Concluding Remarks

The comparison of numerical results with those from eq 1 showed that eq 3 is a good limit, for large N, of eq 1. Quantities previously believed to be unique functions of one parameter h can also depend on N unless h is extremely large (impractically large); some of the quantities such as the Flory constant are unique functions of h_T instead of h. The limit $h \rightarrow \infty$ is a sufficient but not a necessary condition for the appearance of the non-free-draining limit: $h^* \rightarrow 0.25$ causes exactly the same effect. Since experimentally the non-free-draining limit seems to apply to infinite-dilution frictional properties of certain real polymer solutions,[8] the appropriate value of h^* in the Zimm theory must correspondingly be near 0.25. However, it should be noted that the hydrodynamic interaction parameter h^* is defined on a simple model of beads and springs which does not represent the detail of the molecular structure. Thus, $h^* \rightarrow 0.25$ could be the result of forcing the Zimm theory to apply to real molecular systems so that its meaning may be obscure.

Since the mathematical structure is almost the same, analogous considerations have to be applied to the integral equations of Kirkwood and Riseman,[9] and almost the same result is expected. Moreover, one may not have to worry about the mathematical difficulty[10] in this type of problem because the h^* value of interest seems to be restricted to a narrow range where this difficulty does not exist.

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(8) See for example H. Yamakawa, "Modern Theory of Polymer Solutions," Harper and Row, New York, N. Y., 1971, Chapter 6.

(9) J. G. Kirkwood and J. Riseman, *J. Chem. Phys.*, **16**, 565 (1948).

(10) R. Zwanzig, J. Kiefer, and G. H. Weiss, *Proc. Nat. Acad. Sci. U. S.*, **60**, 381 (1968).

Infinite-Dilution Viscoelastic Properties of Poly(α-methylstyrene). Applications of Zimm Theory with Exact Eigenvalues

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ABSTRACT: The storage and loss shear moduli have been measured for solutions of poly(α-methylstyrene) with narrow-distribution molecular weight of 1.43×10^6 in α-chloronaphthalene and decalin. The measurements were performed with the Birnboim–Schrag multiple-lumped resonator at nine frequencies from 100 to 6000 Hz; the data at each frequency were extrapolated to zero concentration to obtain the intrinsic storage and loss moduli. The extrapolated results for poly(α-methylstyrene) as well as previously published results for polystyrene and polybutadiene solutions were compared with the exact numerical result of the bead–spring model theory of Zimm as evaluated by Lodge and Wu for finite numbers of beads and various values of the hydrodynamic interaction parameter h^*. The theory reproduced the experimental data with reasonable values of h^* except for a small deviation at high frequency in the case of poly(α-methylstyrene), which was apparently due to the effect describable by the internal viscosity of the Peterlin theory. Values of h^* obtained from the comparison increased from 0.1 to 0.25 as the solvent power decreased and were not very sensitive to the choice of the polymer and solvent nor to the molecular weight of the polymer. The product $\alpha_\eta h^*$, where α_η is the expansion factor of the excluded volume effect as evaluated from the intrinsic viscosity, had an approximately constant value of 0.21 for most of the systems examined. This result suggested that the assumption of uniform expansion of effective segment length due to the excluded volume effect is sufficient to explain the effect of solvent power on the observed spectrum of viscoelastic relaxation times.

Tanaka and collaborators[1] were the first to succeed in obtaining viscoelastic properties of polymer solutions at infinite dilution. More recently, effort has been devoted to obtaining more extensive data of the same kind over wider ranges of frequency and solvent viscosity. Results for polystyrene solutions in various solvents[2] and polybutadiene in two solvents[3] have been obtained so far with the use of the Birnboim–Schrag multiple-lumped resonator and a computerized data acquisition system.[4] The first purpose of the present publication is to report similar results for poly(α-methylstyrene), which is supposedly stiffer than the polymers studied before and whose molecular weight distribution can be made very narrow.

Recently, extensive numerical calculations for the bead–spring theory of Zimm[5] have been performed by Lodge and Wu,[6] utilizing exact eigenvalues to determine the relaxation spectrum. The eigenvalues, and hence the relaxation spec-

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(1) (a) H. Tanaka, A. Sakanishi, and J. Furuichi, *J. Polym. Sci., Part C*, **No. 15**, 317 (1966); (b) A. Sakanishi and H. Tanaka, *Proc. Int. Congr. Rheol. 5th*, **4**, 251, 259 (1970).

(2) R. M. Johnson, J. L. Schrag, and J. D. Ferry, *Polym. J.*, **1**, 742 (1970).

(3) K. Osaki, Y. Mitsuda, R. M. Johnson, J. L. Schrag, and J. D. Ferry, *Macromolecules*, **5**, 17 (1972).

(4) (a) J. L. Schrag and R. M. Johnson, *Rev. Sci. Instrum.*, **42**, 224 (1971); (b) D. J. Massa and J. L. Schrag, *J. Polym. Sci., Part A-2*, **10**, 71 (1972).

(5) B. H. Zimm, *J. Chem. Phys.*, **24**, 269 (1956).

(6) A. S. Lodge and Y-J. Wu, *Rheol. Acta*, in press.

trum, depend on the number of submolecules N per molecule ($N \leq 222$ for the calculations available at the time the work being reported was done; recent calculations[6] extend to $N = 300$) and the hydrodynamic interaction parameter h^* (related to the friction coefficient for a submolecule), which can be expressed in terms of the parameter h of Zimm as $h^* = h/N^{1/2}$. If N is sufficiently large, the viscoelastic properties at low and intermediate frequencies are determined primarily by h^*, which can be evaluated from a comparison of infinite-dilution viscoelastic data with the theory; the meaning of h^* appears to be clearer than that of the adjustable parameter h, whose theoretical significance has been elusive.[7] The calculation of Tschoegl[8] for intermediate degrees of hydrodynamic interaction, which uses the integrodifferential equation of Zimm[5] to solve the eigenvalue problem, assumes N very large and omits a term in h^*, leading to incorrect results when h is finite.[9] A second purpose of this paper is to show the results of a comparison of experimentally determined viscoelastic properties of polymer solutions at infinite dilution with the Zimm theory as evaluated by Lodge and Wu and to examine the significance of the parameter h^* obtained therefrom.

Materials and Methods

The poly(α-methylstyrene) (PMS) sample (BB5) was one of those prepared and characterized by Kurata and collaborators.[10] The molecular weight M was 1.43×10^6 and the ratio M_w/M_n as determined from the sedimentation method was less than 1.01, showing a very narrow distribution of the molecular weight. The solvents were α-chloronaphthalene from Matheson Coleman and Bell and decalin (approximately half cis and half trans) from J. T. Baker Chemical Co. These are good and poor solvents, respectively; their viscosities at 25.0° were 3.15 and 2.45 cP, respectively. Although cyclohexane was known to be a Θ solvent for this polymer, it could not be used because its low viscosity makes the longest relaxation time much shorter than is observable with the multiple-lumped resonator.

The equipment used for the viscoelastic measurements was the Birnboim–Schrag multiple-lumped resonator together with a computerized data acquisition and processing system.[4] The use of two resonators gave nine working resonance frequencies ranging from 100 to 6060 cps. The ranges of concentration were 0.15–0.58 g/dl for solutions in decalin and 0.072–0.30 g/dl in α-chloronaphthalene. All the measurements were performed at 25.00 ± 0.01°.

Results

The quantities $(G'/c)^{1/2}$ and $(G'' - \omega\eta_s)/c$ were plotted against the concentration c (g/ml), where G' and G'' are the storage and loss shear moduli, ω is the angular frequency, and η_s is the solvent viscosity. Plots of $(G'/c)^{1/2}$ rather than G'/c are more nearly linear and make extrapolation to $c = 0$ easier.[2] The limits as $c \rightarrow 0$ of G'/c and $(G'' - \omega\eta_s)/c$ are, respectively, the intrinsic storage and loss moduli, $[G']$ and $[G'']$. These values for poly(α-methylstyrene) in decalin and in α-chloronaphthalene are shown in Figure 1 as functions of ω with double logarithmic scales. The curves represent the prediction of the Zimm theory[5] as evaluated by Lodge and Wu.[6] A value of 200 was used for N, since the shape of the curves is insensitive to N at lower frequencies if N is large enough, and 222 is the largest for which calculations were available. The values of h^* for which numerical calculations have been performed are 0.05, 0.1, 0.15, 0.2, and 0.25. Thus the value of h^* obtained by curve fitting in Figure 1 includes an uncertainty of ±0.025; however, calculations for intermediate values of h^* would not necessarily result in less uncertainty because the data have some scatter. The vertical and the horizontal positions of the curves are determined by M/RT and $M[\eta]\eta_s/RT$, respectively, where $[\eta]$ is the intrinsic viscosity, R is the gas constant, and T is the absolute temperature. Thus h^* is the only adjustable parameter important at low and intermediate frequencies. The best fit was obtained by the choice of $h^* = 0.1$ and 0.2 for α-chloronaphthalene and decalin, respectively, for which the calculated curves reproduce the data fairly well. However, there is a small but systematic discrepancy in $[G']$ for both solvents: the curves are too high at high frequencies and too low at low frequencies. Choosing smaller values of h^* may remove this deviation but produces an improper fit for $[G'']$. This deviation is probably due to the high-frequency effects which cannot be described by the Zimm theory as discussed below,[11] especially in the α-chloronaphthalene. It should be pointed out that almost the same curves as shown in Figure 1 can be obtained if Tschoegl's evaluation[8] of the Zimm theory is applied in this low and intermediate frequency range ($\omega < 10/\tau_{01}$, where τ_{01} is the longest relaxation time at infinite dilution) with the use of one adjustable parameter h, despite the missing term in this calculation which is discussed elsewhere.[9]

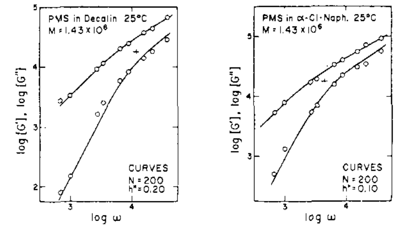

Figure 1. Intrinsic storage modulus $[G']$ (lower curves) and loss modulus $[G'']$ (upper curves) plotted against angular frequency ω for solutions of poly(α-methylstyrene) ($M = 1.43 \times 10^6$) in decalin (left panel) and α-chloronaphthalene (right panel) at 25.0°. Curves from Zimm theory as evaluated by Lodge and Wu with $N = 200$; $h^* = 0.2$ (left panel) and $h^* = 0.1$ (right panel). Crosses correspond to coordinates τ_{01}^{-1}, RT/M.

Discussion

Examination of Frequency Dependence. The slight negative deviation of experimental values of G' from theory at higher frequencies in Figure 1 resembles the behavior observed previously for many dilute polymer solutions[11] and for one polystyrene solution at infinite dilution,[11e] though these were not compared with exact-eigenvalue calculations. Such a comparison is now made in Figure 2 for polystyrene in two solvents at infinite dilution with data from ref 2; here, the curves are calculated with the Lodge–Wu evaluation of the Zimm theory taking $N = 200$ and $h^* = 0.2$ and 0.15 for decalin and α-chloronaphthalene, respectively. In general, the agreement with theory is excellent. In decalin, the dimensionless frequency $\omega\tau_{01}$ does not go high enough to observe any high-frequency effect (note the position of the cross,

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(7) See, for example, J. D. Ferry, "Viscoelastic Properties of Polymers," 2nd ed, Wiley, New York, N. Y., 1970, Chapter 9.

(8) N. W. Tschoegl, *J. Chem. Phys.*, **39**, 149 (1963); **40**, 473 (1964).

(9) K. Osaki, *Macromolecules*, **5**, 141 1972).

(10) M. Abe, K. Sakato, T. Kageyama, M. Fukatsu, and M. Kurata, *Bull. Chem. Soc. Jap.*, **41**, 2330 (1968).

(11) (a) J. Lamb and A. J. Matheson, *Proc. Roy. Soc., Ser. A*, **281**, 207 (1964); (b) J. D. Ferry, L. A. Holmes, J. Lamb, and A. J. Matheson, *J. Phys. Chem.*, **70**, 1685 (1966); (c) W. Philippoff, *Trans. Soc. Rheol.*, **8**, 117 (1964); (d) R. S. Moore, H. J. McSkimin, C. Gienewski, and P. Andreatch, *J. Chem. Phys.*, **47**, 3 (1967); **50**, 5088 (1969); (e) D. J. Massa, J. L. Schrag, and J. D. Ferry, *Macromolecules*, **4**, 210 (1971); (f) K. Osaki and J. L. Schrag, *Polym. J.*, **2**, 541 (1971).

Table I

Hydrodynamic and Coil-Expansion Parameters

Polymer	$M \times 10^{-5}$	Solvent	Temp, °C	η_s, cP	h^*	$[\eta]$, ml/g	$[\eta]_\Theta$, ml/g	$\alpha_\eta h^*$
Polystyrene[a]	8.6	α-Chloronaphthalene	25.0	3.15	0.15	197	76	0.21
		Decalin	16.0	2.95	0.20	76		0.20
		Dioctyl phthalate	22.0	67.8	0.25[f]	76		0.25[f]
		Aroclor 1232	25.0	14.2	0.15	183		0.20
Polystyrene[a]	4.11	Aroclor 1232	25.0	14.2	0.15	111	54.5[c]	0.19
Poly(α-methylstyrene)	14.3	α-Chloronaphthalene	25.0	3.15	0.10	252	91[d]	0.14[g]
		Decalin	25.0	2.45	0.20	135		0.23
1,4-Polybutadiene[b] (55% trans)	9.09	α-Chloronaphthalene	25.0	3.15	0.15	510	(138)[e]	(0.23)
		Decalin	25.0	2.45	0.15	510		(0.23)

[a] Reference 2. [b] Reference 3. [c] Cyclohexane, 34.5° (furnished by manufacturer). [d] Cyclohexane, 38.6° (ref 10). [e] From $[\eta]_\Theta = 145 \times 10^{-3} M^{1/2}$ (dioxane, 34°) for 84% *cis*-polybutadiene [I. Y. Poddubnyi and E. G. Ehrenburg, *J. Polym. Sci.*, **57**, 545 (1962)]. [f] Less reliable because solvent viscosity is at upper limit for operation of multiple-lumped resonator. [g] Low value probably reflects high-frequency effects discussed in text.

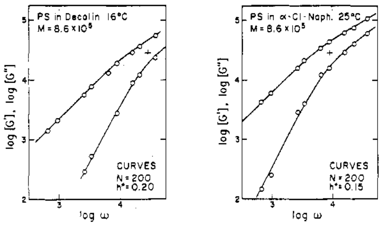

Figure 2. Intrinsic storage modulus $[G']$ (lower curves) and loss modulus $[G'']$ (upper curves) plotted against angular frequency ω for solutions of polystyrene ($M = 8.6 \times 10^5$) in decalin at 16.0° (left panel) and α-chloronaphthalene at 25° (right panel). Curves from Zimm theory as evaluated by Lodge and Wu with $N = 200$; $h^* = 0.2$ (left panel) and $h^* = 0.15$ (right panel). Data from ref 2.

where $\omega\tau_{01} = 1$); in α-chloronaphthalene, there is a small perceptible deviation, though scarcely noticeable in the figure. A similar small deviation has been observed for polybutadiene in α-chloronaphthalene.[3] In all cases, the fit for $[G']$ can be improved by choosing a lower value of h^*, but this results in a poorer fit for $[G'']$.

Better agreement with the data in this frequency range can be achieved by modifying the Zimm theory. For example, the Peterlin theory,[12] with an additional parameter ("internal viscosity") to account for additional energy-loss mechanisms, can reproduce experimental data over a very wide range of frequency.[11e] This successfully describes the data of Figure 1, although it is difficult to obtain definite values of the internal viscosity parameter because the deviation is so small (internal viscosity affects behavior at higher frequencies more strikingly).

Another approach is to assume that the quantities $[G']$ and $([G''] - \omega[\eta']_\infty\eta_s)$ rather than $[G']$ and $[G'']$ represent the contribution from the relaxation mechanism described by Zimm theory,[11a] where $[\eta']_\infty$ is the high-frequency limiting value of the intrinsic dynamic viscosity (equal to zero in the original Zimm theory). Again it is not possible to get $[\eta']_\infty$ from the present data, but if one assumes the values 14 and 22 ml/g for the values of $[\eta']_\infty$ for polystyrene and poly(α-methylstyrene),[11d] respectively, this method also works well. (These minor adjustments are not illustrated here graphically; data may be obtained from the authors on request.) It may be noted that the value of h^* obtained by assuming $[G']$ and $([G''] - \omega[\eta']_\infty\eta_s)$ as the relaxation contribution from the Zimm theory is approximately 0.05 irrespective of the polymer–solvent system. This last result may be convenient for predicting the dynamic mechanical properties of polymers at infinite dilution. However the subtraction of $\omega[\eta']_\infty\eta_s$ from $[G'']$, corresponding to the subtraction of $[\eta']_\infty$ from $[\eta]$ to obtain the intrinsic viscosity due to the relaxation mechanism, is inconsistent with the well established relation[13] between $[\eta]$ and M. The Peterlin theory does not suffer from this feature, and is therefore preferred although the molecular significance of its internal viscosity parameter is uncertain.

Survey of h^* for Various Polymer–Solvent Systems. All values of h^* obtained by fitting experimental data to the Lodge–Wu calculations, with $N = 200$, are given in Table I; the uncertainty is ±0.025. (The results for Θ solutions, such as polystyrene in decalin and in dioctyl phthalate, may have more uncertainty; the data for the former system are restricted to the low frequency range and those for the latter have somewhat larger scattering owing probably to the high solvent viscosity, which is not favorable for good measurement with the multiple-lumped resonator.[4a])

The variation of h^* is quite small; all values lie in the range 0.1–0.25. However, it seems to change systematically with solvent power, as judged by comparison of the measured intrinsic viscosity $[\eta]$ with that obtained in a Θ solvent. The h^* value for a Θ solvent seems to lie near 0.2. The decrease of the hydrodynamic interaction parameter with increasing solvent power is in qualitative agreement with the results obtained at finite concentrations.[7] There does not seem to be much molecular weight dependence of h^*, although the data are not sufficient for a definite conclusion. It may be safely said that the molecular weight is not so important a factor as the solvent power in determining the hydrodynamic interaction.

Some Speculations on h^*. In the Zimm theory, the hydrodynamic interaction parameter h^* is defined as

$$h^* = \zeta/(12\pi^3)^{1/2}\eta_s b \qquad (1)$$

where ζ is the friction constant of a bead and b is the square root of the mean-square distance between neighboring beads.

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[12] A. Peterlin, *J. Polym. Sci., Part A-2*, 5, 179 (1967).

[13] See, for example, H. Yamakawa, "Modern Theory of Polymer Solutions," Harper and Row, New York, N. Y., 1971.

If one assumes a Stokes' effective sphere of radius a to describe ζ, *i.e.*, $\zeta = 6\pi a\eta_s$, then

$$h^* = 0.976a/b \qquad (2)$$

If one wants to visualize the bead–spring model with beads of radius a and springs of length b, the ratio a/b has to be smaller than 0.5 to avoid interpenetration of neighboring beads. The values of h^* in Table I are all consistent with this requirement, so the Zimm theory as evaluated by Lodge and Wu leads to values of h^* that intuitively seem reasonable in terms of this crude model.

Since h^* varies so systematically with $[\eta]$, it seems possible to describe h^* as a function of $[\eta]$. In the last column of Table I is given the product $\alpha_\eta h^*$, where α_η is the linear expansion factor of the excluded volume effect as evaluated from the intrinsic viscosity; $\alpha_\eta^3 = [\eta]/[\eta]_\Theta$. The product $\alpha_\eta h^*$ is essentially constant for all combinations of polymer and solvent, except polystyrene in dioctyl phthalate and poly(α-methylstyrene) in α-chloronaphthalene, for which there are reasons for divergence as described above

$$\alpha_\eta h^* = 0.21 \pm 0.02 \qquad (3)$$

This result supports the statement that the solvent power is the most important factor determining differences in the hydrodynamic interaction parameter. It is convenient because the dynamic-mechanical properties of usual synthetic polymers at infinite dilution may be predicted if the molecular weight and the intrinsic viscosities for a given solvent and for a Θ solvent are known. Equation 3 together with 1 imply that the hydrodynamic interaction parameter for a good solvent system may be obtained by assuming a uniform expansion of segment lengths by the same factor as is observed for the expansion of overall chain dimensions due to the excluded volume effect. This assumption is sufficient to explain the variation of h^* necessary to describe the dynamic-mechanical properties or the spectrum of relaxation times for the solutions described herein. The assumption may not be consistent with recent theoretical considerations[13] of the dependence of the intrinsic viscosity on solvent, but calculation over a wider range of the number of submolecules N is necessary before this dependence can be discussed any further.

Acknowledgment. This work was supported in part by the National Institutes of Health, the Army Research Office (Durham), and the National Science Foundation. The authors are indebted to Professor A. S. Lodge for supplying us with his numerical results prior to their publication.

Molecular Weight Dependence of the Crystallization Kinetics of Linear Polyethylene. I. Experimental Results[1]

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ABSTRACT: The results of a dilatometric study of the crystallization kinetics of molecular weight fractions of linear polyethylene are reported. These data encompass the molecular weight range 4×10^3–8×10^6. Although the usual deviations from the Avrami or Göler–Sachs free-growth formulations are observed, these deviations are systematic with molecular weight and become more pronounced as the molecular weight is increased. There is a one to one correlation between the level of crystallinity at which these deviations occur and the final level of crystallinity that can be attained for each molecular weight. These kinetic results in turn explain the very wide range in values that is observed for all properties. To explain the isotherm shape, we note that over the region of experimental adherance the Avrami exponent is an integral number and varies from four to two as the molecular weight increases. The exponent is independent of temperature except for the very highest crystallization temperatures. At the very highest crystallization temperatures, closer adherance to theory is found, with the implication that if the experiments could be conducted at still higher temperatures the Avrami-type theory would be obeyed. At a fixed temperature the crystallization rate goes through a maximum as a function of molecular weight and the location of the maximum is dependent on the undercooling. Although the very marked negative temperature coefficient gives strong support to nucleation control, it is demonstrated that the rudimentary nucleation theories that have been proposed are not obeyed.

Virtually all thermodynamic, spectral, mechanical and physical properties of linear polyethylene are dependent on molecular weight and on the crystallization conditions.[2-7] A wide range in the values of any specific property is observed for the same chemically constituted polymer. For example, when molecular weight fractions are utilized, the density of melt-crystallized linear polyethylene varies from about 0.99 to 0.92 depending on the molecular weight and the crystallization temperature.[2,8] Based on equilibrium considerations alone, there is no obvious basis for such a range in properties to be observed. Consequently, one is led to seek a kinetic origin for this phenomenon. Since the crystallization of long-chain molecules is by necessity invariably conducted at comparatively large undercoolings, relative to monomeric systems, nonequilibrium properties can easily be expected.

To better understand the factors which govern the properties, therefore, a quantitative molecular understanding of the

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(1) This work was supported by a grant from the Army Research Office (Durham).

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(3) L. Mandelkern, A. L. Allou, Jr., and M. Gopalan, *ibid.*, **72**, 309 (1968).

(4) T. Okada and L. Mandelkern, *J. Polym. Sci., Part A-2*, **5**, 239 (1967).

(5) L. Mandelkern, J. M. Price, M. Gopalan, and J. G. Fatou, *ibid., Part A-2*, **4**, 385 (1966).

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(8) E. Ergoz, Ph.D. Dissertation, Florida State University, Dec 1970.