$$\phi_p{}^0 = \phi_A(\infty) + \phi_B(\infty) \tag{A-7}$$

and the critical value of the polymer volume fraction is given by[2]

$$(\phi_p{}^0)_{cr} = 2/Z\chi_{AB} \tag{A-8}$$

The above result (eq A-6) can be easily derived from eq 2-10 for the symmetric case ($\chi_{AS} = \chi_{BS}$). For the asymmetric case no simplification of eq A-4 takes place.

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Excluded-Volume Effects in Dilute Polymer Solutions. 11. Tests of the Two-Parameter Theory for Radius of Gyration and Intrinsic Viscosity

Y. Miyaki and H. Fujita*

Department of Macromolecular Science, Osaka University, Toyonaka, Japan.
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ABSTRACT: The two-parameter theory for radius of gyration and intrinsic viscosity was tested with experimental data on polystyrene and polyisobutylene published in preceding parts of this series. It was found that the radius expansion factors of the two polymers in different solvents gave a composite curve when plotted against the excluded-volume parameter z, as required by the two-parameter theory. This curve was best fitted by the Domb–Barrett empirical equation. For either polymer, the viscosity expansion factors in different solvents as functions of z did not give a single curve. This implies that intrinsic viscosity does not always obey the two-parameter theory.

One of the most important achievements in modern polymer science is the development of the two-parameter theory for molecular properties of linear flexible polymers in dilute solution. Much work has been done in the past 3 decades to check the predictions of this theory by experiment. The principal results are best summarized and discussed in Yamakawa's monograph.[1] A careful study of them leads us to the conviction that the validity of the two-parameter theory, especially on hydrodynamic properties, is not as yet definitively established.

The purpose of this paper is to check it for mean-square radius of gyration $\langle S^2\rangle$ and intrinsic viscosity at zero shear rate $[\eta]$, mostly using experimental data on polystyrene and polyisobutylene accumulated in our laboratory during the past few years. Except for ones taken from the doctoral thesis of Y. Miyaki, these data were published in preceding parts of this series of papers.

Criteria for the Two-Parameter Theory

According to this theory, the radius expansion factor α_s for linear flexible polymers at infinite dilution should be a universal function of a single variable z called the excluded-volume parameter; i.e.

$$\alpha_s = \alpha_s(z) \tag{1}$$

where α_s and z are defined by

$$\alpha_s{}^2 = \langle S^2\rangle/\langle S^2\rangle_0 \tag{2}$$

$$z = (4\pi\langle S^2\rangle_0/M)^{-3/2}M_0{}^{-2}M^{1/2}\beta \tag{3}$$

with $\langle S^2\rangle$ and $\langle S^2\rangle_0$ the mean-square radii of gyration of a linear flexible polymer in the perturbed and unperturbed state, respectively, M the molecular weight of the polymer, M_0 the molecular weight of its repeat unit, and β the binary cluster integral representing the strength of interaction between a pair of repeat units. The term "universal" in the above statement means that a quantity is independent of the kind of polymer and solvent condition. A solvent condition is defined by the kind of solvent and the temperature.

If, as was assumed by Flory,[2] the polymer molecule in solution behaves as if it were impermeable to solvent, the two-parameter theory predicts that the viscosity expansion factor α_η also should be a universal function of z; i.e.

$$\alpha_\eta = \alpha_\eta(z) \tag{4}$$

where α_η is defined by

$$\alpha_\eta{}^3 = [\eta]/[\eta]_0 \tag{5}$$

with $[\eta]$ and $[\eta]_0$ the intrinsic viscosities of a polymer in the perturbed and unperturbed state, respectively.

If eq 1 and 4 hold, there should exist a universal relation between α_s and α_η. As can be seen in Yamakawa's book,[1] previous tests with well-documented experiments are

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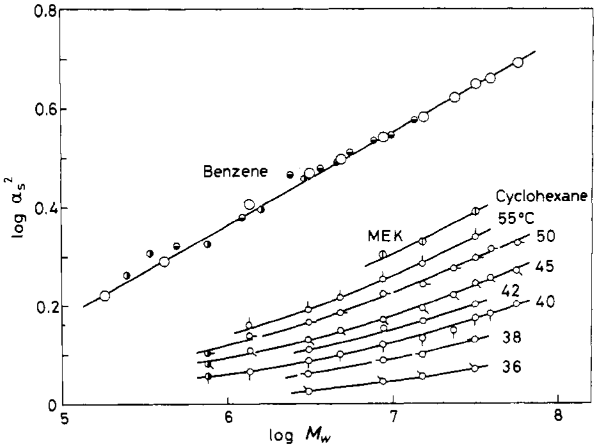

Figure 1. log-log plots of α_s^2 vs. M_w for polystyrene in benzene at 25 and 30 °C, in methyl ethyl ketone (MEK) at 35 °C, and in cyclohexane at the temperatures indicated. Half-filled circles, from ref 4 and 5. Other symbols, from ref 3 and 6.

generally in favor of this prediction. However, we must note that the existence of a universal relation between α_s and α_η is only a necessary condition for eq 1 and 4 to hold. Nonetheless, one might take it as a sufficient condition for the two-parameter theory of $[\eta]$, considering eq 1 to be self-evident theoretically. It is imperative for completeness to verify, in addition to the above-mentioned necessary condition, that either α_s or α_η is a universal function of z.

Now, to a good approximation, the characteristic ratio $\langle S^2\rangle_0/M$ of a polymer may be treated as a constant except in the region of low M. Further, the binary cluster integral β is a function of polymer and solvent condition but not of M. Therefore, to a good approximation, we may write eq 3 as

$$z = KM^{1/2} \tag{6}$$

with K a constant for polymer and solvent condition fixed. The subsequent discussion is limited to the case in which eq 6 is valid.

Criterion A. With eq 6 it follows that if eq 1 holds, plots of log α_s vs. log M for different combinations of polymer and solvent condition can be superimposed on a single curve by appropriate displacement along the horizontal axis.

For a given polymer we choose a relevant solvent condition R as the reference state and denote the value of K for R by K_R. Then, $K_{R'}$, the K value of the same polymer for another solvent condition R′, can be expressed by

$$K_{R'} = K_R(a_M)^{-1/2} \tag{7}$$

if criterion A is obeyed. Here, log a_M is the horizontal distance needed to have the log α_s vs. log M curve for R′ match that for R. We call a_M the shift factor for R′ relative to R. Since K is proportional to β for a given polymer, eq 7 is equivalent to

$$\beta_{R'} = \beta_R(a_M)^{-1/2} \tag{8}$$

Hence, when eq 1 holds, β can be evaluated from experimental determination of the shift factor if one has a means to estimate β_R.

Criterion B. With eq 6 it follows that if eq 4 holds, plots of log α_η vs. log M for different combinations of polymer and solvent condition can be brought on a single curve when displaced horizontally, and the horizontal distance between the plots of a given polymer for solvent conditions R′ and R should be equal to that between the corresponding log α_s vs. log M plots.

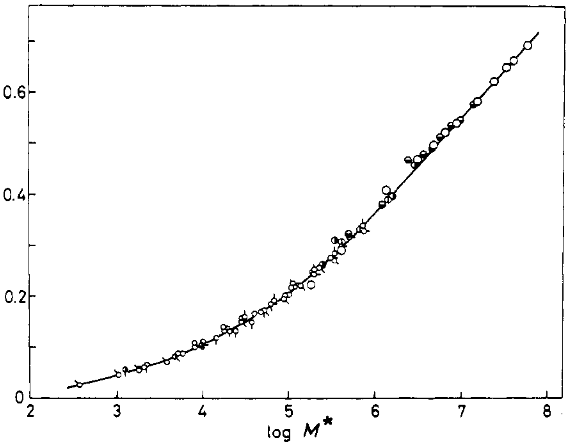

Figure 2. log-log plots of α_s^2 vs. M^* ($\equiv M_w/a_M$) derived from Figure 1. Symbols are the same as in Figure 1.

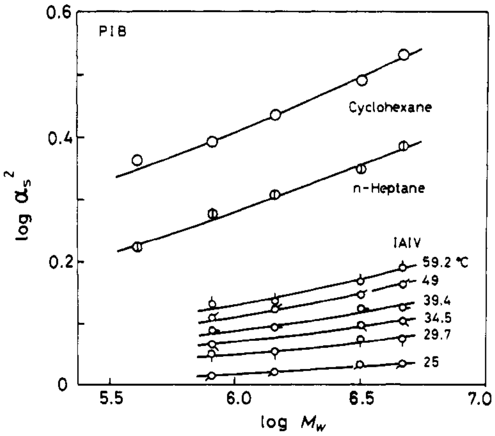

Figure 3. log-log plots of α_s^2 vs. M_w for polyisobutylene in cyclohexane at 25 °C, in n-heptane at 25 °C, and in isoamyl isovalerate (IAIV) at the temperatures indicated.

The latter condition is required by the fact that α_s and α_η are functions of the same variable z.

Radius Expansion Factor

Check of Criterion A. Figure 1 shows double-logarithmic plots of α_s^2 vs. M_w (weight-average molecular weight) for narrow-distribution polystyrene samples in benzene at 25 and 30 °C, in methyl ethyl ketone (MEK) at 35 °C, and in cyclohexane at a series of temperatures above the Θ point (307.7 K).

Figure 2 illustrates how accurately the sets of data points for different solvent conditions in Figure 1 can be brought to a single line by horizontal shifting. Here, M^* is a reduced molecular weight defined by M_w/a_M, with a_M the shift factor relative to 25 °C benzene as the reference state R. We conclude that the polystyrene data in Figure 1 satisfy criterion A.

Figure 3 displays double-logarithmic plots of α_s^2 vs. M_w for polyisobutylene in cyclohexane at 25 °C, in n-heptane at 25 °C, and in isoamyl isovalerate (IAIV) at different temperatures above the Θ point (295.3 K). These data were taken from part 4 of this series.[7] It is seen that there is little or no range of α_s^2 in which values of this quantity in different solvents overlap. This condition makes it difficult to check data unambiguously for the superimposability required by criterion A. However, if the system obeys criterion A, the lines drawn in Figure 3 should be made coincident with the composite curve for polystyrene in Figure 2 by horizontal displacement. Figure 4 demonstrates that this prediction holds. Thus, we can conclude

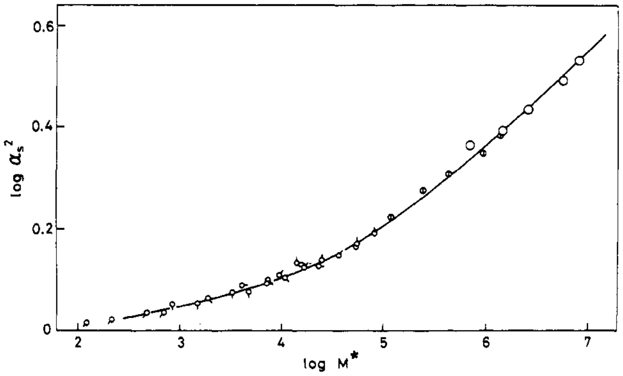

Figure 4. Superimposition of polyisobutylene data on the composite curve (solid line) for polystyrene. Symbols are the same as in Figure 3.

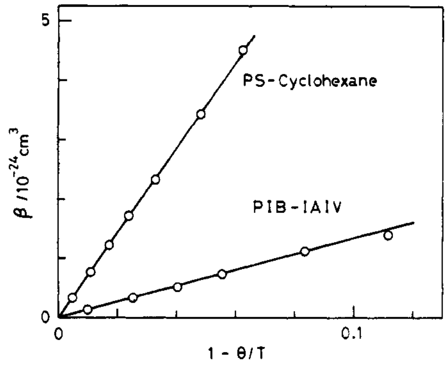

Figure 5. Temperature dependence of binary cluster integral β for polystyrene in cyclohexane and that for polyisobutylene in isoamyl isovalerate.

Table I
Values of Binary Cluster Integral β for Polystyrene in Three Solvents

solvent	T/°C	$\beta/10^{-24}$ cm^3
benzene	25	30
MEK	35	6.3_7
cyclohexane	55	4.5_1
	50	3.4_2
	45	2.3_2
	42	1.7_1
	40	1.2_2
	38	0.77
	36	0.33
	34.5	0.00

that the $\langle S^2 \rangle$ data on polyisobutylene in part 4 also satisfy criterion A.

Evaluation of β. In part 7 of this series,[3] we proposed for evaluation of the binary cluster integral β to use Domb's asymptotic relation[8] $\alpha_s^2 = 1.53z^{2/5}$ derived from computer data on self-avoiding lattice chains and obtained $\beta = 34 \times 10^{-24}$ cm^3 for polystyrene in benzene at 25 °C and $\beta = 14 \times 10^{-24}$ cm^3 for polyisobutylene in cyclohexane at 25 °C. If we use a more accurate value determined recently by Miyaki et al.[9] for the characteristic ratio $\langle S^2 \rangle_0/M$, we find a value of 30×10^{-24} cm^3 for the former.

With this revised value of β taken as β_R in eq 8 we computed β for polystyrene in solvents other than 25 °C benzene from the measured values of log a_M. The results are presented in Table I. These values for cyclohexane at different temperatures T are plotted against $1 - (\Theta/T)$ in Figure 5, in which Θ is the Θ temperature (307.7 K) for polystyrene + cyclohexane. In the range of T examined, the data points are fitted by the relation

$$\beta/10^{-24} \text{ cm}^3 = 72[1 - (\Theta/T)] \qquad (9)$$

Table II
Values of Binary Cluster Integral β for Polyisobutylene in Three Solvents

solvent	T/°C	$\beta/10^{-24}$ cm^3
cyclohexane	25	14
n-heptane	25	5.7_7
IAIV (isoamyl isovalerate)	59.2	1.3_9
	49	1.1_3
	39.4	0.74
	34.5	0.50
	29.7	0.34
	25	0.13
	22.1	0.00

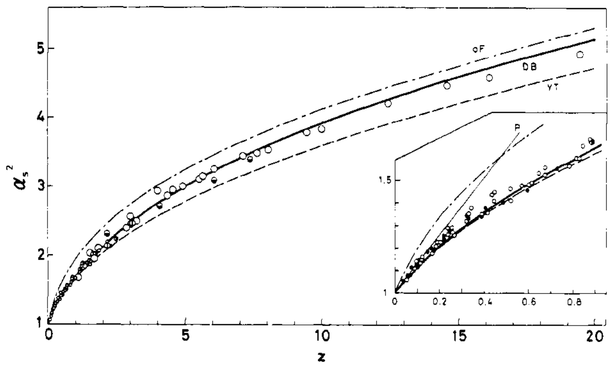

Figure 6. Relations between α_s^2 and excluded-volume parameter z. Solid curve, Domb–Barrett equation; dashed curve, Yamakawa–Tanaka equation; dot–dash curve, "original" Flory equation. Main part: large unfilled circles, PS (polystyrene) + benzene; circles with bar, PS + MEK; bottom-half-filled circles, PIB (polyisobutylene) + cyclohexane; right-half-filled circles, PIB + n-heptane; small unfilled circles, PS + cyclohexane and PIB + IAIV. Insert: unfilled circles, PS + cyclohexane; filled circles, PIB + IAIV.

To evaluate β for polyisobutylene solutions we make use of the relation

$$\beta_{R'} = \beta_R(b_{MR}/b_{MR'})^{1/2} \qquad (10)$$

where log b_{MR} is the horizontal displacement needed to make the log α_s^2 vs. log M_w curve of polyisobutylene for solvent condition R congruent with the composite curve for polystyrene in Figure 2. Equation 10 can be derived from eq 1. With the β value for polyisobutylene in 25 °C cyclohexane taken as β_R in eq 10, we calculated $\beta_{R'}$ for this polymer in solvent condition R′ from the values of log b_{MR} and log $b_{MR'}$ needed to obtain Figure 4 from Figure 3. The results obtained are presented in Table II. These β values for IAIV at different temperatures T are also plotted against $1 - (\Theta/T)$ in Figure 5, where Θ is 295.3 K. Except for one at the highest temperature, the plotted points are fitted by a straight line.

Relation between α_s and z. Using the β values given in Tables I and II, together with the reported values of $\langle S^2 \rangle_0/M$ for polystyrene and polyisobutylene (8.30×10^{-18} cm^2 mol g^{-1} for the former[9] and 9.52×10^{-18} cm^2 mol g^{-1} for the latter[7]), we computed z for all the data points in Figures 1 and 3 and plotted α_s^2 against z in Figure 6. The plotted points compose a smooth curve. Although we must wait for studies on other systems before concluding the universality of this curve, it is interesting to compare it with some typical theories available at present.

Since Flory[2] in 1949 paved the way to dilute polymer solution theory, many theoreticians have made great efforts to approach $\alpha_s(z)$ by calculating statistical dimensions of a randomly coiled chain with volume exclusion. However, no exact solution is as yet found because of the formidable mathematical difficulties contained in this approach. It also still remains unsettled which of the many approximate

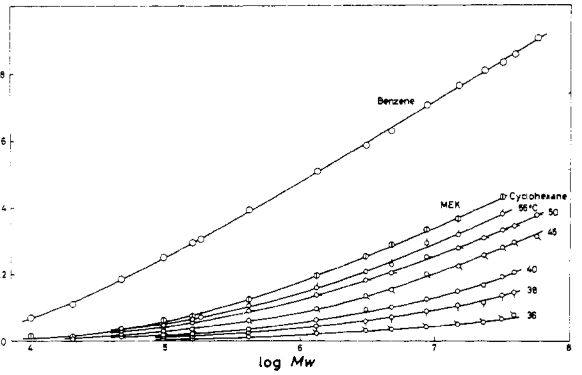

Figure 7. log-log plots of α_η^3 vs. M_w for polystyrene in benzene at 25 °C, in MEK at 35 °C, and in cyclohexane at the temperatures indicated. Benzene data, from ref 12. Other data, from ref 6.

expressions so far proposed for $\alpha_s(z)$ is the most adequate for describing observed relations between $\langle S^2 \rangle$ and M.

Recently, Domb and Barrett[10] presented an empirical expression for $\alpha_s(z)$ which is constructed so as to agree with the perturbation theory[1] for random flight chains and for lattice models[10] at very small z and approach a form close to the above-mentioned Domb asymptotic relation at large z. It can be written

$$\alpha_s^2(z) = [1 + 10z + (70\pi/9 + 10/3)z^2 + 8\pi^{3/2}z^3]^{2/15}[0.933 + 0.067 \exp(-0.85z - 1.39z^2)] \quad (11)$$

In Figure 6, the solid line has been calculated from this equation, while the other lines are results from typical approximate theories:[2,11]

$$\alpha_s^5 - \alpha_s^3 = 2.60z \qquad \text{("original" Flory)} \quad (12)$$

$$\alpha_s^2 = 0.541 + 0.459(1 + 6.04z)^{0.46} \quad \text{(Yamakawa-Tanaka)} \quad (13)$$

It is seen that eq 11 fits the plotted points more accurately than does either eq 12 or eq 13.

The solid straight line P shown in the insert of Figure 6 represents the initial tangent expected by perturbation theory[1] for random flight chains and lattice models.[10] It tangentially touches the plotted points near $z = 0$. This fact implies that Domb's asymptotic relation $\alpha_s^2 = 1.53z^{2/5}$ can be used to estimate β for random flight chains which mimic actual polymers in statistical behavior.

Viscosity Expansion Factor

Check of Criterion B. Figure 7 shows double-logarithmic plots of α_η^3 vs. M_w for polystyrene in different solvents. By inspection we immediately find that this system of curves cannot be brought to a single curve by horizontal displacement; i.e., these data do not obey criterion B. It is interesting to see what happens if the abscissa variable is changed to z computed with the β values given in Table I. The result is shown in Figure 8.

The cyclohexane data for different T and M are seen to fall on a single curve, but this curve is congruent with the line fitting the MEK data only in the region of z above a certain value. What is more interesting is the intersection which occurs between the cyclohexane curve and the line fitting the benzene data. We believe that these discrepancies with criterion B are more than errors in the measurements of α_η^3 and the inaccuracy involved in the determination of β and hence of z.

Another example of the breakdown of the two-parameter theory for $[\eta]$ can be seen in Figure 9, which presents double-logarithmic plots of α_η^3 vs. z for polyisobutylene in various solvents; the values of z were computed by using the β values given in Table II. As is the case with polystyrene in cyclohexane, the IAIV data for different T and M fall on a single curve. However, the n-heptane and cyclohexane data follow lines with different slopes, and neither of these two lines appears to be connected smoothly to the IAIV curve. Further, though not very distinctly, the cyclohexane curve intersects the IAIV curve.

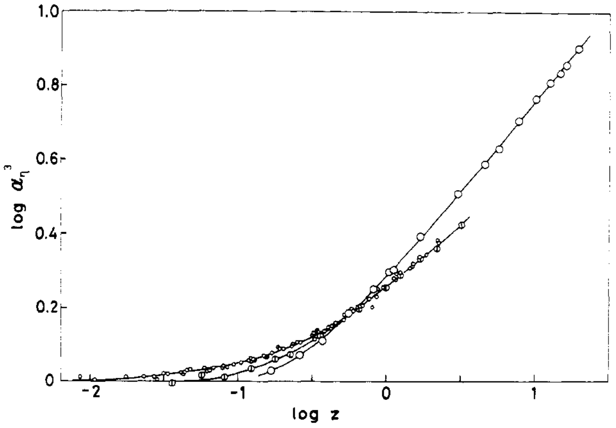

Figure 8. log-log plots of α_η^3 vs. z for polystyrene derived from Figure 7. Symbols are the same as in Figure 7.

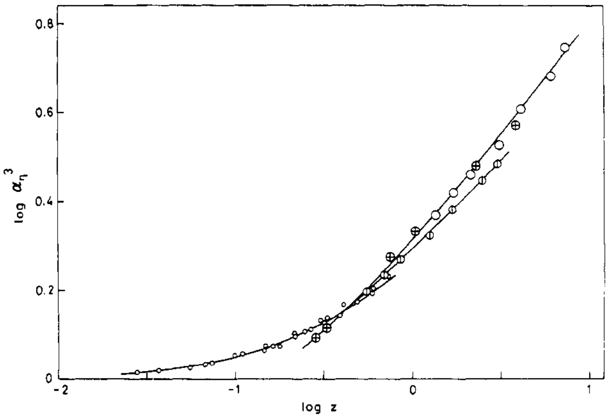

Figure 9. log-log plots of α_η^3 vs. z for polyisobutylene in cyclohexane at 25 °C (large unfilled circles and circles with cross), in n-heptane at 25 °C (circles with vertical bar), and in IAIV at different temperatures (small unfilled circles). Circles with cross, from ref 13. Other data, from ref 7.

Comparing Figures 8 and 9, we find that the cyclohexane line in the former and the IAIV line in the latter are almost exactly superimposable with no further shifting along the horizontal axis. This may be an accident. Nonetheless, we feel it to be an indication of the fact that the two-parameter theory for $[\eta]$ is valid to a good approximation for the variation of solvent condition which is caused by changing T in poor solvent systems (we note that cyclohexane and IAIV are the Θ solvents for polystyrene and polyisobutylene, respectively). As we have shown above, this theory breaks down when the solvent condition is varied by changing solvent from a poor to a good one at fixed T. Thus, we conclude that the effect of solvent condition on $[\eta]$ of a linear flexible polymer does not always appear only through β in the expression for z. Partial free drainage and chain stiffness are the primary factors which come into consideration on this matter.

Relation between α_η and α_s. In Figure 10, double-logarithmic plots of α_η^3 vs. α_s^3 for polystyrene in three solvents are shown. Apparently, all the plotted points cannot be fitted by a single line but are distinctly split into two branches, one consisting of the benzene data and the other of the cyclohexane and MEK data. Since, as we have

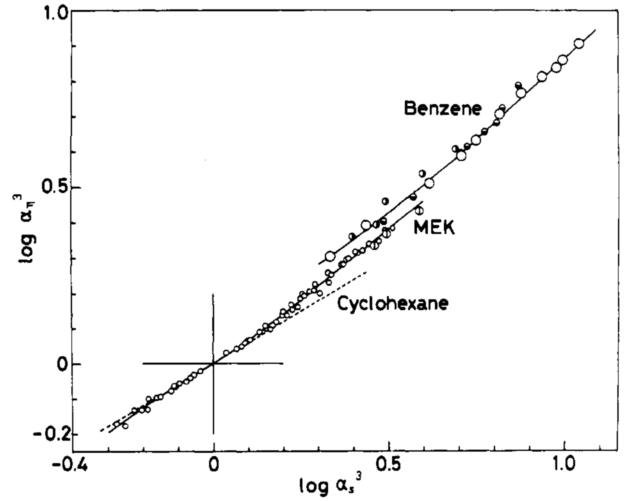

Figure 10. log–log plots of α_η^3 vs. α_s^3 for polystyrene in different solvents. Symbols are the same as in Figure 1. The dashed line is the initial tangent predicted by the perturbation theories for α_s^1 and α_η.[14]

shown above, $\langle S^2 \rangle$ of polystyrene in these three solvents obeys the two-parameter theory, this result is a clear demonstration of the breakdown of the two-parameter theory for $[\eta]$. No previous work has revealed as distinctly as seen here splitting of log α_η^3 vs. log α_s^3 plots for polystyrene in different solvents. Probably, this was due to the fact that previous measurements could not be extended to sufficiently high values of α_s^3 in MEK and cyclohexane because of the unavailability of ultrahigh molecular weight polymer samples.

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Intrinsic Viscosity and Diffusion of Solutions of Flexible Polymer Molecules in Good Solvents

Robert Ullman

Research Staff, Ford Motor Company, Dearborn, Michigan 48121.
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ABSTRACT: The steady-state hydrodynamics of flexible polymer molecules has been treated as a function of solvent power, using the Kirkwood and Kirkwood–Riseman methods with a chain statistics based on the "blob" hypothesis, refined, and smoothed to provide a physically realistic behavior. It provides an asymptotically accurate picture of the second moment of the distance between chain elements in good solvents, with a semiempirical fit in the range intermediate between good and bad solvents. We refer to the model as "quasi-blob" statistics to emphasize its relation to and deviation from the original "blob" model. Calculations of intrinsic viscosity, diffusion constant, radius of gyration, and hydrodynamic radius are performed and presented for several strengths of the excluded-volume interaction over a wide range of molecular weight. These have been compared with experiments on polystyrene solutions. The calculations and experiment are in fair agreement. Among the interesting results of the model are the following: (1) The exponent a in the expression $[\eta] = KM^a$ is a function of both molecular weight and the strength of the excluded-volume interaction. This is also seen in experiments if a large range of molecular weight (3 orders of magnitude or more) is used. (2) In a good solvent, a increases with molecular weight and then decreases. It can be greater than 0.8 in some cases. (3) Weill and des Cloizeaux[8] suggest that intrinsic viscosity and diffusion constants in good solvents approach the asymptotic molecular weight slowly because the hydrodynamic radius approaches this limit slowly. They suggest that the use of the formula $[\eta] \sim R_g^2 R_H / M$ in place of $[\eta] \sim R_g^3/M$ would account for the observed experimental behavior. Our calculations show a marginal advantage for the first of these two formulas.

Introduction

Viscosity and diffusion of polymers in solution provide useful information for characterization of macromolecules. The basis for the characterization rests on the solution of hydrodynamic equations for appropriate molecular models of a polymer chain. For the purpose of calculation, the polymer molecule is regarded as a macroscopic hydrodynamic body immersed in a solvent whose molecular structure is ignored. The solvent plays the role of a viscous fluid in which one or more polymer molecules are dispersed.

The polymer molecule is, on the other hand, treated as a microscopic body in the sense that its undergoes Brownian motion. Therefore, if the flow rate is sufficiently low, Brownian motion eliminates molecular and segmental orientation. It is this combination of the microscopic and