Reviews

Characterization of Branching Architecture through "Universal" Ratios of Polymer Solution Properties

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ABSTRACT: Experimental and Monte Carlo data for the dilute-solution properties of "lightly branched" polymers (stars, combs, rings, ...) are compared with the renormalization group predictions of Douglas and Freed. The comparisons focus on "universal" dimensionless ratios of the mean dimensions of lightly branched polymers, relative to those of linear polymers having the same molecular weight. Complications associated with hydrodynamic solution properties and with the effect of ternary interactions are briefly discussed. Dimensionless ratios involving the polymer second virial coefficient, A_2, are also tabulated and compared with theory.

I. Introduction

Polymer properties can be significantly modified through a variation of molecular architecture because of two basic influences of the topological constraints of branches and loops: (1) The local average polymer density increases relative to that in a linear chain.[1] (2) Cooperative motion of the chain as a whole is restricted by the constrained segmental motion within branches and loops.[2] The first effect is particularly important in the study of dilute-solution properties, while the second effect presumably dominates at high concentrations.[2]

There has been considerable interest lately in using polymers with well-prescribed branching architectures to test molecular theories such as the reptation model.[2,3] Interest also stems from the practical motivation of tailoring the properties of polymeric materials through the control of molecular topology.[4] Interest in chain architectures coincides with recent advances in synthetic procedures,[5] in the theory of polymer solution properties,[6,7] and in the capabilities of Monte Carlo simulation methods.[8] This confluence of motivational factors accounts for the numerous recent papers devoted to the influence of branching on polymer properties.

An experimental study of how chain architecture affects solution properties first requires the synthesis and precise characterization of the model polymer species. Characterization, in turn, necessitates an adequate theory for interpreting experimental data used to assess the "quality" of the synthesized material. The most important means of characterizing the model polymers is through the measurement of dilute-solution properties. For example, a classical measure of branching is the Zimm–Stockmayer ratio,[9] g_s, of the radius of gyration of the branched polymer to that of the linear polymer at the same molecular weight (see below). Other commonly employed "branching parameters" include the g' and h parameters, defined (see below) as the ratios of the intrinsic viscosity and the hydrodynamic radius for the branched to the linear polymer species, respectively.[10,11] Dimensionless virial properties, such as the penetration function, Ψ, have been largely neglected in characterizations of branched polymers because an adequate theory of excluded volume is required to interpret such data and because it is only recently that precise theoretical predictions[6,7] have been made for Ψ of branched polymers. Section III is devoted to these virial ratios.

The present paper compares renormalization group (RG) calculations of Douglas and Freed[6] with an extensive compilation of data for the radius of gyration, hydrodynamic radius, intrinsic viscosity, and second virial coefficient, in which the branching architecture is varied. Comparison is also made with available Monte Carlo simulation data,[12-16] "scaling theory",[17] and classical mean-field calculations.[10] Section II reviews classical Gaussian chain predictions for a uniform star polymer and relates them to RG computations and Monte Carlo simulations. The corresponding results for a chain with excluded volume[6] are summarized, and the relative

Table I
Polystyrene (Good Solvent) Radii of Gyration in Toluene

	sample	$M \times 10^{-5}$	$\langle S^2 \rangle \times 10^{12}$ cm^2	$\langle S^2 \rangle_{\mathrm{Lin}}{}^{a}$	g^*_{s}(exptl)	$g^*_{\mathrm{s}}{}^{b}$	$g^\circ_{\mathrm{s}}{}^{c}$
3-arm[d]					0.79	0.778	0.778
4-arm[e]	S141A	5.37	4.7	8.4	(0.560)	0.631	0.625
	S181A	10.61	11.34	18.6$_3$	0.608		
	S191A	14.4$_4$	16.7$_8$	26.7	0.628		
	A-48.2	18.7	21.0	36.1	0.581		
6-arm[f]	H5041A	5.2	3.8$_6$	8.09	(0.477)	0.453	0.444
	H5051A	11.1	8.6$_5$	19.6$_4$	0.440		
	H5121A	18.9	17.5	36.6	0.478		
12-arm[g]	12PS1B1A	58.0	33.0	135.9	0.243	0.248	0.236
18-arm[g]	18PS1	93.0	48.0	236.2	0.203	0.173	0.161
H-comb[h]	H1A1	4.82	5.0	7.4	0.676	0.720	0.712
	H3A1A	6.82	7.4	11.1	0.666		
	H5A1	10.5	13.0	18.4	0.706		
	H6A1A	17.2	23.7	32.8	0.723		
ring[i]	R19D	3.34	2.5	4.8	0.519	0.516	0.5

[a] Based on $\langle S^2 \rangle_{\mathrm{Lin}} = 1.66 \times 10^{-18} M^{1.17}$. [b] Theory developed in refs 6 and 7. [c] Results reviewed in ref 10. [d] Reference 32. [e] References 22 and 39. [f] Reference 23. [g] Reference 24. [h] Reference 25. [i] Reference 30d.

Table II
Polybutadiene (Good Solvent) Radii of Gyration in Cyclohexane

	sample	$M \times 10^{-5}$	$\langle S^2 \rangle \times 10^{12\,a}$	$\langle S^2 \rangle_{\mathrm{Lin}}{}^{a,b}$	g^*_{s}(exptl)	$g^*_{\mathrm{s}}{}^{c}$	$g^\circ_{\mathrm{s}}{}^{d}$
4-arm	C[e]	1.43$_4$	(1.98)	3.21	(0.616)	0.631	0.675
	B[e]	1.59	2.56	3.63	0.705		
	A[e]	3.75	6.75	10.01	0.674		
	800[f]	8.3	17.0	25.6	0.663		
	1600[f]	13.5$_2$	33.0	45.7	0.723		
18-arm[g]	1518	3.11	(1.54)	8.03	(0.192)	0.173	0.161
	18SSC	3.40	(1.87)	8.92	(0.21)		
	18SC	3.58	1.80	9.48	0.19		
	2518	5.41	3.01	15.45	0.195		
	3718	7.62	3.97	23.17	0.171		
	9918	19.0	11.8	68.28	0.173		

[a] In cm^2. [b] Based on $\langle S^2 \rangle_{\mathrm{Lin}} = 2.55 \times 10^{-18} M^{1.18_3}$. [c] Theory developed in refs 6 and 7. [d] Reviewed in ref 10. [e] Reference 46. [f] Reference 56. [g] Reference 57.

insensitivity of such dimensionless ratios to excluded volume is explained by using the RG theory.

We also discuss the qualitative influence of ternary interactions on the polymer mean dimensions under Θ conditions.[18] Because branching increases the local polymer segmental density, the probability of ternary interactions is increased. Thus, ternary interactions can give rise to a significant contribution to the dimensions of a branched polymer at the Θ point.[6a] Experimental and Monte Carlo data, summarized below, exhibit deviations from the ideal Gaussian chain theory for many-arm stars, which support theoretical expectations of the influence of ternary interactions.[18]

Dimensionless ratios of hydrodynamic properties, while relatively simple to obtain experimentally, present a whole host of problems in their interpretation.[19,20] This issue is addressed briefly in section II.

II. Universal Ratios of Polymer "Size" as Measures of Branching

A common experimental means of characterizing branching architecture is through the ratio of the squared radius of gyration of a branched polymer, $\langle S^2 \rangle_{\mathrm{Br}}$, to the squared radius of gyration, $\langle S^2 \rangle_{\mathrm{Lin}}$, of a linear polymer having the same molecular weight. This ratio is defined as

$$g_{\mathrm{s}} = \langle S^2 \rangle_{\mathrm{Br}} / \langle S^2 \rangle_{\mathrm{Lin}} \tag{2.1}$$

For a uniform star having f Gaussian chain arms (i.e., having arms of equal length) g_{s} is given by the classical Zimm–Stockmayer prediction[9]

$$g^\circ_{\mathrm{s}} = (3f - 2)/f^2 \tag{2.2}$$

where the superscript ° indicates a Gaussian chain property. Equation 2.2, of course, applies only to the limit of long flexible chains. Variations of g°_{s} with branching architecture are reviewed by Yamakawa[10] and Bywater.[11] The experimental problems of incomplete coupling of the star arms to their central vertex and the role of polydispersity of the star arms on g°_{s} are discussed by Bywater.[11] Mansfield and Stockmayer[21] generalize (2.2) to the wormlike star model, which is relevant to stars having relatively short or stiff arms.

A. g_{s} in Good Solvents. It has long been observed that the g_{s} ratios for experimental good solvent systems closely coincide with the predictions of Gaussian chain statistics.[11] Further amplification of this observation is provided by the RG calculations by Douglas and Freed[6] and by Monte Carlo simulations.[15,16] Since recent theoretical studies have reiterated this point, we simply emphasize the experimental data in support of the theoretical predictions and briefly indicate a theoretical explanation of the insensitivity of g_{s} to excluded volume.

Table I summarizes experimental values of g_{s} for 3-, 4-, 6-, 12-, and 18-arm stars, H-combs, and ring polymers for polystyrene in the good solvent toluene. Table II considers 4- and 18-arm polybutadiene stars in the good solvent cyclohexane. A superscript asterisk denotes the good solvent limit (e.g., g^*_{s}). The tables also provide both the renormalization group (RG) calculations of g^*_{s} by Douglas and Freed[6] and the classical Gaussian chain computations for g°_{s}. Agreement between theory and experiment[22,26] is quite reasonable, although it is difficult to conclude anything more quantitative than the approximation $g^*_{\mathrm{s}} \approx g^\circ_{\mathrm{s}}$ given the small difference between the theoretical estimates of g^*_{s} and g°_{s}. The RG prediction that $g^*_{\mathrm{s}} \approx g^\circ_{\mathrm{s}}$ is certainly in good accord with the experimental observations, and the magnitudes of the experimental values of g_{s} in a good

Table III
g_s Lattice Monte Carlo Data for H-Combs

lattice type	simulation: g^*_s(SAW)[a]	theory: g^*_s(RG)[b]	theory: (g°_s)[c]
fcc	0.71 ± 0.02	0.720	0.712
bcc	0.72 ± 0.02		
cubic	0.71 ± 0.02		
tetrahedron	0.70 ± 0.03		

[a] Reference 15b. [b] Theory developed in refs 6 and 7. [c] Theory reviewed in ref 10.

solvent generally agree with the average experimental values cited previously by Douglas and Freed.[6]

Next it is useful to compare Monte Carlo estimates[12-16] of g^*_s and the corresponding RG predictions. Pertinent Monte Carlo data for self-avoiding uniform star polymers have recently been summarized by Barrett and Tremain.[16] Figure 4 of ref 16 compares the RG predictions of Douglas and Freed[6,27] with simulation data for stars with up to 18 arms. The agreement between theory and the Monte Carlo data is quite good over the entire range of f. Table III also lists the H-comb simulations of Lipson et al.[15] for g^*_s on various lattices, where again similar agreement is obtained with RG theory.

It should be appreciated that for many-arm stars the perturbation of the excluded-volume interaction, relative to a linear chain, becomes large so that the renormalization group theory no longer provides a useful description. Application of the RG theory should be restricted to $f < 12$, and only senseless results can be expected from the theory in the infinite-arm limit. The large f limit needs to be treated by separate methods such as scaling theory,[17] mean-field theory,[10,28] or $1/f$ perturbation theory.[6e] No method can be expected to apply over the entire f range. We briefly mention relevant results of the scaling theory and a mean-field approach, discussed in Appendix A, which complement the RG predictions summarized in Table I.

There have been several recent attempts to test the Daoud and Cotton[17] "scaling theory" prediction, $g^*_s \sim f^{-4/5}$ for large f, where the prefactor is unspecified. However, it is difficult to discern from the Monte Carlo or experimental data a small variation of the exponent of f from its classical Gaussian value of −1. Indeed, Whittington et al.[15] find an equally good fit to Monte Carlo data for g^*_s with either the −1 or −4/5 exponents by just adjusting the prefactor. The usefulness of the scaling theory is evidently limited by the uncertainty in the prefactor. An argument is presented in Appendix A, based on the classical modified Flory theory, which gives the Daoud–Cotton scaling result[17] for g^*_s *along with the prefactor* as

$$g^*_s(\text{modified Flory}) \sim 1.94 f^{-4/5} \qquad f \rightarrow \infty \tag{2.3}$$

Equation 2.3 is in reasonably close agreement with the Monte Carlo estimates of Whittington et al.[15] and of Barrett and Tremain.[16] The prefactor is deduced to be about 1.8–1.9 from the simulation data (see Appendix A). DiMarzio and Guttman[29] have also introduced a mean-field theory, augmented by geometrical arguments, that recovers the scaling result $g^*_s \sim f^{-4/5}$ along with an estimate of the prefactor.

Experimental data,[22-26] Monte Carlo and direct enumeration studies,[12-16] and RG calculations by Douglas and Freed[6,27] all point to the simple observation that g^*_s is remarkably close to Zimm and Stockmayer's estimate for Gaussian chains. The reason for this insensitivity of g_s to excluded volume (above the Θ point) is quite simple in the RG theory. Douglas and Freed[6] show that an *arbitrary* static radial polymer property Q, scaling as a radius to the pth power ($Q \sim R^p$), has a *universal* scaling function as a function of excluded volume

$$Q = G_Q \langle S^2 \rangle_0^{p/2} E_p(z_2)\, P_Q(z_2) \tag{2.4}$$

Here $\langle S^2 \rangle_0^{p/2}$ is the radius of gyration of a Gaussian chain, and G_Q is a number (prefactor) obtained by calculating Q in the Gaussian chain limit, where the dimensionless excluded-volume parameter z_2 vanishes and where by definition $E_p(z_2 = 0) = 1$ and $P_Q(z_2 = 0) = 1$. The reader is referred to Douglas and Freed[6] and Freed[7] for a detailed discussion of the specific analytic form of (2.4) and its theoretical derivation. The point to be emphasized here is the "exponent function", $E_p(z_2)$, contains most of the excluded-volume dependence and depends only on z_2 and the power p of the radial property. $E_p(z_2)$ does not depend on the type of radial property (aside from the index p) or on the chain architecture. The "prefactor function", $P_Q(z_2)$, on the other hand, depends on the details of the particular measure of the mean dimensions [e.g., $\langle R^2 \rangle$, $\langle S^2 \rangle$, ...] and on the branching architecture (linear, star, comb, ...) and varies only *weakly* with excluded volume. Further, by forming a dimensionless ratio between measures of polymer size for a branched and a linear polymer at the same molecular weight, we obtain

$$Q(\text{branched})/Q(\text{linear}) = [P_Q(z_2,\text{branched})/P_Q(z_2,\text{linear})]\, g^\circ_Q \tag{2.5a}$$

$$g_Q \equiv Q(\text{branched})/Q(\text{linear}); \quad g_Q(z_2 = 0) \equiv g^\circ_Q \tag{2.5b}$$

so *the predominant contribution to the variation of Q with excluded volume* (i.e., the $E_p(z_2)$ factor) *exactly cancels in forming the ratio* g_Q. This canceling contribution basically reflects the uniform expansion of the polymer dimensions with excluded volume. The ratio $P_Q(z_2,\text{branched})/P_Q(z_2,\text{linear})$ represents the relative variation of P_Q, due to variation of branching architecture, and is even more slowly varying than is either $P_Q(z_2,\text{linear})$ or $P_Q(z_2,\text{branched})$ alone (see Douglas and Freed[6] for details). Consequently, the observed insensitivity of g_s to excluded volume in experiments and Monte Carlo simulations is perfectly understandable on the basis of RG theory. This insensitivity is predicted to apply to a wide class of dimensionless ratios of the type g_Q.

B. Θ Condition Ratios. The measurement of g_s for Θ point polymers is complicated by the possibility that the Θ conditions for a branched polymer and a linear polymer are not generally the same. Shifts of the Θ temperature between branched and linear polymers have been observed in numerous physical systems[23,30] and also in Monte Carlo simulation.[31] A decrease of g_s with additional branching means that the average chain density within a polymer coil is increased and consequently the probability of ternary interactions (i.e., the simultaneous volume interference of three parts of the chain in a single region of space) is greater in the branched chain than in a linear chain of the same molecular weight. The idealized two-parameter model neglects the role of ternary interactions, and when these effects are incorporated into the three-parameter model of polymer excluded volume, a Θ point shift with branching is predicted.[18] Θ point shifts arising from a variation in branching architecture were calculated long ago by Candau et al.[30] using a three-parameter Flory mean-field theory. Recent mean-field calculations by DiMarzio and Guttman[29] also indicate a Θ point shift with branching architecture.

Theoretical predictions based on the three-parameter excluded-volume model indicate that the ratio of the mean dimensions of the Θ star polymer (measured by the average

Table IV
g^{Θ}_s Experimental Data for Star Polymers

f	g^{Θ}_s(exptl)[a]	g^{Θ}_s(exptl)[b]	g^{Θ}_s(exptl)[c]	g°_s[d]
3	0.82			0.778
4	0.63	0.65, 0.63	0.65	0.625
6	0.46	0.46	0.46	0.444
8			0.415	0.344
12	0.28–0.41	0.276	0.33	0.236
18		0.228		0.161
H-comb	0.70			0.712

[a] Reviewed in ref 32. Polystyrene in cyclohexane 34.5 °C. [b] Reviewed in ref 42. Polystyrene in cyclohexane 34.5 °C. [c] Reviewed in ref 42. Polyisoprene in dioxane 32.5 °C. In ref 33 $g^{\Theta}_s = 0.42$, 0.35, and 0.28 for 8-, 12-, and 18-arm stars, respectively. [d] Theory reviewed in ref 10. Deviations from the Gaussian chain theory are expected as a consequence of ternary interactions (see text).

Table V
g_s Lattice Monte Carlo Data under Θ Conditions

		simulation		theory	
f	ϕ_{Θ}	g^{Θ}_s(lattice)[a]	g^{Θ}_s(lattice)[b]	g^{Θ}_s(approx)[c]	g°_s[d]
3	−0.52	0.81	0.83	0.79	0.778
4	−0.50	0.66	0.68	0.65	0.625
6	−0.48	0.49	0.51	0.49	0.444
8	−0.47	0.40	0.42	0.42	0.344

[a] Lattice predictions for g^{Θ}_s of Kolinski and Sikorski[31] on a diamond lattice at cited Θ conditions. Data obtained from Figure 3 of ref 31. ϕ is an attractive nearest-neighbor interaction. [b] Results of Mazur and McCrackin[12] for a simple cubic lattice where the Θ conditions are taken to be that of the linear chain, $\phi_{\Theta} = 0.275$. These authors indicate that a small variation of ϕ_{Θ} with chain architecture is possible but such variations are less than their accuracy in determining ϕ_{Θ}. [c] Estimated roughly on the basis of the three-parameter theory. See discussion in text and ref 18. [d] Theory reviewed in ref 10.

star arm length) to the mean dimensions of the Θ linear polymer is greater than predicted by the Gaussian chain theory and that the deviations *increase with the number of chain arms.*[18] We next provide evidence that Monte Carlo and real experimental data for g_s under Θ conditions (g^{Θ}_s) tend to give larger values of g^{Θ}_s than the idealized Gaussian chain predictions. Observed deviations grow with increased branching[12,14] as predicted by the three-parameter theory.[18]

Table IV lists experimental data for g^{Θ}_s of star polymers over a range of f.[32,33] Note the increased deviation of g^{Θ}_s from g°_s as mentioned above and as emphasized by Huber et al.[34] The experimental values of g^{Θ}_s tend to be dispersed for larger f, suggesting that these ratios *may no longer be universal numbers.* Difficulties in synthesizing "perfect" many-arm stars should be appreciated, however. Observe that deviations from the Zimm–Stockmayer relation (2.2) tend to occur for $f > 6$ (see Bywater[11]). Further, Table V presents g^{Θ}_s from Monte Carlo data of Kolinski and Sikorski,[31] where the g_s values are determined at the values of the lattice polymer–polymer interaction parameter ϕ_{Θ} that these authors identify with the Θ conditions of the star.[35] Mazur and McCrackin[12] previously found that the magnitude of g^{Θ}_s is greater than the predictions for Gaussian chains—about 6% greater for three-arm stars and as much as 15% greater for nine-arm stars. Off-lattice Monte Carlo simulations by Freire et al.[14] display a similar trend for g^{Θ}_s, and data from this work are presented in Table VI. Tables V and VI show that the deviation between the lattice model predictions for g^{Θ}_s and g°_s increases with the number of chain arms. Mazur and McCrackin[12] and Kolinski and Sikorski[31] ascribe the discrepancy between lattice results for g^{Θ}_s and the Gaussian chain predictions of Zimm and Stockmayer[9] to an inadequacy of the ideal Gaussian chain model to describe a polymer under Θ conditions.

Table VI
g_s Off-Lattice Monte Carlo Data

	simulations		theory	
f	g^{Θ}_s[a]	g^{*}_s[a]	g°_s[b]	g^{*}_s(RG)[c,d]
6	0.51 ± 0.01	0.49 ± 0.03	0.444	0.453
12	0.35 ± 0.01	0.33 ± 0.02	0.236	0.248
18	0.28 ± 0.01	0.21 ± 0.01	0.160	0.173

[a] Reference 14. The star arms are relatively short in these simulations. [b] Results summarized in refs 9 and 10. [c] Theory developed in refs 6 and 7. [d] Observe that the RG theory predicts $g^{*}_s/g^{\circ}_s > 1$ while the Monte Carlo data indicates that the corresponding ratio is less than unity for $f \geq 6$.

Calculations for the radius of gyration, $\langle S^2 \rangle$, for stars with ternary interactions have not yet been performed, and this technical calculation is not pursued here. However, a rough estimate of the expansion of g_s under Θ conditions of the star can be obtained from available calculations of the expansion of an arm within a star relative to a linear chain of the same molecular weight under Θ conditions.[18] Assuming for the sake of rough argument that $\langle S^2 \rangle$ for the star expands to the same degree as an individual arm within the star (a uniform expansion-type approximation), neglecting the difference between the Θ condition of the star and linear polymer, and taking the ternary interaction parameter z_3° on the order $z_3^{\circ} \approx 0.01$ (consistent with magnitudes deduced from an analysis of lattice models by Cherayil et al.[18]), we obtain the approximate predictions for g^{Θ}_s given in Table V. The rough three-parameter theory estimates certainly exhibit the correct trend in the data: the estimates yield reasonable magnitudes for the deviation between g^{Θ}_s and g°_s and an increasing deviation between g^{Θ}_s and g°_s as the number of arms is increased. Consequently, we entirely agree with Mazur and McCrackin[12] that the deviation of g^{Θ}_s from g°_s is due to an inadequacy of the noninteracting Gaussian chain model for Θ chains. However, it should be possible to correct this theoretical deficiency by incorporating ternary interactions in RG calculations for star polymers.

According to the RG predictions of the previous subsection, the g_s ratio should vary weakly with excluded volume and should *increase* slightly upon going from a Θ ("ideal") solution to a good solvent. This prediction is in accord with Monte Carlo simulations of g_s for idealized random walks and self-avoiding walks (see Figure 4 of ref 16). Monte Carlo calculations by Mazur and McCrackin[12] on a lattice with a nearest-neighbor attractive interaction, however, yield a rather different variation: g_s *decreases* upon going from a Θ to a good solvent, where the "ideal" value of g_s is only approached in the good solvent limit. This decrease of g_s upon going from Θ to good solvents is also found in the off-lattice simulations of Freire et al. using a 6–12 potential[14] (see Table VI). The difference between g^{Θ}_s and g°_s cannot be attributed to just the difficulty in locating the Θ point of a star since g^{Θ}_s tends to be *always greater* than g°_s (see Figure 6 of Mazur and McCrackin[12]). The wormlike star calculations of Mansfield and Stockmayer[21] indicate that g_s (worm star) is less than g°_s, so the effect cannot be explained as due to chain stiffness in the star arms.

The qualitative trend in Mazur and McCrackin's data for g_s is quite understandable on the basis of the three-parameter model[18] and is worth discussing since it underscores theoretical developments necessary to accurately describe the configurational properties of stars and other lightly branched polymers. As discussed above, the three-parameter theory indicates that the mean Θ-point dimensions of a star polymer relative to those of a linear polymer should generally be larger than predicted by Gaussian chain statistics; however, expansion of the chain decreases the probability of ternary interactions and thus decreases the influence of ternary interactions on the mean dimensions of branched polymers. It is easy to show from scaling considerations (Appendix B) that ternary interactions for long swollen chains are "irrelevant" in three dimensions. However, the RG theory has not yet developed to a point that allows the description of binary and ternary interactions over the full range of both interactions, and the specific manner in which the ternary interactions diminish upon chain expansion cannot yet be described quantitatively. Recently, Douglas and Kosmas[36] have proposed a promising analytic scheme to describe a related type of multiple interaction problem and have applied it to the description of surface interacting polymers with excluded volume. Expansion of a chain at a surface decreases the probability of surface contacts and diminishes the influence of the surface interaction in much the same fashion as expanding a chain in solution diminishes the role of ternary interactions.

Although it is difficult, at present, to quantitatively describe the observed decrease of g_s upon chain expansion, we can understand this basic trend as arising from the decreasing influence of ternary interactions on the mean dimensions combined with the very small increase of ratio g_s coming from binary excluded-volume interactions. Mazur and McCrackin's data[12] underline the necessity of developing a version of the RG theory that allows a consideration of polymer properties over a large range of both binary and ternary interactions.

C. Hydrodynamic Properties. The simplest experimental means of characterizing branching architecture is through measurements of the intrinsic viscosity and the diffusion coefficient (or equivalently the hydrodynamic radius). This situation is natural given the relative complexity of measuring $\langle S^2 \rangle$ by light or neutron scattering. As in the case of the radius of gyration, it is traditional to form ratios of the intrinsic viscosity, $[\eta]$, and of the hydrodynamic radius, R_H, of the branched species to the corresponding linear polymer properties, where the comparison is generally taken such that the branched and linear species have the same molecular weight.[10] Here we denote these ratios as

$$g_\eta = [\eta]_{\mathrm{Br}}/[\eta]_{\mathrm{Lin}} \tag{2.6}$$

$$g_{\mathrm{H}} = R_{\mathrm{H,Br}}/R_{\mathrm{H,Lin}} \tag{2.7}$$

The usual convention is to denote g_η by g' and g_{H} by h, but this notation is avoided because of the proliferation of g ratios for the many properties of interest and because h is already utilized conventionally for the dimensionless hydrodynamic interaction parameter. Barrett and Tremain[16] utilize g' to denote the expansion of an arm in a star polymer relative to a linear chain, and this definition unfortunately overlaps with the traditional hydrodynamic theory notation. The g_Q notation with a subscript Q, indicating specifically what property is being considered in the ratio, is strongly suggested as a standardized notation (see ref 37). The ratio g_Q is given a Θ or * superscript to denote the solvent condition, Θ or good solvent, respectively.

Unfortunately, the relative low cost and simplicity of the measurement of hydrodynamic properties are somewhat counterbalanced by the complexity and relative inadequacy of the corresponding theory of polymer hydrodynamics. The difficulties are, indeed, so severe that we discuss the theoretical and experimental situations with some trepidation. But given the prevalence of estimating various hydrodynamic g_Q ratios we feel compelled to at least comment on some of the complicating factors that should be kept in mind if these hydrodynamic measurements are used to characterize branching architecture.

It has long been recognized that the hydrodynamic g_Q factors for star polymers, calculated from the preaveraged Kirkwood–Riseman and Rouse–Zimm theories, do not agree very well with the experimental data and that the deviation increases with the number of star arms.[11] On the other hand, the claimed agreement for rings between preaveraged hydrodynamic theories and experiment has been reasonably good,[6,38] a result which can only reflect a large cancellation of errors in these hydrodynamic g_Q ratios.[19]

Recent Monte Carlo calculations by Zimm[13] and by Freire et al.[14,49] and analytical dynamical RG calculations[18] stress the importance of the preaveraging approximation, which can affect the absolute magnitudes of the hydrodynamic radius and the intrinsic viscosity of linear chains by roughly 10% in the asymptotic "nondraining" (strong hydrodynamic interaction) limit. Monte Carlo simulations also show that the effect of the preaveraging approximation depends on the chain architecture, so that preaveraging errors are not entirely eliminated by taking ratios of hydrodynamic properties. Near cancellation of preaveraging errors may occur in rings, explaining the apparent success of the preaveraging theory in this case. This suggestion remains to be checked by theoretical calculation.[38]

Another factor to be considered is the presence of ternary excluded-volume interactions that can cause the g_Q factors to deviate from the idealized Gaussian chain theory as discussed in the previous section. Calculations by Cherayil et al.[18] show that hydrodynamic properties such as R_H are *especially sensitive* to ternary interactions.

Finally, hydrodynamic properties have the troubling complication of the "draining effect" (finite hydrodynamic interaction).[20] Expansion of a polymer chain in a good solvent lowers the chain density inside the coil and may thereby diminish the extent of hydrodynamic interaction, thus reducing the effective "hydrodynamic size" of the polymer relative to the "nondraining limit" (i.e., strong hydrodynamic interaction). If this partial draining effect occurs to a different degree in the branched and linear species, the hydrodynamic g_Q ratios could potentially display a sensitivity to the extent of hydrodynamic interaction in good solvents, and this would mean that the hydrodynamic g_Q factors would depend somewhat on the particular polymer–solvent system (an effect not considered in current Monte Carlo simulations). Complications from partial draining should be less problematic under Θ conditions where neglecting the finite magnitude of the hydrodynamic interaction strength should be a better approximation.[10,20]

If the extent of hydrodynamic interaction is not affected significantly by the branching architecture (the dimensionless hydrodynamic interaction parameter in the continuum polymer hydrodynamics theory is not affected by branching), then g_{H} and g_η are expected to vary slowly with excluded-volume and hydrodynamic interactions. Thus, in spite of the theoretical difficulties of including preaveraging corrections, excluded volume, and a hydrodynamic interaction dependent on excluded volume,[19] we can still expect the experimental g_{H} and g_η ratios to be insensitive to excluded volume and to have values similar to those estimated from Monte Carlo simulation[13,14,49] by Zimm and others without employing preaveraging. This expectation is supported by an

Table VII
Variation of g_{H} with Chain Architecture

		experiment		eqs 2.8 and 2.9	
	polymer	g^{Θ}_{H}	g^{*}_{H}	g^{Θ}_{H}	g^{*}_{H}
4-arm star	PS[a]	0.94	0.93	0.94	0.93
	PI[b]		0.92		
6-arm star	PS[c]	0.89	0.86	0.89	0.86
8-arm star	PI[d]		0.82	0.85	0.81
12-arm star	PS[e]	0.81	0.70		
	PS[f]	0.85–0.74	0.83–0.73	0.79	0.73
	PI[d]		0.77		
18-arm star	PS[g]	0.76	0.68	0.73	0.63
	PI[d]		0.64		
	PBd[h]	0.72	0.68		
ring	PS[i]	0.89–0.86	0.83$_5$		
	PS[j]		0.85$_8$		

[a] Polystyrene: Θ solvent, cyclohexane (35 °C); good solvent, toluene (35 °C). Reference 39. [b] Polyisoprene: Θ solvent, dioxane (34 °C); good solvent, toluene (35 °C). Reference 40. [c] Reference 41. [d] Reference 40. [e] One high molecular weight sample. Reference 24. [f] g_{H} decreasing with increasing molecular weight. This set of polymers includes some stars with very small branches. Reference 34. [g] Reference 24. [h] Polybutadiene: Θ solvent, dioxane (26 °C); good solvent, cyclohexane (25 °C). Reference 42. [i] g_{H} decreasing with increasing molecular weight, $1.8 \times 10^4 < M_{\mathrm{w}} < 4.3 \times 10^5$. Reference 26. [j] Reference 43.

Table VIII
Variation of g_η with Chain Architecture

		experiment		eqs 2.8 and 2.9	
	polymer	g^{Θ}_{η}	g^{*}_{η}	g^{Θ}_{η}-(empirical)	g^{*}_{η}-(empirical)
3-arm star	PS[a]	0.85$_6$	0.83$_3$	0.86	0.85
4-arm star	PS[b]	0.76	0.72$_4$	0.76	0.73
	PI[c]	0.77$_2$	0.73		
	PBd[d]	0.76$_0$	0.73		
6-arm star	PS[e]	0.63	0.57	0.63	0.57
	PI[f]	0.62$_5$	0.58$_9$		
8-arm star	PI[g]	0.53$_1$	0.43	0.54	0.47
12-arm star	PS[h]	0.41	0.35	0.43	0.34
	PS[i]	0.42	0.34$_5$		
	PS[g]	0.42$_2$	0.32$_8$		
18-arm star	PS[h]	0.35	0.26	0.35	0.23
	PI[g]	0.29$_8$	0.24$_2$		
	PBd[j]	0.28$_4$	0.22$_5$		
	PBd[k]		0.26		
H-comb	PS[l]	0.80	0.73		
ring	PS[m]	0.66–0.60	0.67–0.56		
	PS[n]	0.71–0.63	0.79–0.68		
	PS[o]	0.71–0.66	0.76–0.56		
	PBd[p]		0.63		

[a] Polystyrene: Θ solvent, cyclohexane (35 °C); good solvent, toluene (35 °C). Reference 32. [b] Reference 39. [c] Polyisoprene: Θ solvent, dioxane (34 °C); good solvent, toluene (35 °C). Reference 5a. [d] Polybutadiene: Θ solvent, dioxane (26 °C); good solvent, toluene (35 °C). References 45 and 46. [e] Reference 23. [f] Reference 5a. [g] Reference 40. [h] One high molecular weight sample. Reference 24. [i] Reference 32. [j] Reference 57. [k] Polybutadiene: good solvent, cyclohexane (25 °C). Reference 42. [l] Reference 25. [m] Decreases with increasing molecular weight. Reference 26. [n] Reference 3b. [o] Decreases with increasing molecular weight $M_{\mathrm{n}} < 30\,000$ in a Θ solvent of 0.67–0.66 except at very low molecular weight $M_{\mathrm{n}} \approx 3000$. [p] Reference 48.

Table IX
Monte Carlo Data for Hydrodynamic Parameters of Star-Branched Polymers

f	g^{Θ}_{H}	g^{*}_{H}	g^{Θ}_{η}	g^{*}_{η}
3	0.97[a]			0.85[a]
4		0.94[a,b]		0.73[a,b]
6	0.89[c]	0.89[a,b]	0.54[c]	0.57,[a] 0.56[b]
12	0.82[c]	0.79[c]	0.39[c]	0.37[c]
18	0.73[c]	0.68[c]	0.28[c]	0.22[c]

[a] Reference 50. [b] Reference 13. [c] References 49 and 14. Simulation values of g_{H} and g_η for Gaussian chains (see Table III of ref 49) are smaller than values of g^{Θ}_{H} and g^{Θ}_{η} for Θ point polymers where the discrepancy increases with the number of arms. This effect is likely due to ternary interactions. Simulation data for chains without excluded volume (i.e., Gaussian chains) should be carefully distinguished from Θ point chain data.

approximate hydrodynamic theory under the assumption that the hydrodynamic interaction is independent of branching structure.[20] Experimental values of the hydrodynamic g_Q ratios are commonly found to be nearly independent of solvent to within experimental precision and to be in relatively good agreement with Monte Carlo simulations,[44] when account of the preaveraging effect is made. We now proceed to discuss the experimental data, keeping in mind the limitations of the hydrodynamic theory.

Tables VII and VIII summarize g_{H} and g_η data for regular stars, rings, and H-combs.[24,26,34,39–48] The data in these tables are obtained by first fitting the linear chain properties Q to a scaling equation $Q \propto M^a$ with M the molecular weight. Properties of linear polymers are calculated from these scaling equations at the molecular weights for which the branched polymer data are available, and the results are combined with the branched polymer data to obtain the cited dimensionless ratios for the viscosity and the hydrodynamic radius. These ratios are then averaged over sets of data for a particular type of branching architecture.

Recent Monte Carlo estimates[13,14,49,50] of g_η and g_{H} have been made without introducing the preaveraging approximation but retaining the rigid-body approximation of the standard Kirkwood–Riseman theory. A summary of recent results is given in Table IX. These Monte Carlo calculations apply to the nondraining limit only. Simulation methods describing variable hydrodynamic interaction have not yet been devised.

Experimental values of g_η and g_{H} in Θ and good solvents are evidently consistent with simulation estimates. Observe that the ratios g_η and g_{H} generally decrease with increasing solvent quality and that this trend is reproduced by the Monte Carlo simulation data. In contrast, the g_Q ratios for static properties and light branching (small f) tend to be increasing functions of excluded volume. The tendency of g_η and g_{H} to increase with solvent quality is not yet understood, but it seems likely that a decrease of ternary interaction with swelling is responsible for part of the trend.

As mentioned before, analytical computations of g_η and g_{H} using the preaveraging approximation tend to be rather inaccurate. Roovers and co-workers[51] have noted useful correlations between g^{Θ}_{η} and g^{Θ}_{H} and the number of star arms f as

$$g^{\Theta}_{\eta}(\text{empirical}) \approx [(3f-2)/f^{2}]^{0.58} \qquad (2.8a)$$

$$g^{\Theta}_{\mathrm{H}}(\text{empirical}) \approx f^{1/4}/[2-f+2^{1/2}(f-1)]^{1/2} \qquad (2.8b)$$

These empirical forms were motivated by results from the preaveraging theory. Further, a semiempirical correlation of the variation of g_η and g_{H} with excluded volume is described by Douglas and Freed.[6] The g_η and g_{H} ratios in good solvents ($f \geq 2$) are given by[6]

$$g^{*}_{\eta}(\text{empirical}) = g^{\Theta}_{\eta}[1-0.276-0.015(f-1)]/(1-0.276) \qquad (2.9a)$$

$$g^*_H(\text{empirical}) = g^{\Theta}_H[1 - 0.068 - 0.0075(f-1)]/(1-0.068) \quad (2.9b)$$

and values of g_η and g_H are listed for comparison in Tables VII and VIII. Equation 2.8 is used to estimate g^{Θ}_η and g^{Θ}_H in (2.9).

There is a remarkable consistency between the experimental and Monte Carlo data and the simple empirical correlations for g_η and g_H in (2.8) and (2.9). In a previous paper we show that the excluded-volume dependence of hydrodynamic properties ([η], R_H) of different polymers can display a significant variation[52] attributed to the "draining effect". The dimensionless ratios g_η and g_H, however, are rather *insensitive* to excluded volume and seem to be insensitive to the particular polymer–solvent system considered. Superficially the experimental data seem to be consistent with the nondraining nonpreaveraged Monte Carlo calculations, even though the hydrodynamic properties of linear polystyrene do not conform very well with the nondraining hydrodynamic theory. The universality exhibited by g_η and g_H seems to be the consequence of a fortuitous cancellation of ternary, hydrodynamic, and excluded-volume effects in these dimensionless ratios. Further experimental work on a variety of polymer–solvent systems is needed to establish whether the apparent universality of g_η and g_H holds generally.

III. Virial Ratios and the Penetration Function, Ψ

The polymer second virial coefficient, A_2, is another property that is sensitive to branching architecture. Until recently, however, the theory of polymer solutions could provide only a rather limited description of A_2, and as a consequence this parameter has been neglected relative to the Zimm–Stockmayer ratio, g_s. Renormalization group calculations by Douglas and Freed[6] give precise predictions for the variation of A_2 with chain branching and excluded volume.

A. Linear Polymers. Before considering how branching architecture affects A_2, it is useful to review theoretical predictions for the linear polymer and to compare these results with available experimental data. The RG theory is, after all, a perturbative method, and this kind of testing is essential in establishing the predictive capability of the theory. Usually, a dimensionless measure of A_2 is used in presenting data in the experimental literature, and the conventional measure is the penetration function, Ψ, defined in three dimensions as[6,7,10]

$$\Psi = (2A_2M^2/N_A)/(4\pi\langle S^2\rangle)^{3/2} \quad (3.1)$$

where M is the polymer molecular weight and N_A is Avogadro's number. Renormalization group theory predicts that the penetration function for long monodisperse samples of linear flexible polymers in three dimensions is a universal constant in good solvent, which in second order equals[6]

$$\Psi^* = 0.269 \quad (3.2)$$

Further, Ψ^* is computed as somewhat smaller for polydisperse samples, marginal solvents, and only modestly long chains.[53] Universal scaling curves describing the crossover of Ψ from its value of zero under Θ conditions to its limiting value of Ψ^* in good solvents are given by Douglas and Freed.[6,7]

Table X
Ψ^* Linear Polystyrene in Toluene at 35 °C

sample	$M_w \times 10^{-5}$	$A_2 \times 10^{4}$ [a]	$\langle S^2\rangle \times 10^{12}$ [b]	Ψ^*(good solvent)
C6bb[b]	2.8_3	3.40	4.18	0.239
PS800f2[c]	6.65	2.8_1	10.6_8	0.265
	6.73	2.7_9	10.8_1	0.265
C7bb[b]	8.60	2.6_2	14.8	0.255
PT[d]	15.3	2.3_3	27.5	0.282
PS1000f2[c]	17.0	2.1_9	35.3	0.225
SS1A[d]	68.0	1.5_7	170	0.244
RG prediction[e]				0.269

[a] In mol·cm^3/g^2; $\log A_{2,\mathrm{Lin}} = -2.15 - 0.242 \log M_w$. [b] $\langle S^2\rangle_{\mathrm{Lin}} = 1.66 \times 10^{-18} M_w^{1.17}$ cm^2 quoted in ref 5b, Table I. [c] Reference 41. [d] Roovers, unpublished data. [e] Theory developed in refs 6 and 7.

Table XI
Ψ^* Linear Polybutadienes in Cyclohexane at 25 °C

sample[a]	$M_w \times 10^{-5}$	$A_2 \times 10^{4}$ [b]	$\langle S^2\rangle \times 10^{12}$ [c]	Ψ^*(good solvent)
PBD 120	1.14	10.5	2.31	0.29_0
165	1.55	10.0	3.50	0.27_4
170	1.64	9.7_6	3.73	0.27_2
180	1.80	9.3_5	4.13	0.26_9
300	2.56	8.6_9	6.64	0.24_8
400	3.61	8.2_7	9.40	0.25_8
800	7.60	6.8_5	22.9	0.26_9
RG prediction[d]				0.269

[a] Samples described in ref 54. [b] $\log A_2 = -1.88_0 - 0.2128 \log M_w$; in mol·cm^3/g^2. [c] $\langle S^2\rangle = 0.0255M^{1.183}$. [d] Theory developed in refs 6 and 7.

Table X provides experimental data[5b,41] for Ψ^* of linear polystyrene in the good solvent toluene at 35 °C along with the associated thermodynamic properties, sample identifications, and references. A similar tabulation of data for polybutadiene in the good solvent cyclohexane[54] is given in Table XI. Agreement between theory and experiment seems to be reasonably good, and the range of values for Ψ^* is consistent with the earlier estimate of Douglas and Freed[6] given by

$$\Psi^*(\text{empirical}) = 0.26 \pm 0.04 \quad (3.3)$$

A precise Monte Carlo simulation of Ψ^* would be welcome.

B. Variation of the Virial Coefficient with Branching Architecture. There are two particularly convenient measures of A_2 that are useful in characterizing branching architecture. First, there is the analogue of the g_s ratio defined by the ratio of A_2 for the branched and linear polymer as[6]

$$g_A = A_{2,\mathrm{Br}}/A_{2,\mathrm{Lin}} \quad (3.4)$$

Renormalization group calculations[6,7] indicate that g^*_A is a constant in a good solvent for a given branching architecture. Table XII presents[22,23,32,39] the ratio g^*_A for three-, four-, and six-arm regular stars of polystyrene in toluene at 35 °C. The RG predictions for these ratios are

$$g^*_A(f{=}3) = 0.968, \quad g^*_A(f{=}4) = 0.923, \quad g^*_A(f{=}6) = 0.808 \quad (3.5)$$

which are to be compared with the experimental values in Table XII. Table XIII lists empirical estimates[24-26,30d,55] of g^*_A for H-combs, rings, and some many-arm stars, where the theoretical estimates of g^*_A(H-comb) = 0.949 and g^*_A(ring) = 0.879 agree reasonably well with the data. It should be borne in mind that the theoretical calculations for rings apply to a kind of "ideal ring" where an equilibrium ensemble of all types of possible knotted structures are implicitly involved in the statistical averaging.[58] "Real rings" do not necessarily correspond to this ideal, and it would be interesting to pursue the question of how specific constraints, corresponding to

Table XII
Ψ^* Regular Star Polystyrenes in Toluene at 35 °C

sample	$M_w \times 10^{-5}$	$A_2 \times 10^4$	$\langle S^2 \rangle \times 10^{12}$	$A^*_{2,\mathrm{Br}}/A^*_{2,\mathrm{Lin}}$	Ψ^*
		Three-Arm Stars[a]			
SS-13	3.92				0.41
SS-14	7.75				0.53
SS-15	9.20				0.40
SS-16	11.9				0.41
RG prediction[b]				0.968	0.384
		Four-Arm Stars[c]			
S141A	5.37	2.80	4.7	0.96_3	0.59_0
S181A	10.6_1	2.34	11.3_4	0.95_0	0.51_6
S191A	14.4_4	2.04	16.7_8	0.89_2	0.46_1
A-48,2[d]	18.7	2.03	21.0	0.94_5	0.55_0
RG prediction[b]				0.923	0.517
		Six-Arm Stars[e,f]			
HS041A	5.20	2.5_1	3.8_6	0.85_7	0.66_7
HS051A	11.1	2.1_5	8.6_5	0.88_2	0.77_6
HS121A	18.9	1.7_9	17.5	0.83_5	0.65_1
RG prediction[b]				0.808	0.793

[a] Reference 32. [b] References 6 and 7. [c] Reference 39. [d] Reference 22. [e] Reference 23. [f] Table IX of Bauer et al.[40] presents Ψ^* for polyisoprene stars over a large range of f. According to this work: Ψ^*(linear) = 0.25, $\Psi^*(f=8) = 0.77$, $\Psi^*(f=12) = 1.43$; $\Psi^*(f=18) = 1.53$. The value of Ψ^* for large f is found to be close to the hard-sphere value $\Psi^*(\mathrm{HS}) = 1.62$ for $f \geq 12$ (see Appendix C).

Table XIII
Virial Properties of Branched Polystyrenes in Toluene at 35 °C

sample	$M_w \times 10^{-5}$	$A_2 \times 10^4$	$\langle S^2 \rangle \times 10^{12}$	$A^*_{2,\mathrm{Br}}/A^*_{2,\mathrm{Lin}}$	Ψ^*
		H-Comb[a]			
H1A1	4.8_2	2.9_5	5.0	0.98_9	0.46
H3A1A	6.8_2	2.6_4	7.4	0.96_3	0.45
H5A1	10.5	2.4_0	13.0	0.97_1	0.42
H6A1A	17.2	2.1_0	$23._7$	0.95_8	0.40
RG prediction[b]				0.949	0.429
		Ring[c]			
R19D	3.3_4	2.9_4	2.5	0.90	0.61_8[d]
RG prediction[b]				0.879	0.687
		12-Arm Star[e]			
12PS1B1A	58.0	0.83	33.0	0.51	1.10[e]
RG prediction[b]				0.336	1.35
		18-Arm Star[e–g]			
18 PS1	93.0	0.57	48.0	0.39	1.10

[a] Synthesis and properties are described in ref 25, Table II. [b] Theory developed in refs 6 and 7. [c] Reference 30d. [d] Reference 26. [e] Properties given in ref 24, Table II. [f] Huber et al. quote different values for this sample in ref 55 leading to $A^*_{2,\mathrm{Br}}/A^*_{2,\mathrm{Lin}} = 0.50$ and $\Psi^* = 0.81$. [g] The RG prediction for the ratio $A^*_{2,\mathrm{Br}}/A^*_{2,\mathrm{Lin}}$ becomes unphysically negative for $f = 18$. This result is expected since we are outside the range of applicability of the RG theory (see section IIA).

Table XIV
Virial Properties of 4-Arm Star Polybutadienes in Cyclohexane at 25 °C

sample	$M_w \times 10^{-5}$	$A_2 \times 10^4$	$\langle S_2 \rangle \times 10^{12}$	$A^*_{2,\mathrm{Br}}/A^*_{2,\mathrm{Lin}}$	Ψ^*
C[a]	1.43_4	9.5_1	(1.98)	0.960	(0.523)
B[a]	1.59	9.0_8	2.56	0.93_8	0.41_8
A[a]	3.75	7.2_8	6.75	0.90_6	0.43_5
PBD4S800B3[b]	8.3	6.4_0	17.0	0.94_7	0.46_9
PBD4S1600B3[b]	13.52	5.8_9	33.0	0.97_0	0.42_3
RG prediction[c]				0.923	0.517

[a] Synthesis given in ref 46. [b] Synthesis given in ref 56. [c] Theory developed in refs 6 and 7.

Table XV
Virial Thermodynamic Properties of 18-Arm Star Polybutadienes in Cyclohexane at 25 °C

sample[a]	$M_w \times 10^{-5}$	$A_2 \times 10^4$	$\langle S^2 \rangle \times 10^{12}$	$A^*_{2,\mathrm{Br}}/A^*_{2,\mathrm{Lin}}$[b]	$\Psi^{*b,c}$
PBD1518	3.11	3.00	(1.5_4)	0.35_8	(1.13_8)
PBD18SSC	3.40	3.0_5	(1.8_7)	0.37_2	(1.02_8)
PBD18SC	3.58	3.1_8	1.80	0.39_2	1.25_8
PBD2518	5.4_1	3.0_3	3.01	0.40_9	1.26_2
PBD3718	7.62	2.4_7	3.9_7	0.35_9	1.35_2
PBD9918	19.0	1.7_9	11.8	0.31_7	1.19

[a] Samples described in ref 57. [b] Quoted mean is 0.37 for $A^*_{2,\mathrm{Br}}/A^*_{2,\mathrm{Lin}}$ and 1.20 for Ψ in ref 57. [c] See footnote g of Table XIII.

different amounts and types of knots, affect configurational properties of ring polymers.

The penetration function, Ψ, provides a second useful measure of the second virial coefficient that is rather sensitive to branching architecture. To first order in the $\epsilon = 4 - d$ (d is the dimension) renormalization group computations of Ψ^*_{Br} yield[6]

$$\Psi^*_{\mathrm{Br}} = (g^\circ_s)^{-d/2}\Psi^*_{\mathrm{Lin}} + O(\epsilon^2), \qquad \Psi^*_{\mathrm{Lin}} = \epsilon/8 + O(\epsilon^2) \tag{3.6}$$

Good qualitative values of Ψ^*_{Br} can be obtained by taking Ψ^*_{Lin} from the second order in the ϵ value $\Psi^*_{\mathrm{Lin}} = 0.269$ (see Appendix D). The renormalization group computations of Ψ^*_{Br} from Douglas and Freed[6] are presented in Tables X–XIV.

Experimental values of Ψ^* for polystyrene stars in toluene at 35 °C are given in Table XII, while those for H-combs, rings, and many-arm stars are listed in Table XIII. Tables XIV and XV summarize similar but more limited data[46,56] for polybutadiene stars in cyclohexane.[46,56,57] Comparison between the theoretical predictions of Tables X–XV and the experimental values shows that the RG theory is rather consistent with the experimental data. Monte Carlo simulations for Ψ^*_{Br} would provide a further test of the RG theory but are not yet available. In summary, the second virial coefficient provides a sensitive probe of branching architecture and can be described to a reasonable level of accuracy by the renormalization group theory.

IV. Conclusion

The preparation of model polymers to test structure–property relationships requires an accurate means to characterize chain architecture. Typically, the characterization involves various measures of molecular "size" (the radius of gyration, second virial coefficient, hydrodynamic radius, intrinsic viscosity, ...), which are compared with the corresponding property of a linear polymer of the same polymer type, of the same molecular weight, and under the same solvent conditions. Ideally the set of g_Q ratios of branched to linear polymer properties provide a "fingerprint", specifying uniquely the branching architecture.

In practice the characterization of branching using the g_Q ratios involves a number of subtle effects. For example, the g_Q ratios measured under Θ conditions are affected by ternary interactions that introduce an increasing deviation from the ideal Gaussian chain theory with increased branching. This effect is an obvious consequence of greater ternary chain interferences with an increased chain density. Theoretical difficulty in treating such ternary effects is complicated by the expected variation of ternary interactions with solvent quality. Hydrodynamic properties have additional complications that limit their usefulness as measures of branching. In addition to a particular sensitivity to ternary interactions, the hydrodynamic calculations involve numerous approximations, with the preaveraging approximation being the most notable. No available analytical scheme allows for an accurate estimation of these preaveraging errors, although useful bounds for this effect are provided by Monte Carlo simulation data. Another problem is that hydrodynamic properties depend on a hydrodynamic interaction in addition to the excluded-volume interactions, and this particularly complicates the interpretation of hydrodynamic properties in good solvents because of the possibility of increased draining through expanded polymer coils. All these difficulties are unfortunate given the relative simplicity of performing hydrodynamic property measurements.

Scaling arguments (Appendix B) show that ternary interactions are less of a problem in good solvents, and a general discussion using the renormalization group theory indicates that the g^*_Q ratios should differ rather little from their Gaussian chain counterparts g°_Q. This situation is rather ironic given the inapplicability of g°_s to estimate g^Θ_s because of deviations due to ternary interactions.

Virial properties are rather sensitive to branching architecture. Hence, good solvent dimensionless ratios, such as the penetration function, are useful parameters for characterizing branching architecture. The virial ratios are especially important in view of the above-cited factors, which complicate the interpretation of the hydrodynamic dimensionless ratios, g_Q. Comparison of the renormalization group theory and the virial ratios of carefully prepared model polymers gives encouraging agreement.

Sometimes data for the mean dimensions of a polymer are summarized in terms of an "equivalent sphere" notation.[40-42] There is a tendency for the properties of many-arm stars to approach those of a hard sphere in the limit of large f. It seems that this limiting behavior starts to set in for $f \geq 20$. The equivalent sphere notation is briefly summarized in Appendix C for those who prefer this notation.

Discussion of our renormalization group calculations conspicuously omits reference to the calculations of Oono and co-workers.[59] Reasons for this omission are described in Appendix D.

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Appendix A. Modified Flory Prediction for g^*_s

The modified Flory theory is derived from a synthesis of the classical two-parameter perturbation theory and the Flory mean-field theory.[10] Classical Flory theory in d dimensions predicts that the linear chain expansion factor of the end-to-end distance, $\alpha_{\mathbf{R}}^2 = \langle \mathbf{R}^2 \rangle / \langle \mathbf{R}^2 \rangle_0$, is equal to

$$\alpha_{\mathbf{R}}^{d+2} - \alpha_{\mathbf{R}}^{d} = C_{\mathbf{R}} z_2 \qquad \text{(A.1)}$$

where z_2 is the Fixman excluded-volume parameter of the two-parameter perturbation theory and $C_{\mathbf{R}}$ is a constant that depends on the spatial dimension d. Stockmayer suggested replacing $C_{\mathbf{R}}$ by an expression consistent with the two-parameter perturbation expansion about the $z_2 = 0$ limit (see ref 10), and more recent renormalized perturbation expansion calculations by Edwards and Singh[28] yield essentially the modified Flory theory as a leading approximation.

Briefly we mention the physical idea behind the modified Flory approximation. Perturbation theory yields the expansion factor $\alpha_{\mathbf{R}}^2$ as

$$\langle \mathbf{R}^2 \rangle / \langle \mathbf{R}^2 \rangle_0 = \alpha_{\mathbf{R}}^2 = 1 + C_{\mathbf{R}} z_2 + O(z_2^2) \qquad \text{(A.2)}$$

where z_2 is given by

$$z_2 = (d/2\pi)^{d/2} \beta_2{}^\circ n^2 / \langle \mathbf{R}^2 \rangle_0{}^{d/2}, \qquad C_{\mathbf{R}}(d=3) = 4/3 \qquad \text{(A.3)}$$

In (A.3) $\beta_2{}^\circ$ is the binary cluster integral and n is the number of statistical segments. The modified Flory expression is obtained by noting that as the chain expands the volume pervaded by the coil increases as $\langle \mathbf{R}^2 \rangle_0{}^{d/2} \rightarrow \langle \mathbf{R}^2 \rangle^{d/2}$. Introducing this replacement into the definition of z_2 in (A.3) gives the *renormalized measure of the excluded-volume interaction*

$$z_2 \rightarrow (d/2\pi)^{d/2} \beta_2{}^\circ n^2 / \langle \mathbf{R}^2 \rangle^{d/2} = z_2 / \alpha_{\mathbf{R}^2}{}^d \qquad \text{(A.4)}$$

The expression on the right-hand side of (A.4) is denoted as $\bar{z}$ in the classical mean-field theory literature.[10] Introducing the correspondence of (A.4) in (A.2) yields the modified Flory result (A.1), which is self-consistent with the perturbation expansion (A.2).

At a more rigorous level the Edwards-Singh approach is based on the simple idea of redefining the reference Hamiltonian such that the excluded-volume perturbation remains small.[28] The method can be summarized in a way that avoids technical complication. We start with an interaction Hamiltonian for chains with excluded volume $H/k_BT = H_0 + H_I$ where H_0 designates the idealized Gaussian chain Hamiltonian and H_I defines the excluded-volume interaction (see Appendix B). We then redefine the Hamiltonian as

$$H/k_BT = \alpha H_0 + [H_I + (1 - \alpha) H_0] \qquad \text{(A.5)}$$

where α is determined by requiring that the contribution to α from the configurational average of $H_I - (1 - \alpha)H_0$ vanishes. This again leads to (A.1) with a value of $C_{\mathbf{R}}$ slightly different than $^4/_3$.[28]

Now that we have schematically explained that there is a theoretical and intuitive basis for the modified Flory theory as an approximation scheme, we may apply it to star polymers. The g_s ratio for chains with excluded volume is defined by

$$g_s = \langle S^2 \rangle(\text{star}) / \langle S^2 \rangle(\text{linear}) = g^\circ{}_S[\alpha_S{}^2(\text{star}) / \alpha_S{}^2(\text{linear})] \qquad \text{(A.6)}$$

where the modified Flory theory gives

$$\alpha_S{}^{d+2} - \alpha_S{}^d = C_{\text{star}} z_2 \qquad \text{(A.7a)}$$

$$\alpha_S{}^{d+2} - \alpha_S{}^d = C_{\text{linear}} z_2, \qquad C_{\text{linear}} = 1.276 \qquad \text{(A.7b)}$$

The two-parameter theory expression for C_{star} is presented in Yamakawa,[10] and for large f we note that[10]

$$C_{\text{star}}(f) \sim 0.430 f^{1/2}, \qquad f \rightarrow \infty \qquad \text{(A.8a)}$$

in three dimensions. Combining (A.6), (A.7a), (A.7b), (A.8), and the observation

$$g^\circ{}_s = (3f - 2)/f^2 \sim 3/f, \qquad f \rightarrow \infty \qquad \text{(A.8b)}$$

we obtain g_s in the good solvent limit as

$$g^*{}_s(\text{modified Flory}) \sim 1.94 f^{-4/5}, \qquad d = 3, f \rightarrow \infty \qquad \text{(A.9)}$$

Equation A.9 is to be contrasted with the estimates of Tremian and Barrett[16]

$$g^*_{\mathrm{s}}(\mathrm{SAW}) \sim 1.86 f^{-4/5}, \quad f \to \infty \tag{A.10}$$

while Whittington et al.[15] obtain

$$g^*_{\mathrm{s}}(\mathrm{SAW}) \sim 1.83 f^{-4/5}, \quad f \to \infty \tag{A.11}$$

The "scaling theory" of Daoud and Cotton[17] is also consistent with (A.9)–(A.11) but does not provide any specific prediction for the important prefactor. A recent mean-field calculation by DiMarzio and Guttman[29] yields the same type of scaling relation as (A.9), except the prefactor is obtained as 1.74.

The modified Flory theory can also be used to estimate g_{s} under Θ conditions in the limit $f \to \infty$. Including the ternary interaction z_3 (see Appendix B) in (A.7) and generalizing the modified Flory theory produces

$$\alpha_{\mathrm{S}}^{d+2} - \alpha_{\mathrm{S}}^{d} = C_{\mathrm{star}} z_2 + D_{\mathrm{star}} z_3 / \alpha_{\mathrm{S}}^{d} \tag{A.12}$$

An estimate of D_{star} can be obtained from the expansion factor of an arm in the star. From the perturbation calculation given in Table II of ref 18 we expect $D_{\mathrm{star}} \sim f^2$ for $d = 3$ with the constant of proportionality unspecified. Taking $z_2 = 0$ in (A.12) and using the definitions (A.6) and (A.8b) implies

$$g^{\Theta}_{\mathrm{S}} \sim f^{-1/2}, \quad f \to \infty \tag{A.13}$$

Interestingly, this is again consistent with the Daoud and Cotton[17] scaling analysis. The qualitative point we infer from (A.13) is that g^{Θ}_{s} is significantly larger than g°_{s} for many-arm stars because of ternary interactions.[6a] Application of the scaling relation (A.13) is limited, however, because the shift of the star Θ point from the linear chain Θ point cannot be generally neglected in the large f limit.

Appendix B. Irrelevance of Ternary Interactions for Swollen Chains in Three Dimensions

The continuous chain model represents the chain configuration by a position vector $\mathbf{R}(\tau)$ where τ is a contour variable ranging between 0 and N, the polymer chain length. A Gaussian chain is described by the configurational Hamiltonian in units of $k_{\mathrm{B}}T$ as[7]

$$H_0/k_{\mathrm{B}}T = (d/2l) \int_0^N |\mathrm{d}\mathbf{R}(\tau)/\mathrm{d}\tau|^2 \, \mathrm{d}\tau \tag{B.1}$$

where l is the Kuhn length and d is the dimension. The binary interaction of the two-parameter model is represented by the interaction contribution to the Hamiltonian[7]

$$H_2 = (\beta_2{}^{\circ}/2!l^2) \int_0^N \mathrm{d}\tau \int_0^N \mathrm{d}\tau' \, \delta[\mathbf{R}(\tau) - \mathbf{R}(\tau')] \tag{B.2}$$

A cutoff, which prevents chain segments from interacting with themselves, is formally neglected in (B.2), and $\beta_2{}^{\circ}$ denotes the usual binary cluster integral. Ternary interactions are similarly represented by the interaction[7,18]

$$H_3 = (\beta_3{}^{\circ}/3!l^3) \int_0^N \mathrm{d}\tau \int_0^N \mathrm{d}\tau' \int_0^N \mathrm{d}\tau'' \, \delta[\mathbf{R}(\tau) - \mathbf{R}(\tau')] \times \delta[\mathbf{R}(\tau') - \mathbf{R}(\tau'')] \tag{B.3}$$

where $\beta_3{}^{\circ}$ is the ternary cluster integral. To understand the effect of chain swelling on H_3, dimensionless units are introduced for the position vector, $\mathbf{R}(\tau)$, and the contour length, τ

$$\hat{\mathbf{r}}(x) = \mathbf{R}(\tau)[d/\langle \mathbf{R}^2 \rangle]^{1/2} \qquad x = \tau/N \tag{B.4}$$

where $\langle \mathbf{R}^2 \rangle$ is the mean-square end-to-end distance of the interacting chain. A chain with strong repulsive binary excluded volume has the asymptotic behavior $\langle \mathbf{R}^2 \rangle \sim N^{2\nu}$, where ν is greater than its Gaussian value of $^1/_2$. Introducing the dimensionless units of (B.4) into (B.3) gives

$$H_3 = (\hat{z}_3/3!) \int_0^1 \mathrm{d}x \int_0^1 \mathrm{d}x' \int_0^1 \mathrm{d}x'' \, \delta[\hat{\mathbf{r}}(x) - \hat{\mathbf{r}}(x')] \times \delta[\hat{\mathbf{r}}(x') - \hat{\mathbf{r}}(x'')](2\pi)^d \tag{B.5a}$$

$$\hat{z}_3 \equiv (d/2\pi\langle \mathbf{R}^2 \rangle)^d \beta_3{}^{\circ} n^3 \qquad N \equiv nl \tag{B.5b}$$

The ternary interaction in (B.5b) scales with chain length as

$$\hat{z}_3 \sim n^{3-2d\nu} \tag{B.6}$$

Thus, near the Θ point in $d = 3$ we have $\nu = {}^1/_2$ and the exponent in (B.6) is zero, indicating that the ternary interactions may affect numerical prefactors. On the other hand, in good solvents, we have $\nu > {}^1/_2$ and the exponent $3 - 2d\nu$ is negative, implying the irrelevance of ternary interactions in swollen chains. (Irrelevance means that the interaction gives no contribution in the limit of long chains.)

Appendix C. "Equivalent Sphere" Notation

Experimental data for dilute polymer solution properties are frequently presented in terms of an equivalent sphere notation rather than the dimensionless ratios given in the text.[24,40–42] We briefly explain how to translate from one notation to another.

Einstein's equation for the viscosity of a dilute suspension of hard spheres yields

$$V_{\eta} = 2[\eta]M/5N_{\mathrm{A}} \tag{C.1}$$

where V_{η} is the equivalent volume of the sphere with radius

$$R_{\eta} = [3[\eta]M/10\pi N_{\mathrm{A}}]^{1/3} \tag{C.2}$$

N_{A} is Avogadro's number. Similarly, Stokes' equation provides the hydrodynamic radius R_{H} as

$$R_{\mathrm{H}} = f/6\pi\eta_{\mathrm{s}} \tag{C.3}$$

where η_{s} is the solvent viscosity and f is the friction coefficient. Also, hard-spherical molecules have the second virial coefficient relation[10]

$$V_A = A_2 M^2/4N_{\mathrm{A}} \tag{C.4}$$

where V_A is the volume of an "equivalent" hard-sphere molecule. Thus, the hard-sphere virial radius R_A is equal

$$R_A = \left(\frac{3M^2 A_2}{16\pi N_{\mathrm{A}}}\right)^{1/3} \tag{C.5}$$

Finally, we have the static radius defined in terms of the radius of gyration as

$$R_{\mathrm{s}} = \langle S^2 \rangle^{1/2} \tag{C.6}$$

If we equate the physical properties on the right-hand side of (C.2), (C.3), and (C.5) with the conventional definitions[10] of the polymer properties, we obtain the "hard-sphere equivalent radii"

$$R_{\eta} \equiv \left(\frac{3(6^{3/2})\Phi}{10\pi N_{\mathrm{A}}}\right)^{1/3} \langle S^2 \rangle^{1/2} \tag{C.7}$$

$$R_{\mathrm{H}} \equiv \left(\frac{P6^{1/2}}{6\pi}\right)\langle S^2\rangle^{1/2} \qquad \text{(C.8)}$$

$$R_A \equiv \left(\frac{3M^2A_2}{16\pi N_{\mathrm{A}}}\right)^{1/3} = \left(\frac{3\pi^{1/2}\Psi}{4}\right)^{1/3}\langle S^2\rangle^{1/2} \qquad \text{(C.9)}$$

and taking the ratios of these radii gives

$$R_{\mathrm{s}}{:}R_{\eta}{:}R_{\mathrm{H}}{:}R_A = 1{:}\left(\frac{3(6^{3/2})\Phi_0}{10\pi N_{\mathrm{A}}}\right)^{1/3}\frac{\alpha_{\eta}}{\alpha_{\mathrm{s}}}{:}\left(\frac{P_0}{6^{1/2}\pi}\right)\frac{\alpha_{\mathrm{H}}}{\alpha_{\mathrm{s}}}{:}\left(\frac{3\pi^{1/2}\Psi}{4}\right)^{1/3} \qquad \text{(C.10a)}$$

In the unperturbed state this reduces to ($P_0 = 5.99$ and $\Phi_0 = 2.5 \times 10^{23}$ are used as estimates without preaveraging[13,14,49] for linear chains)

$$R^{\circ}_{\mathrm{s}}{:}R^{\circ}_{\eta}{:}R^{\circ}_{\mathrm{H}}{:}R^{\circ}_A = 1{:}0.836{:}0.778{:}0 \qquad \text{(C.10b)}$$

while for nondraining good solvents,[6,41] we obtain

$$R^{*}_{\mathrm{s}}{:}R^{*}_{\eta}{:}R^{*}_{\mathrm{H}}{:}R^{*}_A = 1{:}0.805{:}0.777{:}0.710 \qquad \text{(C.10c)}$$

Bauer et al.[40] and Roovers and Martin[42] observe that the static and dynamic properties of many-arm stars approach the limiting behavior of hard spheres for large f. The radius of gyration R_{s} of a uniform density (hyper)-sphere of spatial dimension d is related to the sphere radius R by

$$R_{\mathrm{s}}^{2} = [d/(d+2)]R^2 \qquad \text{(C.11a)}$$

Equation C.11a leads to the hard-sphere ratios (see ref 42 for a discussion of the $d = 3$ case)

$$R_{\mathrm{s}}(\mathrm{HS}){:}R_{\eta}(\mathrm{HS}){:}R_{\mathrm{H}}(\mathrm{HS}){:}R_A(\mathrm{HS}) = 1{:}[d/(d+2)]^{1/2}{:}[d/(d+2)]^{1/2}{:}[d/(d+2)]^{1/2} \qquad \text{(C.11b)}$$

We note that the ratio $R_{\mathrm{s}}(\mathrm{HS}){:}R_A(\mathrm{HS}) = [d/(d+2)]^{1/2}$ implies that the penetration function Ψ in the hard-sphere limit equals

$$\Psi(\mathrm{HS}) = [(d+2)/3]^{d/2}/\Gamma(1+d/2) \qquad \text{(C.12a)}$$

$$\Psi(\mathrm{HS};d{=}3) = (5/3)^{3/2}(4/3\pi^{1/2}) \approx 1.62 \qquad \text{(C.12b)}$$

where Γ denotes the gamma function. Equation C.12 corrects note 36 of ref 6a, which equates the sphere radius R with the radius of gyration R_{s}. For 56-arm polyisoprene stars Bauer et al.[40] find $\Psi(f{=}56.2) = 1.65$, which is consistent with (C.12b).

We also observe that the ratio R_{η}/R_{H} should be rather insensitive to branching architecture. Equation C.10 for linear chains gives the ratios

$$R^{\circ}_{\eta}/R^{\circ}_{\mathrm{H}} = 1.07, \qquad R^{*}_{\eta}/R^{*}_{\mathrm{H}} = 1.03 \text{ (nondraining)}$$

and for a hard sphere we have by definition $R_{\eta}(\mathrm{HS})/R_{\mathrm{H}}(\mathrm{HS}) = 1$. Roovers and Toporowski[41] observed that R_{η}/R_{H} is insensitive branching structure (linear, comb, star) and solvent quality; this ratio varies in the range $R_{\eta}/R_{\mathrm{H}} = 1.03 \pm 0.05$.

Appendix D. Comparison with Other Renormalization Group Calculations

Our discussion of renormalization group calculations of polymer properties has omitted reference to several equilibrium and dynamical computations by Oono and co-workers.[59] This has been done because of technical difficulties in these calculations. Consider first the penetration function, Ψ, which emerges from the renormalized perturbation expansion in the form[6,7]

$$\Psi = u + [7/6 + 4\ln 2]u^2 + O(u^3) \qquad \text{(D.1)}$$

where u is the renormalized dimensionless excluded-volume parameter. In the good solvent limit Ψ^* is obtained by evaluating (D.1) at the fixed point $u \rightarrow u^*$, where[6,7]

$$u^* = (\epsilon/8) + (21/4)(\epsilon/8)^2 + O(\epsilon^3) \qquad \text{(D.2)}$$

When Oono and Freed[60] first computed Ψ^*, the fixed point u^* was obtained only to order ϵ. Inserting the leading $\epsilon/8$ estimate of u^* from (D.2) into (D.1) provides the "one and one half" order approximation

$$\Psi^* \approx (\epsilon/8) + (7/6 + 4\ln 2)(\epsilon/8)^2, \qquad \Psi^*(d{=}3) \approx 0.19 \qquad \text{(D.3)}$$

that omits the order ϵ^2 contribution from (D.2). Using the second-order expression for u^* in (D.1) gives[6,7]

$$\Psi^* = (\epsilon/8) + (21/4)(\epsilon/8)^2 + (7/6 + 4\ln 2)(\epsilon/8)^2 + O(\epsilon^3), \qquad \Psi^*(d{=}3) = 0.27 \qquad \text{(D.4)}$$

We mention that Des Cloizeaux[61] calculated a dimensionless virial coefficient, g^*, closely related to Ψ^* and consistent with (D.4). The error incurred by the $1^{1}/_{2}$-order expression (D.3) is equal 0.08, which is nonnegligible. Calculations by Oono and co-workers[59] still employ the $1^{1}/_{2}$-order approximation leading to lower estimates of Ψ^* as in (D.3).

The problem with the $1^{1}/_{2}$-order approximation becomes more severe for many-arm stars. Renormalization group calculations by Miyake and Freed[6b] employ the $1^{1}/_{2}$-order approximation and lead to values of $\Psi^*(f)$ that have a maximum for $f = 4$, $\Psi^*(f{=}4) = 0.265$, and for larger f the penetration function approaches zero, e.g., $\Psi^*(f{=}15) = 0.0015$. The experimental data and our RG predictions,[6,7] however, indicate a monotonic increase of Ψ^* with f and reasonable values of $\Psi^*(f)$ for $f \leq 12$. However, the RG calculations of Douglas and Freed[6,7] do not predict the approach of Ψ^* to the hard-sphere limit described in Appendix C. The limitations of the continuum model in the large f limit are summarized in section II.A.

Oono and co-workers[59] have also performed dynamical renormalization group calculations leading to hydrodynamic virial expansions of the form (D.1), corresponding to the hydrodynamic radius, R_{H}, and intrinsic viscosity, $[\eta]$. These calculations neglect the second-order contributions to the hydrodynamic fixed point (again the $1^{1}/_{2}$-order approximation) and lead to spurious conclusions. For example, these calculations indicate no preaveraging correction for the hydrodynamic radius, which is in contrast to the significant preaveraging corrections estimated in the simulations by Zimm[13] (about a 10% deviation). Actually, preaveraging should make *no contribution* in the calculations to first order in ϵ given by Oono and co-workers,[59] and the preaveraging effect first arises in a second-order calculation given first by Wang et al.[19] for the Kirkwood–Riseman model. The second-order calculations indicate a leading preaveraging correction of the hydrodynamic radius of about 20% so that the analytical theory is only qualitatively in agreement with the simulation data. (See Wang et al.[19] for discussion.)

The calculations of Oono and co-workers[59] also differ from ours on account of technical procedures relating to the ϵ expansion of prefactors. Oono and co-workers re-exponentiate prefactors while the calculations of refs 6 and 7 do not follow this procedure. The different procedures are illustrated by considering the trivial calculation of the mean-square end-to-end distance of a Gaussian chain. Oono and co-workers[59] use units where $(d/l) = 1$, d is the dimension of space and l is the Kuhn length, so that $\langle \mathbf{R}^2 \rangle$ of a Gaussian chain is equal

$$\langle \mathbf{R}^2 \rangle_0 = dN \equiv 4(1 - \epsilon/4)N \tag{D.5a}$$

where N is the chain length. Oono and co-workers exponentiate $1 - \epsilon/4$ to order ϵ as

$$1 - \epsilon/4 \rightarrow e^{-\epsilon/4} + O(\epsilon^2) \tag{D.5b}$$

to obtain

$$\langle \mathbf{R}^2 \rangle_0 = 4Ne^{-\epsilon/4} + O(\epsilon^2) \tag{D.5c}$$

Reexponentiation as in (D.5b) was followed in the early work by Douglas and Freed,[6a] but this procedure was strictly avoided in later work[6,7] when it was realized that errors could be accumulated after many manipulations of this type. Calculations by Oono and co-workers[54] employ the reexponentiation procedure, and, as the trivial example (D.5) shows, there can be a significant difference between calculations while at the same time being consistent with ϵ perturbation theory.

Finally, we mention that the dynamical renormalization group calculations of Oono and co-workers[59] reach the disturbing conclusion that the hydrodynamic properties of Gaussian chains are independent of the hydrodynamic interaction. While Θ polymers are observed to conform reasonably to the nondraining limit,[20] the application of either the Kirkwood–Riseman or Rouse–Zimm models to Gaussian chains mathematically admits of a crossover from the free-draining to the nondraining limits.[10,19,20]

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Registry No. Polystyrene, 9003-53-6; polybutadiene, 9003-17-2; polyisoprene, 9003-31-0.