

$$R_H = k_B T / 6\pi\eta D_0 \quad (1)$$

where $k_B T$ is the temperature of the solution, η is the viscosity of the solvent, and D_0 is the zero concentration translational diffusion coefficient. It is the latter which is actually measured in a dynamic experiment, e.g., by observing the relaxation in time, of the dynamic scattering function $S(q,t)$ for small momentum transfers $qR_G \ll 1$. The reason for introducing R_H through eq 1 in preference to D_0 is that it is less sensitive to the conditions of the solution, such as the temperature and viscosity, and facilitates comparison with R_G . One may interpret R_H as an equivalent radius, when the polymer is visualized as a rigid sphere with stick boundary conditions, obeying Stoke's law.

It is known that $R_G \sim N^{\nu}$ in a good solvent and for large N , where N is the equivalent number of links in the statistical chain. The scaling arguments by De Gennes¹ and our earlier calculations based on the linear response theory² also yield $R_H \sim N^{\nu}$ for large N . But recent light-scattering experiments by Adam and Delsanti³ in dilute solutions of polystyrene in benzene at room temperature yielded an exponent $\nu' = 0.55 \pm 0.02$ in the molecular weight range 2.43×10^4 to 3.8×10^6 , which differs from the most accurate value of $\nu = 0.588 \pm 0.001$.⁴

In a very recent paper, Des Cloizeaux⁵ proved the inequality

$$R_H > K R_G \quad (2)$$

where K does not depend on N for large N but depends on the type of the chain. He concluded from eq 2 that $\nu' \geq \nu$ must hold even if one postulates⁶ the existence of a new dynamical exponent ν' in $R_H \sim N^{\nu'}$.

Des Cloizeaux⁷ suggested that this discrepancy may be due to the fact that R_H does not reach its asymptotic power law behavior, as predicted by the theory, within the range of experimental values of the molecular weight.

The aim of this paper is to study this question quantitatively by comparing the theoretical calculations of R_G ⁸ and R_H ² as a function of the molecular weight and temperature in the nonasymptotic regions with the experi-

mental data on polystyrene in different solvents and at different temperatures. The reason for studying both R_G and R_H together in this paper is to eliminate the unspecified proportionality constants in the “blob” theory of polymer statistics^{6,8,9} using R_G data and compare the theory and experiment on R_H without any adjustable parameters. Temperatures above the Θ point are considered in this study.

The Variation of R_G with T and M_w

The radius of gyration is calculated from its definition

$$R_G^2 = \frac{1}{2N^2} \sum_{m,n=1}^N \langle |R_{mn}|^2 \rangle \quad (3)$$

$$R_G^2 = \frac{1}{N^2} \sum_{n=1}^N (N-n) \langle |R_n|^2 \rangle$$

where N is the number of beads in the equivalent statistical chain.

In the temperature “blob” theory of polymer statistics,^{9,10} $\langle |R_n|^2 \rangle$ is modeled as

$$\langle |R_n|^2 \rangle = l^2 n, \quad n \leq N_r$$

$$\langle |R_n|^2 \rangle = l^2 N_r^{1-2\nu} n^{2\nu}, \quad n \geq N_r \quad (4)$$

where l is the statistical length and N_r is a temperature-dependent cutoff to separate Gaussian and excluded volume regimes. The value of N_r is estimated from

$$N_r \sim (l^3/\nu)^2 \quad (5)$$

where ν is the usual binary cluster integral which will be approximated here as¹⁰

$$\nu = \nu_\infty \left(1 - \frac{\Theta}{T} \right), \quad \text{for } T > \Theta \quad (6)$$

In (6), ν_∞ is treated as a constant to be determined from comparison of theory and experiment. Combining (5) and (6) we find

$$N_r = \alpha/\tau^2 \quad (7)$$

where

$$\tau = (T - \Theta)/T \quad (8)$$

and the proportionality constant $\alpha \sim (l^3/\nu_\infty)^2$ is an adjustable parameter, which may depend insensitively on the type of the solvent and the structure of the monomer units.

Substituting (4) into (3) yields

$$\alpha_S^2(x) = x^2(3 - 2x) + 6x^{1-2\nu} \left(\frac{1 - x^{2\nu+1}}{2\nu + 1} - \frac{1 - x^{2(\nu+1)}}{2(\nu + 1)} \right) \quad (9)$$

where $x \equiv N_r/N$, and α_S is the linear expansion factor defined by $\alpha_S \equiv R_G(x)/R_G(\Theta)$ where $R_G(\Theta)$ is the value of R_G at the Θ temperature, i.e.,

$$R_G(\Theta) = l(N/6)^{1/2} \quad (10)$$

Equation 9 was first given by Farnoux et al.⁸

In (9), x varies from N^{-1} to unity when the solvent changes from “good” to “poor”, respectively. In the good solvent limit $x \leq N^{-1}$ one has

$$R_G(\text{good}) = lN^\nu/[2(\nu + 1)(2\nu + 1)]^{1/2}$$

$$R_G(\text{good}) = 0.377lN^{0.6} \quad (\nu = 3/5) \quad (11)$$

and²⁵

$$\alpha_S(\text{good}) = 0.923N^{0.1} \quad (12)$$

The variation of α_S with $X^{-1} = N/N_r$ is presented in Figure 1 with the Flory value $\nu = 3/5$ although the most accurate value of ν is reported to be 0.588.⁴ The accuracy

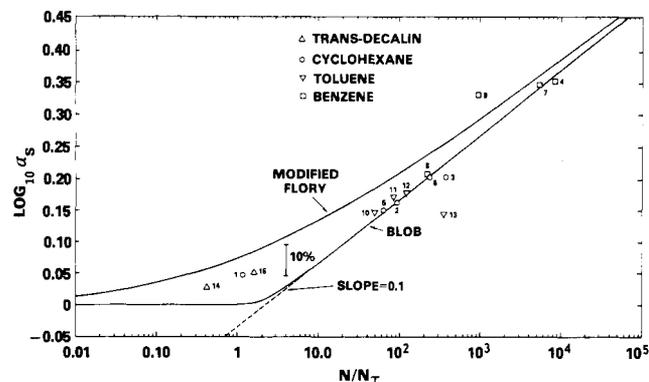


Figure 1. The variation of the expansion factor α_S for radius of gyration with N/N_r , that combines both the molecular weight and temperature dependence. The experimental points with labeled numbers corresponding to Table I are adjusted to fit the blob theory.

of the Flory value is sufficient for the purpose of this paper.

The asymptotic behavior of α_S for large N/N_r follows from (9) as

$$\alpha_S \rightarrow [3/(2\nu + 1)(\nu + 1)]^{1/2} (N/N_r)^{\nu-0.5}$$

$$\alpha_S = 0.923(N/N_r)^{0.1}, \quad (\nu = 3/5) \quad (13)$$

It is interesting to compare (9) to the original Flory equation,¹¹ $\alpha_S^5 - \alpha_S^3 = \gamma z$, where z is the excluded volume parameter

$$z = (3/2\pi)^{3/2} (\nu/l^3) N^{1/2} \quad (14)$$

and $\gamma = 2.60$ in the original theory and 1.276 in its modified version.¹⁰ It is observed from (5) and (14) that

$$N/N_r = Cz^2 \quad (15)$$

where C is a numerical proportionality constant. Matching the asymptotic behavior (eq 13) to that $[\alpha_S \rightarrow (\gamma z)^{1/5}]$ predicted by the Flory equation, one can estimate C as $C = \gamma^2/0.923^{10}$ which yields²⁶ $C = 3.63$ for $\gamma = 1.276$ and $C = 6.215$ for $\gamma = 1.67$, which is more appropriate for large z .¹⁰ The variation of $\alpha_S(z)$ in Flory theory with $C = 3.63$ is compared to (9) in Figure 1. It is observed that the Flory theory predicts a slower approach to the asymptotic behavior than the blob theory does. The latter reaches the power law region as early as $N \geq 5N_r$. Since it reproduces the exact first-order perturbation theory result for small z , the modified Flory theory may be expected to be more accurate for smaller values of $N/N_r \leq 1$. Below, we use the blob theory to analyze the experimental results, because, being essentially a model for the equilibrium distribution of the vector distance between monomer pairs, it provides a general mathematical framework to consistently calculate other static and dynamic quantities such as hydrodynamic radius R_H which we consider in this paper.

The measured values of α_S are given as a function of temperature and molecular weight (see Table I). In order to enter the experimental points in Figure 1, we must express N/N_r in terms of M_w and T :

$$\frac{N}{N_r} = \frac{\tau^2 M_w}{\alpha n A} \quad (16)$$

where A is the molecular weight per monomer ($A = 104$ for polystyrene) and n is the number of monomer units in a statistical length. The product αn is the only adjustable parameter needed for a quantitative comparison of the theory and experiment. We have determined it as $\alpha n \approx 4$ by matching the experimental and theoretical values

TABLE I. R_G AS A FUNCTION OF M_w & TEMPERATURE

SOLVENT	T(°C)	$M_w(10^{-3} \text{g/mol})$	$R_G(T)(\text{Å})$	$\Theta(°C)$	$R_G(\Theta)(\text{Å})$	$z^{-1} = N/N_T$	$R_G(T)/R_G(\Theta)$	REFERENCE	NO.	
C_6H_{12} (CYCLOHEXANE)	36.4	43.8	2,400	36.4	2,170	1.1	1.11	SLAGOWSKI (17)	1	
	46		3,170			98.0	1.46		2	
	56		3,480			378.0	1.89		3	
C_6H_6	40	27.8	4,810	-50	1,580	8.71×10^3	2.22	BERRY (19)	4	
C_6H_{12}	46		2,230	80.9		1.41	5			
C_6H_6	56		2,490	238.0		1.58	6			
C_6H_6	40	1.3	3,470	-50	344	5.63×10^3	2.20	CARPENTER (18)	7	
C_6H_6	36		568	238.0		1.82	8			
C_6H_6	30		1,471	682		968.0	2.15		9*	
C_7H_8 (TOLUENE)	12	0.82	305	-41	216	51.5	1.41	BERRY (19)	10	
			106			282	87.3		1.47	11
			156			366	128.7		1.50	12
			4.40			662	678		306.0	1.40
TRANS-DECALIN	30	0.178	138	20.5	130	0.42	1.062	CHU (20)	14	
	40		146			1.87	1.122		15	

* $R_G(\Theta)$ VALUE OF NO. 9 AND NO. 13 ARE NOT CONSISTENT WITH OTHERS.

of α_S for polystyrene in cyclohexane, for which the Θ temperature is known to be about 35.4 °C. More explicitly, we have first calculated α_S from the experimental values of $R_G(T)$ and $R_G(\Theta)$ listed in Table I as a function of T and M_w . Then we have computed the theoretical value of (N/N_T) corresponding to α_S using eq 9 which gives α_S as a function of (N/N_T) . These results are also tabulated in Table I. Finally, we have substituted N/N_T , M_w , $\tau = (T - \Theta)/T$, and $A = 104$ in (16) to obtain αn . We have considered only the experimental points designated by 2, 5, and 6 in Table I and Figure 1, because the values of α_S corresponding to these points are well in the asymptotic region and follow N^ν power law, and the blob theory is expected to be more accurate in this region. The value $\alpha n \approx 4$ represents a rounded average of αn for these points. A more precise determination of αn employing least-squares fitting of a power law to data in this region was not considered necessary for the main purpose of this paper. Besides, we had only few experimental points in the asymptotic region to obtain a precise value for αn .

The Θ temperatures for benzene and toluene are not accurately known. We have estimated them in the vicinity of -50 °C and -41 °C, respectively, by assuming that αn is the same in these solvents as in cyclohexane. αn is expected to be insensitive to the type of solvent for a given polymer because the dominant solvent dependence is accounted for explicitly through the Θ temperature in $N_T = \alpha/\tau^2$. Had the Θ temperatures been known for benzene and toluene, this assumption would be unnecessary, and in fact αn could be obtained the same way for these solvents as illustrated above for cyclohexane, and the solvent dependence of αn could be investigated. We emphasize that other values of Θ for these solvents can be accounted for by allowing αn to be different in different solvents. The interpretation of the experimental results for the hydrodynamic radius in such solvents at room temperature, or above, is very insensitive to the value of the Θ temperature, so that the above estimates are adequate for our purpose.

A value of the parameter α can be obtained from an independent estimate of n , i.e., the number of monomers in a statistical length, using, for example, the characteristic ratios calculated by Flory¹³ for various chain models. For a Gaussian polystyrene chain one obtains values in the vicinity of $n = 15$ –20. As a typical value we choose $n = 20$ and obtain $\alpha \approx 0.2$. We use this value in the following discussions, where we indicate the temperature region in which the behavior of α_S as function of T is most sensitive to the choice of value of α and suggest the possibility of experimental evaluation α from comparison of theory and experiment in this region.

Figure 2 shows the variation of α_S with the reduced temperature τ for polystyrene with $M_w = 44.4 \times 10^6$. The

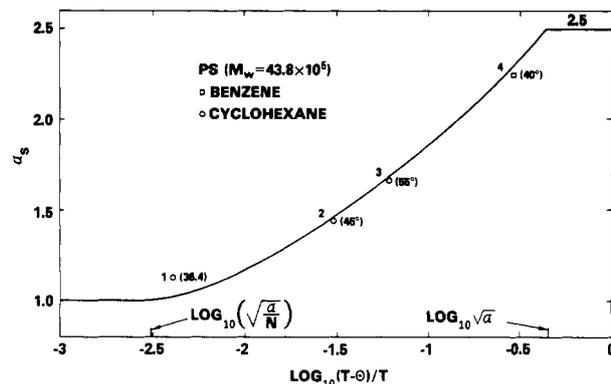


Figure 2. The variation of α_S with the reduced temperature at a fixed molecular weight.

three temperature regions are to be observed. The Θ region extends up to the transition temperature

$$T_m = \Theta(1 - [\alpha/N]^{1/2})^{-1} \quad (17)$$

where T_m and Θ are in degrees Kelvin. For polystyrene with $M_w = 44.4 \times 10^6$ in cyclohexane ($\Theta = 308$ K) we find $T_m \approx 36.5$ °C. For $M_w = 1.79 \times 10^6$, $T_m \approx 51$ °C.

The upper transition temperature T_M , if it exists, marks the beginning of the good solvent limit, which corresponds to the maximum swelling of the chain for fixed N . It is given by

$$T_M = \Theta(1 - \alpha^{1/2})^{-1} \quad (18)$$

when $\alpha < 1$. The case $\alpha > 1$ implies that the maximum swelling is not attained at any temperature. For benzene eq 18 yields $T_M \approx 130$ °C with $\Theta = -50$ °C and $\alpha = 0.2$. This result, admittedly very crude, seems to indicate that polystyrene in benzene is not quite in the good solvent regime, where α_S becomes independent of temperature. This point may be verified by measuring α_S in benzene at higher temperatures with fixed M_w .

In summary, we find, for large N ,

$$\alpha_S = [3/(\nu + 1)(2\nu + 1)]^{1/2} N^{\nu-0.5} \quad (19)$$

for $T > T_M$,

$$\alpha_S = [3/(\nu + 1)(2\nu + 1)]^{1/2} \tau^{2\nu-1} (N/\alpha)^{\nu-0.5} \quad (20)$$

for $T_m < T < T_M$, and $\alpha_S = 1$ for $T < T_m$.

The Variation of R_H

The calculation of R_H through its definition (eq 1) requires an expression of the diffusion coefficient D_0 . Such an expression can be obtained from the fact that $D_0 q^2$ is the slope of $|\ln S(q,t)|$ for small momentum transfers q satisfying $qR_G \ll 1$, where $S(q,t)$ is the normalized scattering function with $S(q,0) = 1$. However, D_0 may be calculated as the limit as $q \rightarrow 0$ of a generalized q -dependent diffusion coefficient^{2,14}

$$D(q) = \Omega(q)/q^2$$

where $\Omega(q)$ is the initial slope of $|\ln S(q,t)|$. $D(q)$ may be interpreted as the diffusion coefficient of part of the chain within a wavelength of momentum transfer, whose diffusion dominates the initial decay of $S(q,t)$. When $qR_G \ll 1$, this initial diffusion involves the entire molecule so that $S(q,t)$ becomes an exponential function of t for all times and $D(q)$ reduces to D_0 .

The general expression for $D(q)$ was obtained earlier² as

$$D(q) = \frac{1}{q^2} \frac{\sum_{m,n} \langle D_{mn} \exp(iq \cdot R_{mn}) \rangle : q q}{\sum_{m,n} \langle \exp(iq \cdot R_{mn}) \rangle}$$

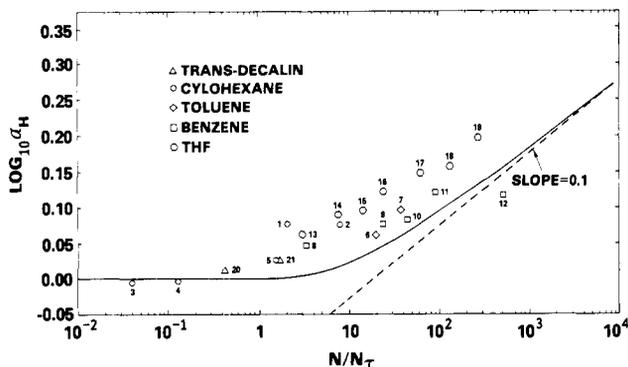


Figure 3. The variation of the expansion factor α_H for hydrodynamic radius with N/N_T . No adjustable parameters are involved in comparison of theory and experiment. Experimental points are labeled corresponding to Table II.

where D_{mn} is the diffusion tensor, and R_{mn} denotes, in the limit of zero concentration, the vector distance between two beads of the same chain. In the limit of $q \rightarrow 0$ and with D_{mn} chosen as the conventional diffusion tensor in Kirkwood-Riseman theory,¹⁰ $D(q)$ reduces to

$$D_0 = \frac{k_B T}{\xi} \left[\frac{1}{N} + \left(\frac{\xi}{6\pi\eta} \right) \frac{1}{N^2} \sum' \left\langle \frac{1}{|R_{mn}|} \right\rangle \right] \quad (21)$$

where ξ is the friction coefficient per segment. Using the temperature blob model to perform the equilibrium averages, Benmouna and Akcasu² calculated D_0 as a function of temperature. We present their result directly in terms of the hydrodynamic radius:

$$\frac{1}{R_H} = \frac{1}{lN^{1/2}} \frac{12}{(6\pi)^{1/2}} x^{1/2} \left[2 \left(1 - \frac{x}{3} \right) + \frac{1}{1-\nu} (x^{\nu-1} - 1) - \frac{1}{2-\nu} (x^{\nu-1} - x) \right] \quad (22)$$

where as before $x = N_T/N$.

Equation 22 yields

$$R_H(\theta) = ([6\pi]^{1/2}/16) lN^{1/2} \quad (23)$$

in a θ solvent with $x \geq 1$, and

$$R_H(\text{good}) = ([6\pi]^{1/2}/12)(1-\nu)(2-\nu)lN^\nu \quad (24)$$

in the good solvent limit with $x \leq 1$.

The expansion factor $\alpha_H = R_H(x)/R_H(\theta)$ is then obtained from (22) as

$$\alpha_H(x) = \frac{4}{x^{1/2}} \left[2(3-x) + 3 \left(\frac{x^{\nu-1} - 1}{1-\nu} - \frac{x^{\nu-1} - x}{2-\nu} \right) \right]^{-1} \quad (25)$$

Figure 3 shows the variation of $\alpha_H(x)$ with N/N_T , as calculated from (25) with $\nu = 3/5$. The asymptotic behavior for large (N/N_T) is

$$\alpha_H(x) \rightarrow \frac{4}{5}(1-\nu)(2-\nu)(N/N_T)^{\nu-0.5} \quad (26)$$

$$\alpha_H(x) = 0.747(N/N_T)^{0.1}$$

Figure 4 presents the variation of $\alpha_H(x)/\alpha_G(x)$ as calculated from (25) and (9) with $\nu = 3/5$. We find that

$$R_H(\theta)/R_G(\theta) = \frac{3}{8}\pi^{1/2} = 0.664 \quad (27)$$

in θ solvents, and

$$\frac{R_H(\text{good})}{R_G(\text{good})} = \frac{\pi^{1/2}}{2(3)^{1/2}} (2-\nu)(1-\nu)[(\nu+1)(2\nu+1)]^{1/2} \quad (28)$$

$$\frac{R_H(\text{good})}{R_G(\text{good})} = 0.537 \quad (\nu = 3/5)$$

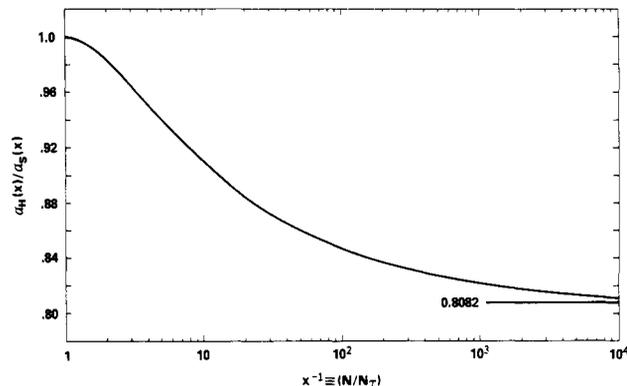


Figure 4. The variation of the ratio of the hydrodynamic radius to radius of gyration.

TABLE II. R_H AS A FUNCTION OF M_w & TEMPERATURE

SOLVENT	T (°C)	M_w (10^{-1} g/mol)	R_H (Å)	θ (°C)	R_H (Å)	$x^{-1} = N/N_T$	$R_H(T)/R_H(\theta)$	REFERENCE	NO.
C ₈ H ₁₂ CYCLO- HEXANE	46	0.800	267	36	211.3	2.14	1.19	HAN (21)	1
	56		262			8.04	1.19		2
	38	93.7	84.2		0.04	0.986	3		
	40.4	84.1	84.2		0.13	0.986	4		
	85	84.7	84.2		1.6	1.08	5		
C ₆ H ₆ TOLUENE	23	0.179	107	-41	84.2	20.1	1.14		6
	56		118			38.8	1.25		7
C ₆ H ₆ BENZENE		0.0246	39.0		34.8	3.38	1.11	ADAM & DELSANTI (3, 22)	8
		0.174	112		92.8	23.8	1.19		9
	20	0.334	157	-50	128.7	48.8	1.21		10
		0.864	242		181.5	91	1.32		11
		3.8	574		434.1	521	1.31		12
THF		0.0204	37		31.8	3.1	1.16	MANDEMA & ZELDENRUST (23)	13
		0.0610	82		50.3	7.78	1.23		14
		0.0972	87		66.4	14.8	1.25		15
	25	0.180	119	-50	88.1	24.4	1.33		16
		0.411	202		142.8	62.8	1.41		17
		0.880	298		206.5	131	1.44		18
		1.8	471		288.8	274	1.576		19
TRANS- DECALIN	30	0.179	93.8	20.5	81.1	0.42	1.030	S. CHU (20)	20
	40		86.8			1.67	1.082		21

(18) $R_H(\theta)$ is calculated from $R_H(\theta) = 0.2227 M_w^{1/2}$

(19) $R_H(T)$ is calculated by using $T = 283^\circ\text{C}$ and $\zeta_0 = 0.847$ c.p.

in a good solvent. Both of these results are consistent with the inequality of (2) of Des Cloizeaux.⁵

The experimental results on R_H are compiled in Table II as a function of M_w and T for polystyrene in various solvents. We have used

$$\frac{N}{N_T} = \frac{M_w}{104.4} \tau^2$$

to calculate (N/N_T) in the table, which corresponds to $n\alpha = 4$ determined from the data on the radius of gyration, as discussed in the previous section. The θ temperature for THF was taken as -50°C (the same for benzene) in the absence of any more accurate data. The experimental results are shown in Figure 3.

The main observation is that the data fall in the non-asymptotic region of the theoretical curve, where a simple power law $R_H \sim N^\nu$ is not obeyed, as suspected by Des Cloizeaux.⁶ It also follows that any power law fit to the data is bound to yield an exponent less than 0.6, as observed by Adam and Delsanti.³ The value of the exponent in such a fit should depend on the range of (N/N_T) corresponding to the experimental values of M_w and T .

A final remark about the discrepancy between the data and the theoretical curve is that the blob theory is expected to be crude for small values of N/N_T due to the discontinuous transition from the Gaussian to excluded volume behavior in modeling $\langle |R_n|^2 \rangle$. On the basis of the com-

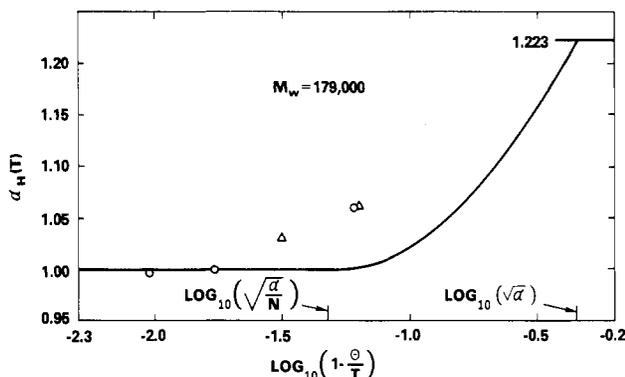


Figure 5. The variation of α_H with the reduced temperature at a fixed molecular weight.

parison made in Figure 1 between the blob theory and the modified Flory theory for α_S , one may conclude that the blob theory of R_H should predict lower values in the transition region $N/N_r \sim 1$ than the actual values. The experimental results seem to confirm this trend in Figure 3.

Figure 5 presents the variation of α_H with the reduced temperature $(1 - \theta/T)$ for $M_w = 179\,000$, along with the experimental values in cyclohexane and *trans*-decalin.

Discussions and Conclusions

We regard the blob theory of chain statistics essentially as a model for the equilibrium distribution of the vector distance between monomer pairs in the same chain. When supplemented with a dynamical model for the time evolution of polymer solution, it provides a powerful computational tool within the framework of the linear response theory,^{15a,15b,16} by which various equilibrium and dynamic polymer properties can be calculated in a self-consistent manner. This aspect of the blob theory, which has been demonstrated in this paper by actually computing the radius of gyration and the hydrodynamic radius, is perhaps its most attractive feature over the other classical two-parameter theories, such as the modified Flory theory.

The mathematical framework described above does not leave any room for a new dynamical exponent ν' in $R_H \sim N^{\nu'}$ for large N , which is independent of, and numerically different from, the exponent in $R_G \sim N^{\nu}$. This implication of the theory is in agreement with Des Cloizeaux's conclusion (eq 5) mentioned in the introduction and calculations by Adler and Freed.²⁴

The single chain properties such as the expansion factors α_S and α_H considered in this paper are expressed in terms of a single parameter $N/N_r \sim z^2$ where z is the excluded volume parameter. The unspecified proportionality constant in $N/N_r \sim z^2$ introduces a further lack of precision in quantitative comparison of theory and experiment, in addition to the difficulties encountered in other two-parameter theories in expressing the binary cluster integral in z as a function of temperature. We have removed these uncertainties in this paper by adopting Flory's form for the binary cluster integral and eliminating the unknown quantities, which are lumped into a single parameter, by matching the theory and experiment for the radius of gyration.

The data for the hydrodynamic radius R_H have been compared in Figure 3 with the theory which is now free of any adjustable parameter. The main conclusion is that the experimental values R_H for various molecular weights

and temperatures all fall in a region, where, as suspected by Des Cloizeaux,¹⁷ R_H cannot be represented by a power law $N^{\nu'}$ as a function of N . Interpretation of the data by a simple power law is therefore expected to yield a value for ν' less than ν , as reported by Adam and Delsanti. The numerical value of ν' obtained by this procedure would depend on the range of molecular weights used in the experiment.

Figure 3 also shows that the blob theory predicts consistently lower values than the experimental data in the transition region centered about $N/N_r \sim 1$. The same trend is also observed in Figure 1 where the data on R_G are compared with the blob and modified Flory theories. The inadequacy of the blob theory in this region is due to the discontinuous jump from the Gaussian to excluded volume behavior in modeling $\langle |R_n|^2 \rangle$. This numerical inaccuracy in the transition regions seems to be a price one pays for the simplicity and clarity of the blob theory.

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- Note that (11) yields the ratio of the conventional expansion factors α_R and α_S as $(\alpha_R/\alpha_S) = [(2\nu + 1)(\nu + 1)/3]^{1/2}$ which yields 1.0832 for $\nu = 0.6$ and 1.0739 for $\nu = 0.5888$. Using $\alpha_R^5 = 1.333z$ and $\alpha_S^5 = 1.276z$ where z is the excluded volume parameter [ref 10, p 118], one finds $(\alpha_R/\alpha_S) = 1.0088$. The Monte-Carlo calculations for tetrahedral and simple cubic lattices give respectively 1.0328 and 1.0247 [ref 10, pp 12 and 123].
- Setting $N_r = 1$ in (15), we obtain an estimate of (ν/l^3) that corresponds to maximum swelling for fixed N as $(\nu/l^3) \approx (2\pi/3)^{3/2}/C^{1/2}$. One finds $(\nu/l^3) \approx 1.59$ with $\gamma = 1.276$ and 1.216 with $\gamma = 1.67$. Recall that $(\nu/l^3) = 1.53$ for the tetrahedral lattice.¹⁰ The consistency of the numerical values is noteworthy.