has been used for the theoretical treatment of swelling in binary solvents[24] (the first use of that parameter was made by Read,[25] concerning preferential sorption). The necessity of introducing the ternary χ_T parameter may be due to a deviation of the numbers of molecular contacts from those given by the Flory-Huggins theory. Recently it has been suggested that molecular "surface" fractions[26] (or "site" fractions[27]) should replace the familiar volume fractions, and the formal introduction of the χ_T parameter into the Flory-Huggins theory equation seems to be justifiable by this step. Allowing also for the dependence of χ_{13} and χ_{23} on polymer concentration as given by eq 1, we see after performing the necessary calculation (*cf.* ref 24 and 28), that the eq 8 should be replaced by

$$\bar{\chi} = u_1(\chi_{13}{}^0 + \chi_{13}{}'\phi_3) + u_2(\chi_{23}{}^0 + \chi_{23}{}'\phi_3) - u_1u_2[\chi_{12} - 2\chi_T(1 - \phi_3)] \quad (10)$$

The experimental results[19-22] are fitted if the ternary parameter is assumed to be of the same sign as χ_{12} but of numerical value smaller than $\chi_{12}/2$. We can thus write

$$\chi_T = (\gamma/2)\chi_{12} \quad 0 < \gamma < 1 \quad (11)$$

The term with χ_{12} is thus diminished by a factor $1 - \gamma$ for very dilute systems ($\phi_3 \rightarrow 0$), but at the same time its dependence on polymer concentration is apparent. The expression $[(1/3) - \chi']$ in eq 4 for ξ_2 or B_2 is now replaced by

$$\frac{1}{3} - \bar{\chi}' = \frac{1}{3} - (u_1\chi_{13}{}' + u_2\chi_{23}{}') + \gamma\chi_{12}u_1u_2 \quad (12)$$

Assuming γ constant for a given polymer in different solvent mixtures, the proportionality of the last term to χ_{12} is valid. Inspecting eq 12 together with eq 4 and eq 2 or 6, this term offers an explanation of the deviation of the K_θ value, found in mixed solvents, from additivity. For $\chi_{12} = 2$, $\gamma = 0.8$, $u_1 = u_2 = 0.5$, we get a change of B_2, due to χ_{12}, which is at least of order 0.2, with a corresponding change of ~20% in the apparent value of K_θ. The sign of this effect would change with χ_{12} as found experimentally. Thus when mixed solvents are used, there may be an important influence of the thermodynamic interactions on the extrapolation procedure for K_θ.

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Infinite-Dilution Viscoelastic Properties of Poly(dimethylsiloxane)

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Measurements of storage and loss shear moduli have been made recently on several polymers in solution at concentrations sufficiently low to permit extrapolation of the data to infinite dilution for comparison with the predictions of molecular theories.[1] Data for linear polystyrene,[2] poly(α-methylstyrene),[3] and 1,4-polybutadiene[4] agree well with the predictions of the Zimm theory,[5] as evaluated by Lodge and Wu[6] with an arbitrary degree of hydrodynamic interaction, provided the frequency range does not extend far above the reciprocal of the longest relaxation time. Moreover, the degree of hydrodynamic interaction appears to be related to the expansion factor of the random coil as gauged by the intrinsic viscosity relative to that in a Θ solvent.[3]

In the present report, additional measurements on two samples of poly(dimethylsiloxane) (PDMS) are presented and compared with the Lodge-Wu evaluation of the Zimm theory. This polymer is somewhat different from those previously studied in having atoms other than carbon in the backbone; it is generally thought of as having a very high internal flexibility.

Two samples of PDMS with narrow molecular weight distribution were generously provided by Dr. Neal R. Langley of Dow Corning Corp. In order to place the relaxation times in a range appropriate for the frequency scope of our experimental method, it was necessary to use solvents of somewhat higher viscosity than the conventional ones for other dilute-solution measurements such as osmotic pressure and light scattering, and there is a narrow choice of liquids in which PDMS is soluble. We used PDMS oligomer liquids in which there were no components of high enough molecular weight to contribute any viscoelastic effects; these were also kindly furnished by Dr. Langley. Their viscosities (η_s) were determined by the multiple-lumped resonator in the course of the viscoelastic measurements. Intrinsic viscosities of the polymers in their respective oligomer solvents were determined by conventional capillary viscosimetry at 25°. Intrinsic viscosities in toluene were reported by Dr. Langley. Characterization of the polymers and solvents is summarized in Table I, including average molecular weights ($\bar{M}_w$, $\bar{M}_n$) determined at the Dow Corning Corp. No $\bar{M}_n$ is available for the sample of higher molecular weight, but its $\bar{M}_w$:$\bar{M}_n$ ratio was judged to be 1.10 to 1.15 from gel permeation chromatography.

The storage and loss shear moduli, G' and G'', of the solutions were measured by the Birnboim-Schrag multiple-lumped resonator[7] with computerized data acquisition and processing system.[8] The use of two resonators gave 9 working frequencies from 100 to 6060 Hz. The ranges of concentration (c) were 0.003-0.007 g/ml and 0.002-0.007 g/ml for the polymers of lower and higher molecular weights, respectively. All measurements were made at 25.00 ± 0.01°.

The quantities $(G'/c)^{1/2}$ and $(G'' - \omega\eta_s)/c$, where ω is radian frequency, were plotted against c and extrapolated to zero c at each frequency as described in previous studies[2-4] to give the corresponding intrinsic quantities $[G']$ and $[G'']$. The initial concentration dependences, derived from the slopes of these plots, could not be determined as precisely as usual because the concentration range was more limited. However, the ratios $\gamma' = (G'/c)^{-1}\mathrm{d}(G'/c)/\mathrm{d}c$, and γ'' which is the corresponding expression with $G'' - \omega\eta_s$ substituted for G', decreased substantially with in-

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Table I
Characterization of Polymers and Solvents

Polymer code no.	177-4	235-2
$\bar{M}_i \times 10^{-6}$	0.42	
$\bar{M}_w \times 10^{-6}$	0.45	1.44
$[\eta]$, toluene, ml/g, 25°	113	298
$[\eta]$, PDMS solvent, 25°	54.5	189
Solvent code[a]	DC-200, 20 cs	DC-200, 5 cs
η_s, 25.0°, P	0.183	0.048_5
ρ_s, 25.0°, g/ml	0.949	0.920

[a] The second number is the nominal viscosity in centistokes.

Table II
Hydrodynamic Interaction Parameters and Relaxation times

$M_w \times 10^{-6}$	0.45	1.44
h^*	0.15	0.15
S_1	2.11	2.11
Log τ_{01} (sec)	−4.06	−3.60
Log (τ_{01}/η_s)	−3.32	−2.29
α_η	1.00	1.25
$\alpha_\eta h^*$	0.15	0.19

creasing frequency as usually observed; this behavior is consistent with the hypothesis that the longest relaxation time is much more strongly concentration dependent at very low concentrations than are the other relaxation times.[2]

The extrapolated values are reduced to $[G']_R = [G']M/RT$ and $[G'']_R = [G'']M/RT$, with M taken as the weight-average value, and plotted logarithmically against $\omega\eta_s[\eta]M/RT$ in Figure 1. These coordinates are convenient for comparison with the shapes of theoretical curves.[9] The points were matched to logarithmic plots of $[G']_R$ and $[G'']_R$ *vs.* $\omega\tau_{01}$, where τ_{01} is the longest relaxation time at infinite dilution, calculated from the Lodge-Wu evaluation[6] of the Zimm theory with $N = 300$ (number of submolecules) and various values of h^* (hydrodynamic interaction parameter). The match involves a horizontal shift of the abscissa to make $[G'']_R$ coincide at low frequencies; this shift is log S_1, where $S_1 = \Sigma(\tau_{0p}/\tau_{01})$, the τ_{0p} being the individual relaxation times evaluated for a particular h^*. The theoretical curves are drawn in Figure 1 and the values of h^*, S_1, and τ_{01} ($= \eta_s[\eta]M/RTS_1$) are given in Table II. The curves agree with the data quite well, though the uncertainty in h^* is at least ±0.03. The deviation in $[G']_R$ at low frequencies for the sample of higher molecular weight is in the direction to be expected from a small degree of molecular weight heterogeneity.

In previous work on linear polymers,[3] h^* has been found to be approximately inversely proportional to α_η, where α_η^3 is the ratio of intrinsic viscosities in a particular solvent and in a Θ solvent. For PDMS, the Θ-solvent intrinsic viscosity can be calculated from data reviewed by Stockmayer and Kurata,[10] for example, in methyl ethyl ketone at 20°, as 54.2 and 97.2 ml per g, respectively; the latter agrees also with a value measured in bromocyclohexane at the Dow Corning Corp. From these, the values of α_η given in Table II are obtained. It appears curious that the 20-cs oligomeric PDMS used for the polymer of lower molecular weight is a Θ solvent, whereas in the 5-cs oligomer used for the other polymer α_η is greater than unity. However, it is generally accepted[11] that a polymer molecule surrounded by others of its kind has unperturbed dimensions, and the average molecular weight in the 20 cs solvent may be sufficiently high to provide these conditions.

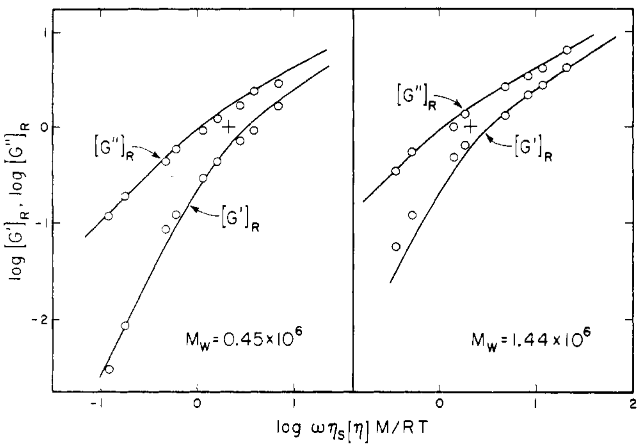

Figure 1. Reduced intrinsic storage and loss moduli plotted logarithmically against $\omega\eta_s[\eta]M/RT$ for samples with weight-average molecular weights as indicated. Curves drawn from Zimm theory evaluated by Lodge and Wu with $N = 300$, $h^* = 0.15$. At cross, $\omega\tau_{01} = 1$.

The product $\alpha_\eta h^*$ is, for both samples, somewhat smaller than the average of 0.21 previously observed,[3] but the differences are not sufficiently outside the uncertainty of curve fitting to judge their significance. In any case, the predictions of the Zimm theory, which are rather insensitive to the choice of the single adjustable parameter h^*, agree closely with the data both in absolute magnitude and in frequency dependence, providing additional evidence of the utility of the bead-spring model in this frequency range. Effects which are specific to the detailed chemical structure may be anticipated at higher frequencies.[1,12]

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On the Molecular Weight Determination of EPM and EPDM Rubbers

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The molecular characterization of copolymers of ethylene and propylene (EPR, EPM) and of terpolymers of these two and a third, diene, monomer (EPDM), often meets with problems. Recently, Baldwin and Ver Strate[1] in an extensive review of ethylene-propylene elastomers discussed the conflicting molecular weight values found for such polymers, and mentioned incomplete dissolution as a possible cause of the discrepancies. Dissolution at low temperature might not be effective enough in removing molecular aggregates and, in consequence, might cause abnormally large values of molecular weight to be found by light scattering. The problem is analogous to that indicated by

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