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Some Unsolved Problems on Dilute Polymer Solutions

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ABSTRACT: In contrast to the prevailing notion, our understanding of polymer behavior in dilute solutions still leaves much to be desired. This fact is illustrated here by discussing some typical unsolved problems regarding the following subjects: intrinsic viscosity, hydrodynamic factors, second virial coefficient, and the onset of the excluded-volume effect on the statistical radius.

It is misleading to consider that polymer behavior in dilute solutions has been worked out so thoroughly in the past decades that few problems of fundamental importance on this subject remain unsolved or unexplored. If we study the existing literature somewhat carefully, we will soon come across many important experimental results which are waiting for adequate theoretical explanations in terms of molecular parameters. The aim of the present paper is to illustrate this fact by discussing some unsolved problems regarding four typical subjects: intrinsic viscosity, hydrodynamic factors, second virial coefficient, and the onset of the excluded-volume effect on statistical radius. In so doing, we will confine our object to the behavior of monodisperse flexible linear polymers in a single solvent, except in the last subject which is concerned with semiflexible polymers.

Intrinsic Viscosity

The Houwink–Mark–Sakurada Relation. One of the most surprising generalities observed in polymer systems is that the intrinsic viscosity $[\eta]$ of a series of polymer homologues increases with the polymer's molecular weight M following a simple power law usually called the Houwink–Mark–Sakurada (HMS) relation, i.e.,

$$[\eta] = KM^{\nu} \tag{1}$$

where K and ν are constant for a given polymer + solvent system. A vast amount of experimental data[1] indicates the empirical rule that ν in Θ solvents where the second virial coefficient A_2 of the solution becomes zero is always 0.5, while it is found between 0.5 and 0.8 in non-Θ solvents where A_2 is positive. Generally, this index for a given kind of polymer is larger for a better solvent which is conveniently defined as one giving a larger second virial coefficient.

When data for log $[\eta]$ of a series of polymer homologues are graphed as a plot of log $[\eta]$ against log M, we seldom see a discernible curvature, sometimes it is seen in the region of relatively low molecular weight, and as a rule the slope of the plot is steeper for a better solvent, as sketched in Figure 1. This is another version of what was stated in the preceding paragraph explaining the HMS relation.

The upper bound of M accessible to experimental work is limited, implying that the asymptotic behavior of $[\eta]$ at indefinitely large M is beyond the reach of our measurement. What can actually be done is to make an estimation guess of it from experimental data obtained over a limited range of M, and for a surer estimate it is desirable to acquire data extended up to M so high that polymer behavior is considered to obey an asymptotic law. Recently, such data were obtained by Einaga et al.[2,3] for narrow-distribution polystyrene (PS) in benzene and by Meyerhoff and Appelt[4] for PS in toluene; the highest molecular weight of PS studied was as large as 6×10^7 for the former and 4×10^7 for the latter. Interestingly, for both systems, the log $[\eta]$ versus log M plots were perfectly linear over the range of at least 2 decades up to these M values. It is difficult to suspect that even in the region of such "ultrahigh" molecular weights the viscosity behavior of a linear polymer in dilute solution does not yet become asymptotic; i.e., the HMS relations established by the above authors will fail to hold if the measurement is extended to "superhigh" molecular weights. If this is the case, it would virtually be impossible to approach by experiment the asymptotic polymer behavior at high M, and theoretical calculations with infinitely long chains would become a matter of mere mathematical interest. On the basis of the vast amount of available experimental information, the author maintains the opinion that once found valid over a sufficiently broad range of M, say more than 2 decades, the HMS relation should be valid up to any higher molecular weights and that this should be taken as the fact or truth that has to be explained by molecular theory.

Theoretical Predictions

Polymer transport properties in dilute solutions have so far been formulated on the basis of the Kirkwood–Riseman integral equations[5] or the Kirkwood generalized diffusion equation.[6] Despite the great many efforts of theoreticians no exact solution to these equations is as yet found for flexible polymers. Thus, some typical theoretical predictions for $[\eta]$ described below are based on approximate solutions whose accuracy is not easily assessed.

Θ-Solvent Systems. Theories of $[\eta]$ and other transport properties such as the diffusion coefficient are greatly simplified when we are concerned with Θ-solvent systems in which the complications due to excluded-volume effect are considered to disappear. In what follows, $[\eta]$ in such a system is given a subscript Θ.

In 1948, Kirkwood and Riseman (KR)[5] and independently Debye and Bueche (DB)[7] presented the first mo-

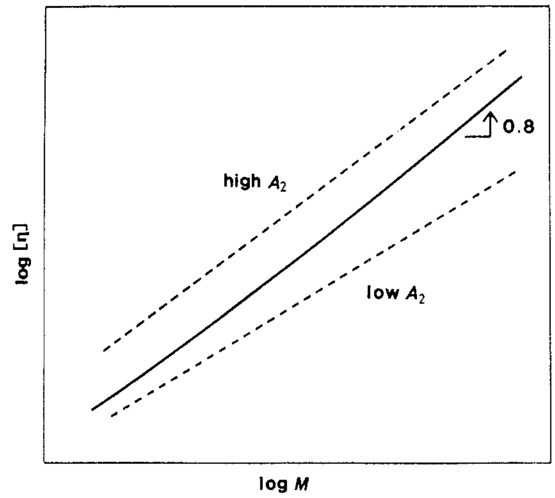

Figure 1. Molecular weight dependence of intrinsic viscosity $[\eta]$ for homologous flexible linear polymers (schematic): solid line, theoretical prediction (note its weak upward curvature); dashed lines, experimental (showing no discernible curvature).

lecular theories of $[\eta]_\Theta$, using somewhat different models for the polymer coil. The results from the two theories were essentially the same, predicting that the index ν in eq 1 changes continuously from 1.0 to 0.5 with increasing M and thus failing to explain the empirically known fact that ν in Θ solvents is 0.5 independently of M.

According to the KR or DB theory, ν varies with M owing to the hydrodynamic effect that makes the polymer coil less permeable (draining) to solvent as the chain gets longer. Thus, the fact that $\nu = 0.5$ in Θ solvents implies that actual polymer coils in such solvents behave hydrodynamically as if they completely immobilize solvent inside them regardless of chain length. It is worth noting that Kuhn[8] had proposed complete solvent immobilization early in the 1930s and that later Flory[9] adopted Kuhn's idea as a postulate in formulating his famous theory of dilute polymer solutions. However, no persuasive theoretical justification of this postulate is as yet found, as far as the author is aware. Since a substantial part of a polymer coil is occupied by solvent molecules, it seems quite difficult to rule out the so-called partially draining polymer model.

Actual polymer molecules are not perfectly flexible as assumed in the KR or DB theory but have a certain stiffness for both bending and twisting. Yamakawa and Fujii[10] extended the KR theory to unperturbed (i.e., free from volume exclusion) wormlike chains, a typical model of semiflexible polymers, and showed that chain stiffness expressed in terms of persistence length q gives rise to an effect which suppresses the effect of solvent draining on intrinsic viscosity. In fact, when a value of about 0.8 is assigned to q/d, where d is the diameter of the chain, their theory gives $[\eta]$ which varies linearly with $M^{0.5}$ over a much wider range of M than predicted by the KR theory for perfectly flexible chains, thus appearing to be able to explain the observed fact in Θ-solvent systems. However, it is not likely that q/d happens to be 0.8 for any pair of polymer and Θ solvent. This ratio may vary from system to system.

Non-Θ Solvents. Volume exclusion of chain segments affects dynamic as well as static properties of linear polymers in non-Θ solvents. Theoretical formulation of its effects on transport properties is especially difficult, but significant progress in recent years by renormalization group methods[11] is worth noting.

The theories presented to date for $[\eta]$ in non-Θ solvents (in which A_2 is positive) predict in common that, as schematically shown by a solid line in Figure 1, log $[\eta]$ plotted against log M follows a curve which is weakly bent upward and asymptotically approaches a straight line with a slope of 0.8. Importantly, this asymptote is reached regardless of solvent quality (unless the system is under the Θ condition) and the value of draining strength, though the rate of approach to it varies with these parameters. Here the draining strength is proportional to the well-known drainage parameter h divided by $M^{1/2}$.

These results are at variance with what the author has inferred above as fact from observed information; i.e., log $[\eta]$ may increase linearly with log M with no upper bound of M and the slope of this linear relation, ν in eq 1, should be larger for a better solvent. Actually, the good-solvent limit of ν for flexible polymers remains unestablished. Benzene and toluene are typical good solvents for PS. Einaga et al.[2] obtained $\nu = 0.75$ for the former and Meyerhoff and Appelt[4] found $\nu = 0.724$ for the latter. For poly(methyl methacrylate) in a good solvent, acetone, Kashiwagi et al.,[12] who measured $[\eta]$ over a range of M up to $M = 3 \times 10^7$, found an even smaller value of 0.70 for ν. In fact, the theoretically predicted good-solvent limiting value of 0.8 for ν is seldom reported in well-documented experimental work.

The observed constancy of ν over a virtually infinite range of M may be explained by allowing the draining strength to vary with M, as was done by Wang et al.[13] in their recent approach to intrinsic viscosity and the diffusion coefficient. However, the renormalization group theory they used does not answer the question of why such a variation of the draining strength emerges.

Summarizing the above discussions, we may conclude that no persuasive theory is as yet established for the experimental fact that the intrinsic viscosity of flexible linear polymers almost invariably follows the HMS relation. Probably, among other things, what has to be uncovered first would be the molecular mechanism responsible for the Kuhn–Flory postulate that polymer coils moving in dilute solutions behave as though they are impermeable to solvent.

Hydrodynamic Factors

Experimental Information. One of the most firmly established facts in dilute polymer solution studies is that the mean-square radius of gyration $\langle S^2\rangle$ of a series of flexible linear polymer homologues in a Θ solvent is directly proportional to M except in the region of low M, i.e., $\langle S^2\rangle_\Theta = K'M$, with K' independent of M. As mentioned above, we have $[\eta]_\Theta = KM^{0.5}$ experimentally. Hence, the quantity Φ_Θ defined by

$$\Phi_\Theta = [\eta]_\Theta M/(6\langle S^2\rangle_\Theta)^{3/2} \tag{2}$$

is independent of M, being equal to $K/(6K')^{3/2}$. Well-documented studies have led to Φ_Θ in the range (2.0–2.7) $\times 10^{23}$ mol^{-1}, nearly independently of polymer and solvent. The most reliable value of this quantity for the most thoroughly studied system of PS and cyclohexane seems to be that of Miyaki et al.,[14] 2.55×10^{23} mol^{-1}.

Accurate measurements of D_Θ, the translational diffusion coefficient at infinite dilution, for flexible linear polymers in Θ solvents have established an empirical relation $D_\Theta = K''M^{-0.5}$ over a wide range of M, with K'' constant for a given polymer + solvent system. The quantity $R_{h\Theta}$ defined by

$$R_{h\Theta} = kT_\Theta/(6\pi\eta_0 D_\Theta) \tag{3}$$

is called the Stokes radius of a polymer coil in a Θ solvent. Here, k is the Boltzmann constant, T_Θ the Θ temperature, and η_0 the solvent viscosity. Figure 2 illustrates typical

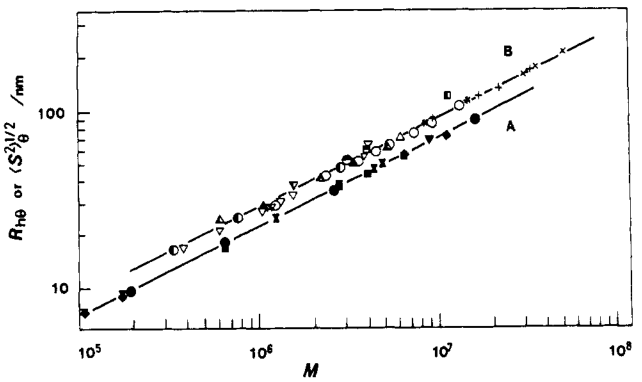

Figure 2. Typical data of gyration radius $\langle S^2\rangle_\Theta^{1/2}$ (B) and Stokes radius $R_{h\Theta}$ (A) for polystyrene in Θ solvents; different marks distinguish work of different authors: solid lines, drawn with slope 0.5.

PS data for $\langle S^2\rangle_\Theta^{1/2}$ and $R_{h\Theta}$ as functions of M.

We define a dimensionless quantity ρ_Θ by

$$\rho_\Theta = \langle S^2\rangle_\Theta^{1/2}/R_{h\Theta} \tag{4}$$

which is the static radius relative to the hydrodynamic one of a polymer coil in a Θ solvent. It can be shown that

$$\rho_\Theta = 6\pi\eta_0 K''(K')^{1/2}/kT_\Theta \tag{5}$$

which indicates ρ_Θ to be independent of M. Using the data illustrated in Figure 2, Schmidt and Burchard[15] estimated ρ_Θ for PS to be 1.27; see also Tsunashima et al.[16] ter Meer and Burchard[17] reported the value of 1.16 for poly(methyl methacrylate) in a Θ solvent.

Mandelkern and Flory[18] long ago introduced a dimensionless quantity P_Θ defined by

$$P_\Theta = kT_\Theta/[(6\langle S^2\rangle_\Theta)^{1/2}\,\eta_0 D_\Theta] \tag{6}$$

It can be shown that

$$P_\Theta = 6^{1/2}\pi/\rho_\Theta \tag{7}$$

The P_Θ values corresponding to $\rho_\Theta = 1.27$ (for PS) and 1.16 (for PMMA) are 6.05 and 6.63, respectively. With many reported data[19] in consideration, we may conclude that P_Θ is universal (or nearly so) and its average value is in the range 5.8–6.0; the scatter of reported values is narrower for the former than for the latter.

Theoretical Values

A great many authors have made various attempts to evaluate the hydrodynamic factors Φ_Θ and P_Θ by solving the relevant basic equations analytically or numerically; see Yamakawa's book[20] for previous attempts and Oono's review[11] for recent ones. In many cases, the "nondraining" approximation was introduced in view of the fact that for a yet unknown reason either $[\eta]_\Theta$ or D_Θ as a function of M shows no symptom of solvent permeation through the polymer coil and also for the reason that this greatly simplifies mathematical analysis.

The most crucial point in computing the hydrodynamic factors concerns the Oseen tensor which describes hydrodynamic interactions between chain segments. At present, it does not appear feasible to solve the basic equations analytically unless what is called the "preaveraging" approximation to this tensor is invoked, as was originally done by Kirkwood and Riseman.[5]

The most reliable values of the hydrodynamic factors obtained by using this approximation are as follows:[20] $\Phi_\Theta = 2.85 \times 10^{23}$ mol^{-1} and $P_\Theta = 5.20$ ($\rho_\Theta = 1.48$). The former value is 13% higher than Miyaki et al.'s experimental value of 2.55×10^{23} mol^{-1} for PS, while the latter is 16% lower than Schmidt and Burchard's estimate for the same polymer. These differences are rather small but must be considered significant because of the high reliability of the experimental values.

Recently, using the renormalization group method but limiting the calculation to first order in ϵ ($=4 - d$, d is the dimensionality of space), Oono[11] obtained 2.36×10^{23} mol^{-1} for Φ_Θ and 6.20 for P_Θ. Both compare more favorably with the experimental values than do the previous theoretical estimates. However, it should be noted that Oono's results have nothing to do with preaveraging. Use of this approximation becomes imperative for evaluating the hydrodynamic factors to second order in ϵ, as shown by Wang et al.[21]

Zimm[22] and subsequently Garcia de la Torre et al.[23] undertook the Monte Carlo method to solve numerically the Kirkwood–Riseman integral equations without invoking the preaveraging approximation. The results obtained by Zimm are $\Phi_\Theta = 2.51 \times 10^{23}$ mol^{-1} and $P_\Theta = 5.99$ ($\rho_\Theta = 1.28$). These are very close to the experimental values quoted above and thus appear to convince us that the previous estimates of the hydrodynamic factors were inaccurate mainly owing to the use of the preaveraging approximation. But Fixman[24] criticized the rigid-body treatment of a polymer invoked in the Kirkwood–Riseman approach and suggested by Brownian dynamic simulation that the error due to the preaveraging approximation be about 8% for Φ_Θ but about 1% for P_Θ. According to him, Zimm's method of computation gives the upper bound to the true value.

If Fixman's suggestion is correct, there still remains a disagreement of several percent between measured and calculated values of Φ_Θ, and this fact has to be given an adequate theoretical explanation. Calculations of this factor and also P_Θ, either analytical or numerical, have so far been made for an idealized chain in which intramolecular interactions of any order are absent. However, actual polymers in Θ solvents are ones in which the combined effect of these interactions on the second virial coefficient A_2 happens to vanish. Such a difference may account for the above-stated remaining gap between theory and experiment for the hydrodynamic factors. With only binary and ternary interactions of chain segments taken into account (this approximation is well justified for long chains), several authors have investigated the statistical dimensions of a linear flexible polymer near the Θ point (see Bruns[25] and Cherayil et al.[26] for recent work), but as far as the author is aware, this type of calculation is as yet unattempted for transport properties and hence for the hydrodynamic factors.

In this connection the following remark may be in order. It can be easily shown that if the polymer still has a significant ternary segment interaction at the Θ point the Θ temperature of the system should measurably depend on the polymer's chain length. However, no experimental data have ever been reported finding a definite molecular weight dependence of Θ, except in the region of oligomers.

In conclusion, no unquestionable theoretical evaluation of the hydrodynamic factors is as yet achieved. This unsolved problem will keep attracting the interest of polymer theoreticians in the years to come, but it is apparent that experimentalists have to make further efforts toward the determination of more accurate and reliable values of the these factors. Regrettably, not much attention is currently being paid to the value of such efforts.

Second Virial Coefficient

Experimental Information. The second virial coefficient A_2 for flexible linear polymers has as long a history

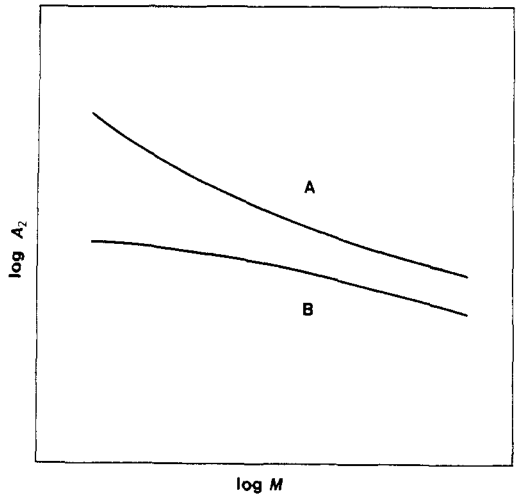

Figure 3. Molecular weight dependence of second virial coefficient A_2 for homologous flexible linear polymers in good solvents (schematic): line A, experimental; line B, theoretical. Note that these lines differ in curvature.

of being researched as the intrinsic viscosity and the diffusion or sedimentation coefficient. Yet there are some serious gaps between typical experimental results and current theoretical predictions about its molecular weight dependence.

Good Solvents. Usually, the M dependence of A_2 for a series of flexible linear polymer homologues in a good solvent can be described well by an empirical relation

$$A_2 \sim M^{-\delta} \tag{8}$$

with a constant δ found in the range 0.2–0.3. Thus, when plotted against log M, log A_2 decreases linearly with a slope of $-\delta$. However, it has been shown that when taken over a sufficiently wide range of M the data plotted on a log–log graph give a *convex-downward* curve like line A in Figure 3.[27] So, more generally, δ in eq 8 must be considered a function of M which decreases weakly with increasing M. Its asymptotic value is not yet firmly established experimentally but appears close to 0.2 regardless of the kind of solvent, as long as it is a good one for the polymer under investigation. Measurement of A_2 at low M is difficult even in very good solvents. Thus, available information on δ at such M is quite limited and divergent.

As far as the author is aware, no log A_2 versus log M data following a *convex-upward* curve have ever been reported for flexible linear polymers in good solvents and even in poor solvents. This seems to be a very significant common observed fact.

Below the Θ Point. Available data on A_2 in poor solvents below Θ is scant and fragmentary. Recently, we[28] tried careful measurement of this quantity on PS in cyclohexane and on poly(isoprene) in dioxane below the Θ temperatures of the respective systems and obtained similar results for both. Figure 4 illustrates the data on the former. What is worth noting and probably not expected is the finding that A_2 is virtually independent of M. Whether specific or not to the systems studied, this fact does not appear consistent with any theories available at present. It is worth adding that very recently and independently Perzynski et al.[29] reported A_2 data which substantiated our finding for PS in cyclohexane below Θ.

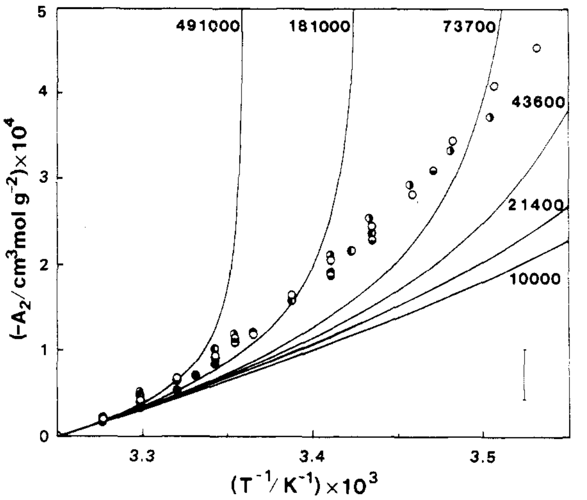

Figure 4. Second virial coefficient A_2 for polystyrene in cyclohexane below the Θ temperature. Different marks indicate data for different molecular weights. Solid curves, calculated by the Tanaka–Solc two-parameter theory for indicated molecular weights.

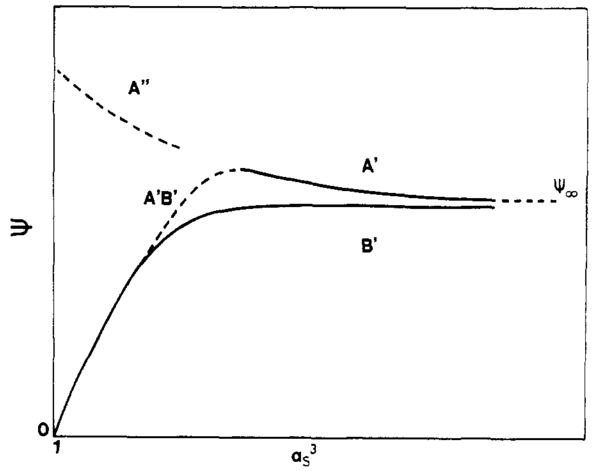

Figure 5. Penetration function Ψ plotted against the cube of radius expansion factor α_S. Lines A' and A", experimental findings in good solvents; line B', prediction by two-parameter theories; dashed part A'B', predicted crossover from poor to good solvent.

Comparison with Theory

The M dependence of A_2 for flexible linear polymers has been formulated by two-parameter theory[20,30–32] and by renormalization group theory.[11,33–37] All the available theories predict in common that the penetration function Ψ should be a universal function of the radius expansion factor α_S, where

$$\Psi = A_2M^2/(4\pi^{3/2}N_A\langle S^2\rangle^{3/2}) \tag{9}$$

$$\alpha_S{}^2 = \langle S^2\rangle/\langle S^2\rangle_\Theta \tag{10}$$

with N_A being the Avogadro constant. The form of $\Psi(\alpha_S)$ depends on theory, but, except for Gobush et al.'s value,[30] it has a common feature as illustrated by the line B' in Figure 5; i.e., Ψ starts from zero at $\alpha_S = 1$, sharply increases, then rather abruptly levels off, and slowly approaches a limiting value Ψ_∞ with increasing α_S.

Ample experimental evidence is available showing $\langle S^2\rangle_\Theta \sim M$ and $\langle S^2\rangle \sim M^{1.2}$ in good solvents (except at low M). With this information it follows from eq 9 that the line B' predicts for good solvent systems such a relation between log A_2 and log M as depicted by the line B in Figure 3. Line B has curvature opposite to that of line A, indicating that the current theories fail to explain the common feature of the M dependence of A_2 for flexible linear polymers in good solvents. It can be shown[27] that line A in Figure 3 leads to Ψ which decreases asymptotically toward Ψ_∞ as illustrated by line A' in Figure 5. In fact, behavior like line A' was observed when A_2 and $\langle S^2\rangle$ of some typical linear polymers in good solvents were measured up to very high molecular weights.[38] But, until a very recent experiment by Huber et al.,[39] which will be mentioned below, it remained unexplored how Ψ in good solvents varies as α_S is decreased toward unity. The reason is simple. To lower α_S in a good solvent we must lower M, but this is accompanied by a sharp decrease in the accuracy of radius of gyration measurement by conventional light scattering. Thus, in good solvent systems, it is not always easy for experimentalists to approach the region of α_S close to unity.

According to the two-parameter theory (and renormalization group theory as well), the behavior of Ψ in this region of α_S could be elucidated by measuring A_2 and $\langle S^2\rangle$ of a given polymer in a poor solvent near the Θ condition as a function of temperature and M. In fact, such measurements were performed by many authors[20] on a variety of polymer + solvent systems, with the finding that the data followed closely line B′ in Figure 5, though limited to the region of α_S where Ψ sharply increased. This was considered a triumph of the formulation of Ψ by the two-parameter concept and led to the following prediction: a smooth curve connecting line A′ and the rising part of line B′ as indicated by the dashed line A′B′ would represent the correct picture of $\Psi(\alpha_S)$ obtained if this function in good solvents could be determined experimentally over a broad range of α_S from unity up to a very large value. The line A′B′ predicts the appearance of a broad maximum, but no convincing experimental evidence is yet presented. In this connection, we remark that the theory of Gobush et al.[30] deduced a $\Psi(\alpha_S)$ curve exhibiting a broad maximum.

Very recently, using small-angle neutron scattering, Huber et al.[39] have succeeded in measuring A_2 and $\langle S^2\rangle$ for PS in toluene down to as low an M value as 1200. Interestingly, when used to calculate Ψ and α_S, their data yield Ψ which increases first gradually and then sharply as α_S approaches unity. This important finding suggests that Ψ for flexible linear polymer + good solvent systems does not decrease to zero but monotonically increases as shown by line A″ in Figure 5 with lowering α_S or M (see Huber and Stockmayer[40]). In other words, the maximum of Ψ predicted for such systems may not be observed. It is highly desirable that experiments similar to that of Huber et al. be undertaken for other systems containing marginal as well as good solvents.

The appreciable difference between the lines A″ and B′ indicates the breakdown of the two-parameter approximation to A_2 for short-chain PS. However, it does not seem necessary to take this finding too seriously, in the sense that short polymers are not the object pertinent to two-parameter theory. For example, such chains must be treated as semiflexible, a condition not considered in two-parameter formulations of polymer properties. In fact, Huber et al.[39,40] showed that if chain stiffness is taken into account, it is possible to explain the M dependence of A_2 as represented by the line A in Figure 3. But their theory contains much to be improved. In any event, there exist many theoretical and experimental problems of considerable interest that have to be solved to understand short-chain polymers in good solvents.

The solid curves in Figure 4 show the prediction of the two-parameter theory due to Tanaka and Solc.[31] The known two-parameter theories of A_2 by other authors[20] predict similar behavior. Interestingly, these curves exhibit appreciable deviations from the data points which show that A_2 below the Θ temperature is virtually independent of M within the ranges of M and temperature studied. Here, we see a definitive breakdown of the two-parameter formulation, but presently we do not know how to explain this finding. Polymer behavior in dilute solutions below Θ is highly challenging.

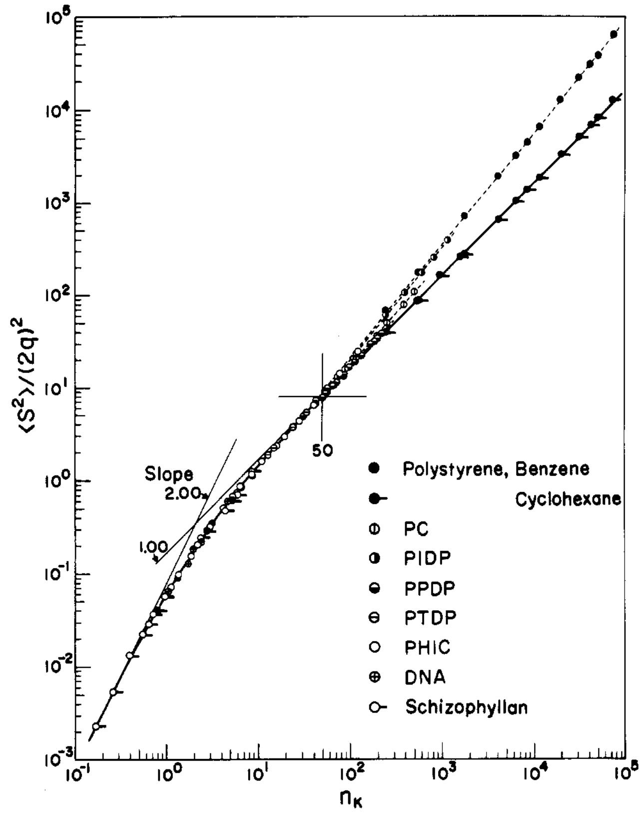

Figure 6. Reduced mean-square radius of gyration as a function of the number n_K of Kuhn's segments for linear polymers with different chain stiffness (or persistence length q): solid line, unperturbed wormlike chain.

Onset of the Excluded-Volume Effect

Efforts to formulate excluded-volume effects on dilute polymer solutions have been mostly concerned with perfectly flexible chains, an idealization of actual polymer molecules. In such a model chain, volume exclusion of chain segments does not vanish down to the limit of zero chain length. This is not the case for actual polymers which have a certain flexibility and hence should be treated as semiflexible. In a semiflexible chain, the probability of segment collision ought to vanish before its contour length L diminishes below some nonzero value $L_c{}^*$, which should be larger for a stiffer chain. It is intriguing to investigate the relation that exists between this critical chain length and the persistence length q, which is the familiar parameter characterizing chain stiffness. However, this problem remains almost untouched, despite its basic importance in any attempt to unify dilute solution properties of flexible and stiff polymers in one theoretical framework.

Probably it is too simple-minded to consider that the excluded-volume effect becomes experimentally detectable as soon as L exceeds $L_c{}^*$. In fact, the critical chain length L_c at which this effect is visible in a measurable quantity should be larger than $L_c{}^*$ and their difference should depend on the polymer, the solvent, and the property concerned.

Figure 6 shows plots of log $\langle S^2\rangle/(2q)^2$ versus log n_K for several polymer + solvent systems covering a broad range of q.[41] Here, n_K is the number of Kuhn segments contained in a chain and given by $n_K = M/(2qM_L)$, with $M_L = M/L$ (the molar mass per unit contour length of the chain). In

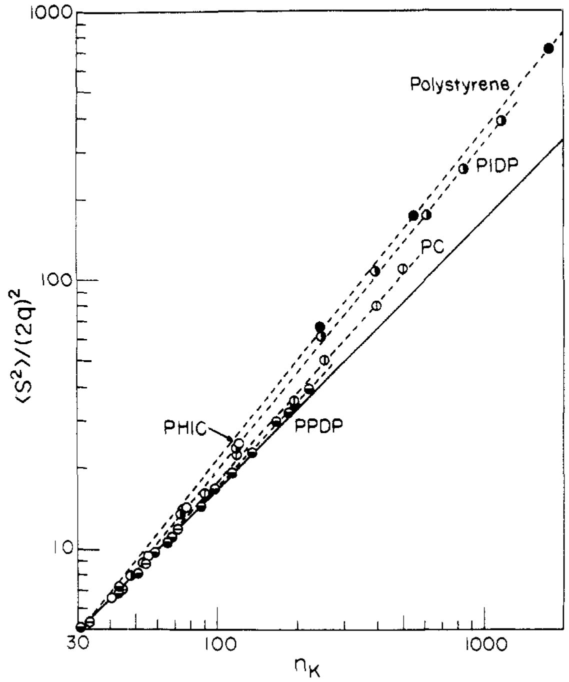

Figure 7. Enlarged version of Figure 6. Note the departure of dashed lines from the solid line for unperturbed wormlike chain.

constructing Figure 6, q and M_L were evaluated by applying the Doty–Benoit expression[42] for $\langle S^2\rangle$ of unperturbed, i.e., volume-exclusion free, Kratky–Porod wormlike chains.[43] The solid line in Figure 6, drawn according to this expression, fits closely the data points for different systems up to n_K of about 50. However, Figure 7, which magnifies the plots for n_K above 30, reveals that, more precisely, the plotted points begin deviating upward from the solid line at n_K ranging from 30 to 80, depending on the system. Therefore, Norisuye and Fujita[41] concluded that the excluded-volume effect on the polymer's statistical radius becomes experimentally visible at $n_K \sim 50$, roughly independent of polymer + solvent system. Because $L = 2qn_K$, this conclusion means

$$L_c \sim 100q \qquad (11)$$

Developing a first-order perturbation theory on wormlike chains, Yamakawa and Stockmayer[44] concluded that the radius expansion factor α_S should start deviating from unity at $n_K \sim 1$, which means

$$L_c^* \sim 2q \qquad (12)$$

Comparison with eq 11 shows that L_c estimated by Norisuye and Fujita is at least 1 order of magnitude larger than L_c^* deduced by Yamakawa and Stockmayer. Though L_c is expected to be larger than L_c^*, this discrepancy seems to be too large to be accepted literally.

To estimate the latter more accurately, Yamakawa and Shimada[45] made computer simulations of polymethylene-like rotational isomeric chains with excluded volume. Figure 8 shows the computed results schematically. The solid and dashed lines refer to a perturbed and an unperturbed chain, respectively. The asymptotic linear part of the former fits experimental data for PS in benzene. The dotted line is the extension of this part and intersects with the dashed line at point E. The solid line starts deviating from the dashed one at point E*.

What was actually estimated by Norisuye and Fujita is the value of n_K at E, designated n_{Kc} in Figure 8. At E, the solid line appears significantly above the dashed line, implying that n_{Kc} cannot be assigned to the onset of the excluded-volume effect on statistical radius. Theoretically, this effect begins appearing at n_{Kc}^*, i.e., n_K at point E*, which for PS in benzene was estimated by Yamakawa and Shimada to be 3–5. This value is somewhat larger than the previous estimate, ~1, by Yamakawa and Stockmayer, but still about 10 times smaller than $n_{Kc} \sim 30$ for the same polymer + solvent system (see Figure 7).

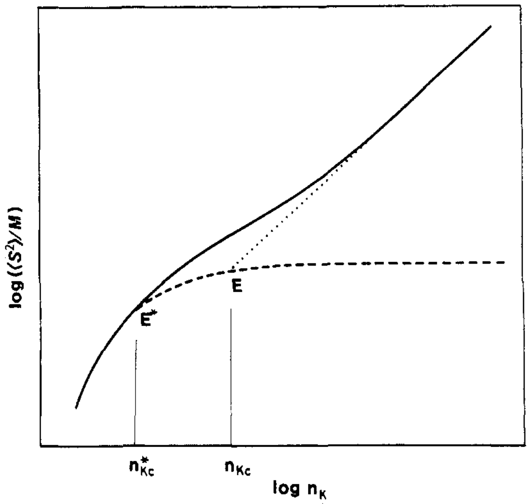

Figure 8. Characteristic ratio $\langle S^2\rangle/M$ as a function of the number n_K of Kuhn's segments: solid line, Yamakawa–Shimada theory; dashed line, theory for an unperturbed wormlike chain; dotted line, extrapolation of the asymptotic linear part of the solid line. E* and E point to the theoretically predicted and the experimentally determinable onset of the excluded-volume effect in a semiflexible polymer, respectively.

Such a marked difference between n_{Kc} and n_{Kc}^* is associated with the behavior of the calculated curve of log $(\langle S^2\rangle/M)$ which rises gradually over a range of short chains before starting to increase sharply with chain length. However, since the computation of Yamakawa and Shimada refers to a polymethylene-like chain, this theoretical finding may not be valid in general. In fact, the experimental data reported by Murakami et al.,[46] who made an extensive study of poly(n-hexyl isocyanate) in n-heptane, showed that soon after it became apparent the excluded volume was followed by a sharp rise in log $(\langle S^2\rangle/M)$. Thus, in this system, $n_{Kc}^* \sim n_{Kc} \sim 50$. As Yamakawa and Shimada put it, their theory will have to be reconsidered for polymers with high stiffness.

Transport properties may also show the onset of volume effects at a certain critical chain length. It is interesting to investigate how such a chain length can be estimated experimentally or theoretically, but this problem has received little attention. The author looks forward to seeing whether renormalization group methods, which have proved so powerful in dealing with flexible polymers, can be applied successfully to formulate semiflexible polymers with excluded volume.

There are a lot of problems other than those discussed above which still remain unsolved in the field of study of dilute polymer solutions. This is especially true concerning dynamic properties. However, it is beyond the author's ability to enter the relevant description and comments on such problems. This paper contains nothing new, but the author hopes that it is of some use to dispell the misleading notion that polymer behavior in dilute solutions is a closed subject of research or too classical to be worthy of further exploration.

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Zigzag Polyamides Comprising Rodlike Segments Connected by Freely Rotating or Stiff Joints

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ABSTRACT: Six fully aromatic zigzag polyamides were synthesized and characterized. The angles between their rigid rodlike segments are all fixed at 119° and 120°. Three of the polyamides have joints between the rodlike segments with free torsional rotation, and three have rather stiff joints. In solution and the amorphous bulk they all adopt a random coil configuration. The behavior of all polymers in dilute solution is dictated by their equilibrium rigidity, with no significant difference between those having freely rotating joints and those having stiff joints. With increased concentration effects of kinetic rigidity become more prominent because the slowness or rapidity of torsional motion interferes in varying degrees with the free movement of interpenetrated coils and their segments. Two groups of radii of gyration were measured in dilute solution for all polymers. The large R_G's are a measure of the coil dimensions, while the smaller R_G's and the hydrodynamic radius reflect the fact that in coils with long rodlike segments only a small fraction of the solvent in the volume pervaded by the coil is actually interacted with the coil and hydrodynamically affected by its presence.

Introduction

In this paper solution properties of six fully aromatic polyamides will be described. Each of these polymers comprises rodlike segments of identical length connected to one another by joints having either high degree or low degree of torsional mobility. When the chains of the six polyamides are fully extended in a plane, they appear as long zigzags and hence their name. The six polyamides are divided into two groups. One includes three polyamides whose joints are essentially freely rotating. These polymers were briefly described recently.[1] The second group contains three additional zigzag polyamides whose joints are substantially stiffer, severely reducing the torsional rotation freedom of their rodlike segments.

The behavior of the zigzag polyamides in dilute and concentrated solutions appears to be controlled by two important structural features. The first is the length l_o of the rodlike segments characteristic of each polymer. In our case this length corresponds to the length of the average virtual bond of the polymer. The second feature is the degree of freedom for torsional rotation around the joints connecting these segments. These two structural