Dynamic Viscoelastic Properties of Polystyrene in High-Viscosity Solvents.
Extrapolation to Infinite Dilution and High-Frequency Behavior

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ABSTRACT: The storage (G') and loss (G'') shear moduli of solutions of four polystyrenes with narrow-distribution weight-average molecular weights (M) from 19,800 to 860,000 have been measured over a frequency range frpm 0.02 to 634 Hz. The solvents were two Aroclors (chlorinated diphenyls) with a viscosity range from 2 to 7000 P over a temperature range from −5 to 25°. The Birnboim transducer, with several modifications including a computerized data acquisition and processing system and provision for Segel–Pochettino geometry, made possible the extrapolation of data to infinite dilution and also measurements at sufficiently high solvent viscosities and frequencies so that the dynamic viscosity approached a limiting value. For $M = 860{,}000$, the zero-concentration limits of G'/c and $(G'' - \omega\eta_s)/c$ in Aroclor 1248 (where ω is radian frequency, η_s solvent viscosity, and c concentration in grams per cubic centimeter) were determined as a function of frequency. The results fit the Peterlin modification of the bead-spring theory which takes into account internal viscosity and a finite number of submolecules; P/N (monomer units per submolecule) was 11.6, ϕ/f (ratio of internal to external friction) was 1.5, and h^* (reduced hydrodynamic interaction parameter) was 0.30. One solution of each of the four molecular weights, with concentration chosen to give a relative viscosity between 5 and 8, was studied over a wide enough range of frequencies and temperatures to encompass the transition of dynamic viscosity η' from its steady-flow value η to its high-frequency limiting value η_∞'. The limiting inherent viscosity $(\eta_\infty' - \eta_s)/\eta_s c$ was about 20 cm^3/g with apparently little dependence on concentration and molecular weight in this range. The shapes of the frequency dependence could be described very well by the Peterlin theory quoted with about the same value of P/N, ϕ/f from 1.5 to 2.5, and h^* decreasing from 0.3 to 0.1 with increasing molecular weight; these parameters agreed very well with those obtained by Thurston and Schrag from dynamic birefringence data. At these finite concentrations, the fit with the Peterlin theory requires that the molecular weight be treated as an adjustable parameter, but it turns out not far from the correct value except for the sample with lowest molecular weight. The success of temperature superposition shows that ϕ/f is independent of temperature and therefore of solvent viscosity over wide ranges; it is also nearly the same in two different solvents with a 30-fold viscosity difference. Thus the "internal viscosity" is proportional to solvent viscosity. The limiting high-frequency value of the storage modulus is proportional to volume fraction of polymer without regard to molecular weight, and their ratio is about 4.6 × 10^6 dyn/cm^2. The steady-state compliances calculated from the limiting behavior at low frequencies, where internal viscosity plays no role, are intermediate between the predictions of the Rouse and Zimm theories except for $M = 19{,}800$, whose steady-state compliance is abnormally low.

Extensive studies of dynamic viscoelastic properties of polystyrenes and other polymers, dissolved in high-viscosity solvents at quite low concentrations, have been reported previously from this laboratory.[1–5] Although in conjunction with molecular theory they have provided considerable insight into the origin of viscoelasticity, they have had two significant limitations. First, it has not been possible to make precise measurements at concentrations low enough to extrapolate to infinite dilution, for quantitative comparisons with molecular theory in which intermolecular interactions are not taken into account. Second, within the frequency range of the original Birnboim transducer[6] (0.01–400 Hz) and the range of then usable solvent viscosities, behavior reflecting motions of short macromolecular segments could not be explored; the frequency dependence of the storage and loss shear moduli corresponded to the predictions of the bead-spring theories of viscoelasticity in which internal molecular structure is ignored and dissipation of energy occurs only through frictional resistance of the solvent regarded as a continuum. Deviations from such behavior must occur at sufficiently high frequencies and/or high solvent viscosities;[7–10] they have been rather loosely referred to as effects of incomplete flexibility, internal stiffness, or internal viscosity.

Extrapolation of viscoelastic data to infinite dilution has been achieved for low-viscosity solvents by Tanaka and Sakanishi[11] with torsional piezoelectric crystal resonators, and very recently in this laboratory[12] with a multiple-lumped resonator[13] driven electromagnetically. However, these cannot be used for high-viscosity solvents; the upper limit for solution viscosity for the latter instrument is 2 P. Effects of incomplete flexibility can be seen in measurements at extremely high frequencies,[7–10] but data are sparse because of the limited number of frequencies available when piezoelectric resonators are used.

Recent modifications[14,15] of the original Birnboim transducer apparatus,[6] in particular the use of a computerized data acquisition and processing system with a cross-correlation calculation of phase differences and amplitudes in sinusoidal

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(2) N. W. Tschoegl, J. E. Frederick, and J. D. Ferry, *ibid.*, **68**, 1974 (1964).

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(13) J. L. Schrag and R. M. Johnson, *Rev. Sci. Instrum*, in press.

(14) D. J. Massa, Ph.D. Thesis, University of Wisconsin, 1970.

(15) D. J. Massa and J. L. Schrag, to be submitted for publication.

deformations with greatly improved precision, have made it possible to extrapolate data in high-viscosity solvents to infinite dilution and also to observe high-frequency behavior (*i.e.*, manifestation of incomplete flexibility) at audiofrequencies by use of solvent viscosities as high as 7000 P. Examples of such measurements are presented here.

Experimental Section

Materials. The polystyrenes with narrow molecular weight distribution, 2a, S-102, S-108, and 6a, have been described previously;[2-4] their weight-average molecular weights were 19,800, 82,000, 267,000, and 860,000 respectively. They were dried at 60° *in vacuo* overnight before use. The solvents, Aroclors 1248 and 1254, have also been described elsewhere;[2-4] data on their densities and viscosities at various temperatures are available.[14] Solutions were made up by weight, with moderate heating (65°) and very gentle stirring. Solution densities and concentrations in grams per cubic centimeter were calculated assuming additivity of volumes.

Method. The modified Birnboim transducer, equipped with data acquisition and processing system, was used for measurements over a frequency range from 0.02 to 633.6 Hz. The most important modifications, aside from the computerization with its greatly improved precision, were the adoption of open-ended (Segel–Pochettino) geometry instead of annular pumping geometry for solutions of very high viscosity and the reduction of the volume below the oscillating rod when annular pumping geometry was used.[14,15] Open-ended geometry was used for all solutions with viscosities greater than 500 P; otherwise, annular pumping geometry with either medium or wide annular gaps depending on the viscosity. Measurements were made at selected frequencies equally spaced on a logarithmic scale, five to a decade, and calculated as the storage and loss shear moduli, G' and G'', in dynes per square centimeter.

Results

Data for Extrapolation to Infinite Dilution. The sample with molecular weight 860,000 was measured in Aroclor 1248 at 15.01° at concentrations (c) of 0.002, 0.004, 0.006, and 0.008 g/cm^3, and at each of 19 frequencies the ratios G'/c and $(G'' - \omega\eta_s)/c$ were plotted against c to extrapolate to zero c, giving the intercepts $[G']$ and $[G'']$, respectively—the intrinsic storage and loss shear moduli. Here η_s is the solvent viscosity, measured in the instrument under identical conditions (or with a small temperature correction if temperatures did not match exactly); high accuracy is essential since the difference $G'' - \omega\eta_s$ becomes small at low c. Examples of extrapolation at selected frequencies are shown in Figure 1. Both components extrapolate linearly over this range, though at somewhat higher concentrations G' is expected[12] to show more curvature than $G'' - \omega\eta_s$. Since the slopes cannot be determined as accurately as with the multiple-lumped resonator,[13] no attempt has been made to analyze their interrelations.[12]

The extrapolated values $[G']$ and $[G'']$ are plotted logarithmically against frequency in Figure 2. The frequency dependence is intermediate between the predictions of the Zimm[16] and Rouse[17] theories; its description by a modified molecular theory is discussed below.

Data Revealing High-Frequency Effects. To obtain data corresponding to motions of short macromolecular segments, one solution each of the three lower molecular weights was made in Aroclor 1254 and one of the highest molecular weight in Aroclor 1248, at concentrations ranging from 0.015 to 0.076 g/cm^3, chosen so that each solution had a relative (zero frequency) viscosity in the range from 5 to 8; the product $c[\eta]$, where $[\eta]$ is intrinsic viscosity, ranged from 1.2 to 2.8, giving a gauge of the degree of molecular overlapping.

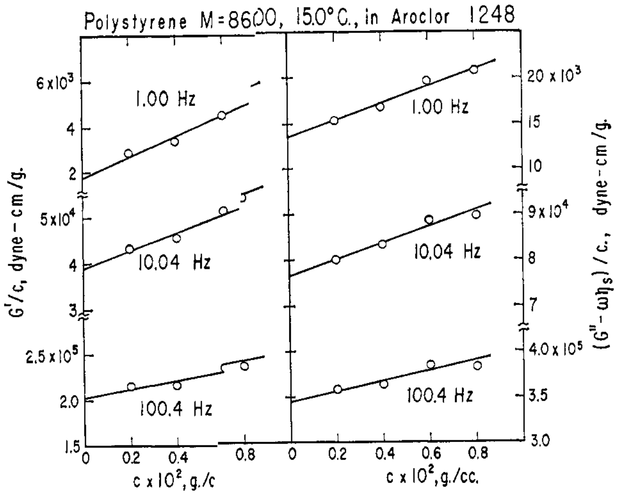

Figure 1. Extrapolation of G'/c and $(G'' - \omega\eta_s)/c$ to infinite dilution, for M = 860,000 in Aroclor 1248 at 15.0°, at three selected frequencies as indicated. Note that each line has a different ordinate scale.

The concentrations are given in Table I together with other derived data which will be discussed below. Each solution was measured at ° and at two other lower temperatures at least (one at th), and the data were reduced to 25.0° by the method of reduced variables. For the two lower molecular weights, the shift factor a_T was calculated from the temperature dependence of $\eta - \eta_s$;[18] for the others, it was determined from empirical shifts on the logarithmic frequency scale. At lowest temperatures, because of the enormous temperature dependence of Aroclor viscosities, the solution viscosities were very high (up to [illegible]0,000 P) and of course open-ended geometry was used.

Logarithmic plots of G' and $G'' - \omega\eta_s$ against frequency are shown in Figures 3–6. The high precision of the data is

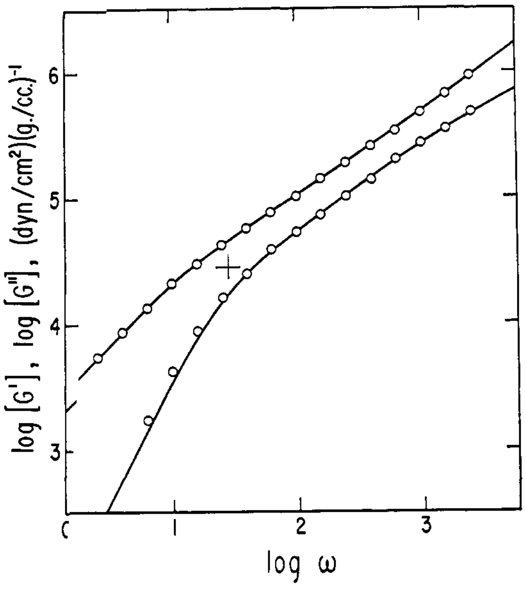

Figure 2. Extrapolated $[G']$ and $[G'']$ from Figure 1 and data at other frequencies, plotted logarithmically against radian frequency. Curves drawn from the Peterlin theory with P/N = 11.6, ϕ/f = 1.5, and h^* = 0.

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

(17) P. E. Rouse, Jr., *ibid.*, **21,** 1272 (1953).

(18) J. I Ferry, "Viscoelastic Properties of Polymers," 2nd ed, Wiley, New York, N. Y., 1970.

Table 1
Parameters at Low and High Freqcies Reduced to 25.0°

Sample	2a	S-10.	S-108	6a
$M_w \times 10^{-3}$	19.8	82	267	860
c, g/cm^3	0.0757	0.05	0.0274	0.0152
$c[\eta]$	1.2	1.9	2.1	2.8
η, P	358	455	440[a]	19.8
η_s, P	70	70	70	2.57
η_∞', P	~200	146	102	3.28
$(\eta_\infty' - \eta_s)/\eta_s c$	~24	21	17	18
Log J_e^0	−5.96	−4.87	−4.15	−3.19
S'/S^2	0.16	0.29	0.26	0.37
N	18	68	222	716
P/N	10.6	11.6	11.6	11.6
ϕ/f	2.5	1.5	1.55	2.0
ϕ/f, birefringence[b]	2.0	2.0	2.0[c]	2.0[d]
h^*	0.40	0.30	0.20	0.09
h^*, birefringence[b]	0.3	0.3	0.2[c]	0.1[d]
Log M_{ve}/M_w	−0.36	0.03	0.09	0.18
Log τ_1, sec	−3.15	−1.90	1.13	−1.54
Log G_∞'	5.52	5.32	5.05	4.74
Log (G_∞'/v_2)	6.66	6.63	6.63	6.58

[a] Estimated from data of ref 3. [b] G. B. Thurston and J. L. Schrag, *J. Polym. Sci., Part A-2*, **6**, 1331 (1968). [c] For M = 239,000. [d] For M = 968,000.

apparent, and the superposition of data from different temperatures is excellent. For the highest molecular weight (Figure 3), the frequency dependence reveals the customary slopes of 2 and 1 for G' and G'', respectively in the terminal (low frequency) zone, followed at higher frequencies by the "power-law" region in which both have a slope of approximately two-thirds (as specified by the Zimm theory). At still higher frequencies, G'' reverts to a slope of one (*i.e.*, constant dynamic viscosity $\eta' = G''/\omega$) and G' appears to be approaching a limiting value. (Measurements of G'' can be carried to frequencies about a decade higher than those of G', because the latter are affected by an inertial term which cuts precision at high frequencies.[14]) This is the behavior seen earlier in very high-frequency measurements in solvents of lower viscosity;[7-10] the present data afford a more detailed description because of the continuous frequency range available. The high-frequency regime would be called the glassy zone in an undiluted polymer; here, it might be termed a zone of configurational immobility. At lower molecular weights, the pattern is similar, but with diminishing molecular weight the power-law region shrinks and for M = 19,800 it is essentially absent; the terminal zone is adjacent to the immobility zone and G'' undergoes only a slight inflection between two segments of unit slope. A related feature is that $G'' - \omega\eta_s$ is everywhere much larger than G'; their ratio is never less than 4, as contrasted with the values of 1.73 and 1.0 predicted in the power-law region for Zimm and Rouse behavior, respectively.

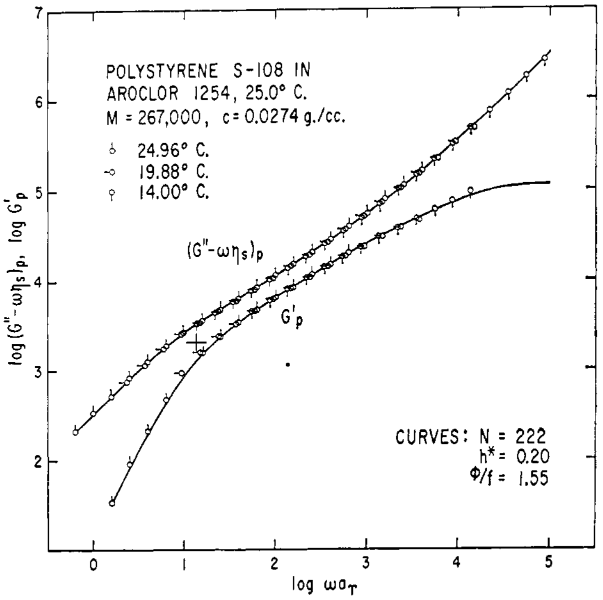

Figure 4. G' and $G'' - \omega\eta_s$ for M = 267,000, reduced and plotted as in Figure 3, from data at three different temperatures as indicated.

Whereas a limiting high-frequency value G_∞' cannot be measured directly, it can be derived in principle from the measurements of η' (or G'') by an integration analogous to the Kronig–Kramers relations[19] as follows

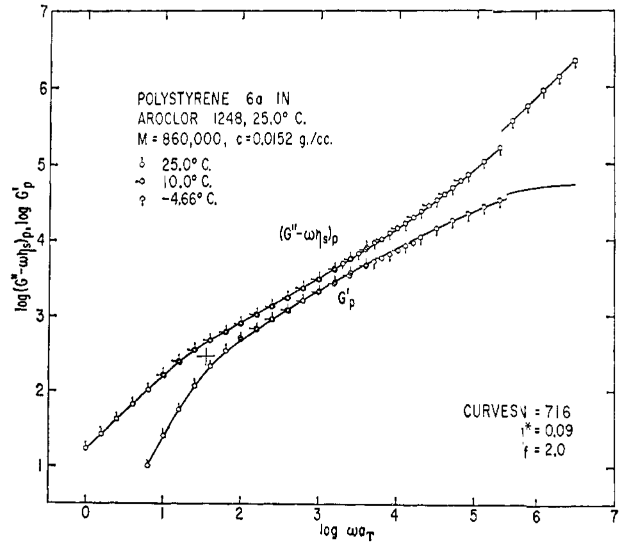

Figure 3. G' and $G'' - \omega\eta_s$ plotted logarithmically against frequency reduced to 25°, from data at three different temperatures as indicated, for M = 860,000, c = 0.015 g/cm^3. Subscript p denotes multiplication by $T_0\rho_0/T\rho$ where ρ's are solution densities and subscript 0 refers to 298°K. Curves drawn from Peterlin theory with parameters listed in Table I.

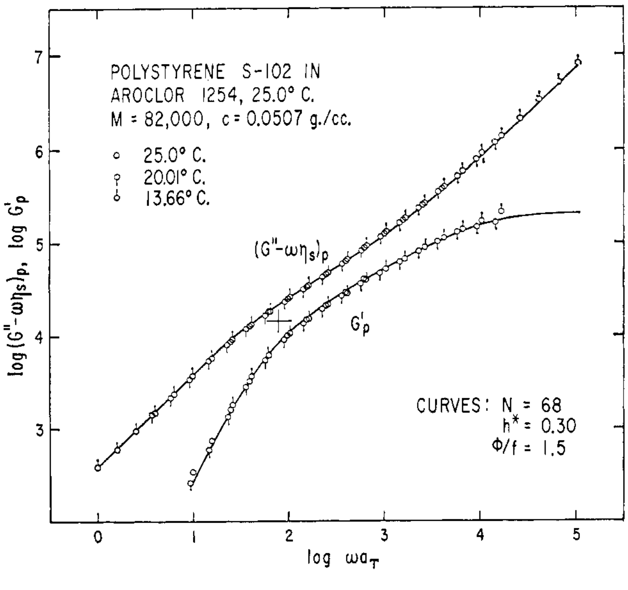

Figure 5. G' and $G'' - \omega\eta_s$ for M = 82,000, reduced and plotted as in Figure 3, from data at three different temperatures as indicated.

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(19) We are indebted to Dr. K. Osaki for verifying this equation.

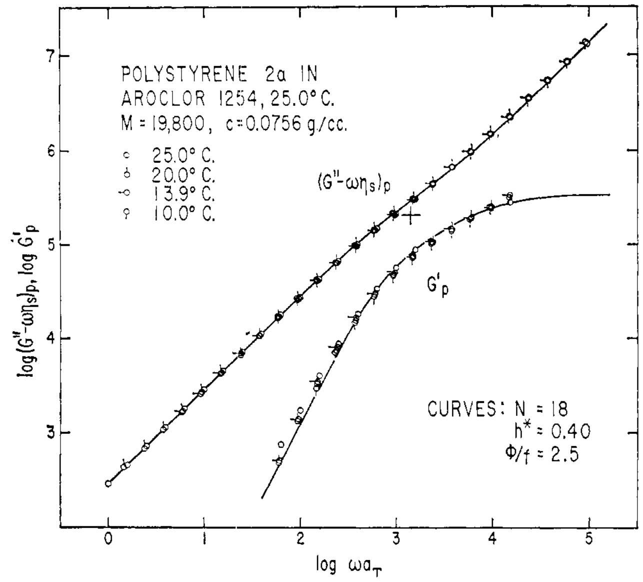

Figure 6. G' and $G'' - \omega\eta_s$ for M = 19,800, reduced and plotted as in Figure 3, from data at four different temperatures as indicated.

$$G_\infty' = \frac{2}{\pi}\int_{-\infty}^{\infty} (\eta' - \eta_\infty')\omega \mathrm{d}\ln\omega \qquad (1)$$

where η_∞' is the limiting value of η' at high frequencies (see below). In practice, very high precision is required for η' in the vicinity of η_∞' to evaluate the integral. For M = 860,000, planimetric integration of the appropriate graph provided log G_∞' = 4.66 ± 0.10. For the other samples, the η' data were not sufficiently precise.

In Figure 7, $\eta' - \eta_s$ is plotted against log ω for all four solutions. In each case, a finite limiting high-frequency value is approached, rather well defined except for the lowest molecular weight; otherwise, of course, $G'' - \omega\eta_s$ would go through a maximum and vanish at high frequencies in Figures 3–6. Values of η_∞' are included in Table I and are substantially higher than η_s. This behavior contrasts sharply, of course, with the predictions of the Rouse–Zimm theories in which the assumption of complete flexibility leads to $\eta_\infty' = \eta_s$.

Discussion

Limiting Low-Frequency Behavior. Besides the steady-flow viscosity η, the important parameter characterizing linear viscoelastic behavior at low frequencies is the steady-state compliance

$$J_e^0 = \lim_{\omega\to 0} [G'/(\omega\eta)^2]$$

Values calculated from the data of Figures 3–6 are included in Table I. They agree quite well with values previously reported for these samples in earlier studies[3,4] which focused attention on low-frequency behavior only—except for M = 19,800, whose J_e^0 is somewhat higher than cited before.[4] The earlier values for this low molecular weight are in error because of slight yielding of the apparatus, before its reconstruction, when annular pumping geometry was used with very high-impedance solutions.[14]

A related parameter is the dimensionless ratio we have denoted by S'/S^2 (others[20,21] call it J_{eR}), which is

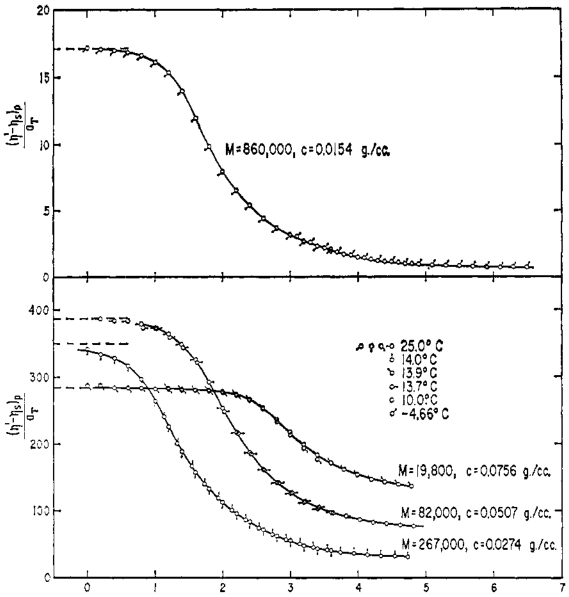

Figure 7. Reduced contribution of polymer to dynamic viscosity, $(\eta' - \eta_s)_p/a_T$, plotted against log ωa_T, for the solutions of Figures 3–6.

$$\lim_{\omega\to 0} [G'cRT/M\omega^2(\eta - \eta_s)^2]$$

This number is 0.206 for the Zimm theory and 0.400 for Rouse; the values for our solutions (Table I) are intermediate, as previously observed,[3,4] except that for M = 19,800, which is abnormally low. This abnormal behavior is less marked (0.16) than previously reported[4] for a similar solution (0.07), the latter being subject to error as explained above, but it is a distinct deviation from the bead-spring theories. In the framework of the Peterlin theory,[22–24] it is primarily associated with the low value of N (see below).

Limiting High-Frequency Behavior. The dependence of η_∞' on c and M cannot be examined here because both variables changed in the present series; it will be discussed in a later communication.[25] However, it has been noted that the concentration dependence of the ratio $(G'' - \omega\eta_s)/c$, and hence of $(\eta' - \eta_s)/c$, diminishes progressively with increasing frequency,[12] and $(\eta_\infty' - \eta_s)/c$ appears to be independent of c up to substantial concentrations. In fact, the high-frequency inherent viscosity, $(\eta_\infty' - \eta_s)/\eta_s c$, is quite similar for all four solutions despite the wide molecular weight range, being about 20 cm^3/g (Table I). It may be tentatively concluded that $(\eta_\infty' - \eta_s)/\eta_s c$ varies little with either concentration or molecular weight.

Application of the Peterlin Theory with Finite Number of Submolecules. The existence of a nonzero $\eta_\infty' - \eta_s$ can be deduced from a modification of the bead-spring theories which assumes an additional energy dissipation from the motion of one bead relative to another as well as from the motions of beads relative to the solvent.[22] This extra dissipation is referred to as a manifestation of "internal viscosity." As developed by Peterlin[23,24] for intermediate degrees of hydrodynamic interaction and a finite number of submolecules per macromolecule, the shape of the frequency dependence of both dynamic mechanical properties and dy-

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(20) N. W. Tschoegl, *J. Chem. Phys.*, **44**, 2331 (1966).
(21) H. Janeschitz-Kriegl, *Advan. Polym. Sci.*, **6**, 170 (1969).
(22) A. Peterlin, *J. Polym. Sci., Part A-2*, **5**, 179 (1967).
(23) A. Peterlin and C. Reinhold, *Trans. Soc. Rheol.*, **11**, 15 (1967).
(24) G. B. Thurston and A. Peterlin, *J. Chem. Phys.*, **46**, 4881 (1967).
(25) K. Osaki, J. L. Schrag, and J. D. Ferry, in preparation.

namic birefringence can be described with three parameters: N, the number of submolecules per molecule; ϕ/f, a ratio which gauges the relative magnitudes of frictional forces from internal deformations of the macromolecule and the motions of beads (submolecules) relative to the solvent; and h^*, a measure of the strength of the hydrodynamic interaction between beads. Despite some arbitrary features of this treatment, it has described with remarkable success intrinsic viscosity and dynamic birefringence data for solutions of polystyrenes in Aroclor over a very wide range of molecular weights.[26]

In applying the Peterlin theory to the data of Figures 3–6, the values of N were taken from the analysis of dynamic birefringence data by Thurston and Schrag[26] which included two of the same polystyrene samples and two closely similar to the others, since the fit of birefringence to theory is primarily sensitive to N. In the latter analysis, N was found to be close to directly proportional to the degree of polymerization P with a ratio P/N of about 11. Curves for G' and $G'' - \omega\eta_s$ were then calculated by computer (Varian 620i) for various values of ϕ/f and h^* and the best ones selected for fit as drawn in Figures 3–6. (In this calculation, the eigenvalues of Pyun and Fixman were used; details are presented elsewhere.[14]) The agreement with experiment is clearly extremely good, and the values of the parameters listed in Table I are quite close to those derived from the birefringence measurements.

Strictly speaking, application of the theory here to data at finite concentration (as in its application to dynamic birefringence[26]) is not quite appropriate since intermolecular interactions are ignored in the theory. In fact, the agreement cited is concerned with the shape of the frequency dependence only, while one more adjustable parameter is needed to specify the positions of the curves on the logarithmic axes. This amounts to treating the molecular weight as an adjustable parameter, M_{ve}; it is specified by the position of the cross on each plot, which corresponds to cRT/M on the ordinate scale. Values of log M_{ve}/M are included in Table I; evidently, M_{ve} is a little larger than the true molecular weight except for the sample with $M = 19{,}800$, for which the concentration is the highest. The position of the cross on the abscissa scale is $-\log \tau_1$, where τ_1 is the terminal relaxation time; these values are also given in the table. (When M_{ve} is chosen, τ_1 is determined through the measured viscosity η.)

The data for Figure 2, at infinite dilution, can also be fit to the Peterlin theory; although they do not extend to high enough frequencies to reach limiting values, the characteristic changes in curvature which herald this event are evident. The curves drawn correspond to the same value for P/N as in the finite-concentration plot for this molecular weight (Figure 3) with $\phi/f = 1.5$ and $h^* = 0.3$. In Figure 2, the fit with theory is absolute, since the data have been extrapolated to infinite dilution; the curves are drawn for the true molecular weight. It may be noted that the experimental values of G' at the lowest frequencies are a little high, but this is to be expected from some degree of molecular weight distribution.

When regarded in the framework of the Peterlin theory, a remarkable feature of the data in Figures 3–6 is the fact that measurements at different temperatures superpose with the identical shape of frequency dependence, even at high frequencies where the internal viscosity has a dominant effect, despite the enormous temperature dependence of solvent viscosity. In other words, the ratio ϕ/f appears to be independent of solvent viscosity. Moreover, it is about the same for sample 6a as for the others despite a 30-fold difference in solvent viscosity. In the usual concept of internal viscosity, the coefficient ϕ is supposed to be a property of the macromolecule and is not expected to depend on the solvent, whereas the friction coefficient f is of course proportional to solvent viscosity and changes with temperature accordingly. It must be concluded that ϕ also is proportional to solvent viscosity.

The molecular origin of this internal viscosity has remained obscure, though the concept goes back 25 years to the assumption of Kuhn[27] that a force is required to move the ends of a random coil relative to each other, proportional to their relative velocity. In view of the preceding paragraph, the solvent must play a crucial role; the effect cannot be understood in terms of an isolated macromolecule. Perhaps the extra energy is dissipated by deformation of a sheath of solvent molecules in the immediate vicinity of the macromolecule, as distinguished from the energy dissipated in long-range configurational motions in which the solvent plays the role of a structureless continuum as postulated in the bead-spring models.

The limiting high-frequency values of G' obtained by the Peterlin theory fit are of interest in representing a limiting elasticity in the configuration–immobile zone; they are included in Table I. For $M = 860{,}000$, the value agrees quite well with that calculated from eq 1. Also listed are the logarithms of the ratio G_∞'/v_2, where v_2 is volume fraction of polymer. It is essentially constant, corresponding to a modulus of 4.6×10^6 dyn/cm^2, but the significance of this figure is not clear at present.

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[26] See Table I, footnote *b*.

[27] W. Kuhn and H. Kuhn, *Helv. Chim. Acta*, **28**, 1533 (1945); **29**, 71, 609, 830 (1946).