Effects of Concentration and Thermodynamic Interaction on the Viscoelastic Properties of Polymer Solutions

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ABSTRACT: We report linear viscoelastic measurements for solutions of a high molecular weight polybutadiene covering the entire range of concentration from pure polymer to pure solvent at 25 °C. Two solvents were employed that have glass transition temperatures near that of polybutadiene: dioctyl phthalate is nearly a Θ solvent at 25 °C and phenyloctane is a good solvent. We find three regimes of concentration for the viscosity in each solvent. In dilute solution ($\phi < \phi^*$) the viscosities are well represented by the Huggins equation, although with quite different intrinsic viscosities and Huggins coefficients in the two solvents. In the entangled semidilute range ($\phi_c < \phi < 0.1$) and the concentrated regime ($\phi > 0.1$) the free volume adjusted viscosity is identical in the two solvents and obeys power laws of $\phi^{4.7}$ in semidilute solution and $\phi^{3.6}$ in concentrated solution. Elastic response is also identical for the two solvents, with $G°_N$ (inferred from G''_m) $\propto 1/J°_e \propto \phi^{2.3}$ for $\phi > 0.02$. The results in semidilute solution compare favorably with the predictions of a recent two-parameter scaling theory. The observations also suggest that the concentration dependences of the characteristic molecular weights M_e and M_c are somewhat different.

Introduction

In this paper we examine the effects of thermodynamic interactions on the viscoelastic properties of polymer solutions over a very wide range of concentrations. Zero shear viscosity was obtained for polybutadiene solutions from the dilute range to the melt in phenyloctane, which is a thermodynamically good solvent for polybutadiene, and dioctyl phthalate, which is a near-Θ solvent at the temperature of measurement. Elastic response was also measured over the widest range of concentrations possible with our instrument. The glass transition temperature is well below ambient and similar for all components, allowing the convenience of measurements near ambient temperature over the full concentration range and also making free volume corrections for the viscosity relatively small.

Experimental Section

A. Synthesis and Characterization. The polybutadiene sample used in this study is the sample designated B4 in ref 1. It was prepared under vacuum line conditions by anionic polymerization. The polymerization was conducted at ambient temperature in a 9/1 cyclohexane–benzene mixture with initiation by *sec*-butyllithium. The molecular weight of the sample is 925 000, as determined by light scattering. The sample has a narrow molecular weight distribution, $M_w/M_n < 1.1$ and $M_z/M_w < 1.1$, as determined by size-exclusion chromatography. Its chemical microstructure is 50% cis 1,4, 42% trans 1,4, and 8% 1,2 (vinyl), as determined by proton NMR. Density ρ, thermal expansion coefficient α, and viscosity η at 25 °C are given in Table I.[1]

Solvents of low volatility were used to minimize solvent evaporation during the rheological measurements. Dioctyl phthalate (bis(2-ethylhexyl) phthalate, Aldrich Chemical Co.) was selected as the Θ solvent, and phenyloctane (Aldrich Chemical Co.) was selected as the good solvent. Values of ρ, α, and η are given in Table I. The basis for this choice of solvents is described in the Appendix. An original estimate of $\theta = 21.5$ °C for the

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Table I
Selected Properties of the Solution Components

	ρ, g mL^{-1} (25 °C)	$10^4\alpha$,[a] K^{-1}	η, P (25 °C)
polybutadiene	0.895	7.0	4.5×10^8
phenyloctane	0.852	8.1	0.023_4
dioctyl phthalate	0.980	7.4	0.58_1

[a] Obtained from density measurements at 25 and 60 °C.

Table II
Intrinsic Viscosity and Huggins Coefficient

solvent	T, °C	$[\eta]$, dL g^{-1}	k_H
phenyloctane	25.0	4.51	0.46
	50.0	4.47	0.46
dioctyl phthalate	16.5	1.47	0.95
	21.5	1.62	0.77

polybutadiene–dioctyl phthalate system, based on cloud point determinations, proved later to be incorrect. A better estimate is ~13 °C, as explained in the Appendix, so the rheological measurements, mainly at 25 °C, correspond only to "near-Θ" conditions. The intrinsic viscosity and the Huggins coefficient for the polymer in these solvents at two temperatures are given in Table II. The following Mark–Houwink–Sakurada equations were obtained from data for a series of polybutadienes of similar microstructure (see Appendix):

$$[\eta] = 5.02 \times 10^{-4}M^{0.661} \quad (\text{dL g}^{-1}) \tag{1}$$

in phenyloctane at 25 °C and

$$[\eta] = 9.03 \times 10^{-4}M^{0.549} \quad (\text{dL g}^{-1}) \tag{2}$$

in dioctyl phthalate at 21.5 °C.

B. Solution Preparation. Solutions were prepared on a weight basis, and the volume fraction of polymer ϕ was calculated from the pure component densities assuming negligible volume change on mixing. The dioctyl phthalate solutions were prepared with benzene as a cosolvent to speed dissolution. The benzene was subsequently removed under vacuum at room temperature. The solutions were dried to constant weight (a weight loss of less than 0.001 g in the final week of drying; the rate of dioctyl phthalate evaporation under these conditions is negligible, and no benzene was detected in the dried solutions by infrared. The phenyloctane solutions were prepared without a cosolvent.

Table III
Glass Transition Temperatures for Pure Components and
Selected Solutions

	ϕ	T_g, K
dioctyl phthalate	0	185[a]
	0.0214	187
	0.157	184
	0.306	183
	0.523	181
phenyloctane	0	152[b]
	0.0274	150
	0.140	152
	0.280	154
	0.488	157
polybutadiene	1.0	174

[a] Values for dioctyl phthalate and its solutions extrapolated to zero scan rate from data at 5, 10, and 20 K min⁻¹. [b] Values for phenyloctane and its solutions obtained at a scan rate of 20 K min⁻¹.
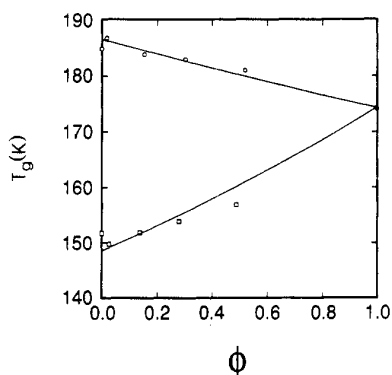
Figure 1. Glass transition temperatures for solutions. Circles are DOP solutions; squares are PHO solutions. Curves are the Fox equation $(1/T_g = \phi/T_{gp} + (1 - \phi)/T_{gs})$.

Approximately 0.02 wt % of an antioxidant, Ionol, was added to all solutions during their preparation, and all were stored in the dark until use (for a minimum of 2 weeks after the solutions appeared to be homogeneous).

C. Glass Transition Measurements. Values of the glass transition temperature T_g were obtained for the pure components and selected solutions by differential scanning calorimetry (DSC-2, Perkin-Elmer Instrument Co.). The equilibrium melting temperature for both solvents is approximately –30 °C, so the solvent and solution samples were quenched rapidly to minimize crystallization. Crystallization was never avoided completely and was particularly troublesome for the phenyloctane solutions, where T_g was estimated as the incipient crystallization temperature for $\phi < 0.1$. The values obtained are listed in Table III and plotted in Figure 1.

D. Viscoelastic Measurements. Kinematic viscosity $\nu = \eta/\rho$ for the pure solvents and the solutions of low concentration ($\phi < 0.02$) was determined with calibrated glass capillary viscometers (Cannon Instrument Co.), equipped with automatic timers (Wescan Instruments, Inc.). Results for the pure solvents at various temperatures are given in Table IV and for the solutions at 25 °C in Table V. Solvent crystallization prevented the measurement of viscosity below –30 °C. The likelihood of liquid–liquid phase separation in the dioctyl phthalate solutions at temperatures much below 25 °C and solvent evaporation from the phenyloctane solutions much above 25 °C placed additional restrictions on the measurement ranges.

Linear viscoelastic properties were measured for the solutions of higher concentration with a System Four rheometer (Rheometrics, Inc.), equipped with a 10 000 g cm transducer. Parallel platens and the oscillatory shear mode were used to determine the storage modulus $G'(\omega)$ and loss modulus $G''(\omega)$ over a range of frequencies, 2×10^{-4} rad/s $< \omega < 4 \times 10^2$ rad/s. Gap settings of 1–2 mm were used; 50-mm platens were used for solutions of low viscosity ($\eta < 10^5$ P) and 25-mm platens for solutions of higher viscosity. Results at 25 °C are shown in Figures 2 and 3.

Table IV
Kinematic and Shear Viscosity Measurements on Pure Solvents at Various Temperatures

|	T, °C	ν,[a] S	η,[b] P
dioctyl phthalate	–26		87.5
	–2		4.18
	21.5	0.726	
	25	0.592	0.549
	30	0.447	
	48		0.18
phenyloctane	–20	0.0971	
	0	0.0494	
	25	0.0259	
	50	0.0166	
	75	0.0119	

[a] Measured by capillary viscometry. [b] Measured by oscillatory rheometry.

Table V
Viscosity of Polybutadiene Solutions at 25 °C

dioctyl phthalate		phenyloctane	
ϕ	η, P[a]	ϕ	η, P[b]
0	5.81×10^{-1}	0	2.34×10^{-2}
1.17×10^{-3}	6.87×10^{-1}	6.15×10^{-4}	2.99×10^{-2}
1.76×10^{-3}	7.51×10^{-1}	1.03×10^{-3}	3.49×10^{-2}
2.35×10^{-3}	8.27×10^{-1}	1.54×10^{-3}	4.23×10^{-2}
3.53×10^{-3}	1.02	2.05×10^{-3}	5.01×10^{-2}
5.29×10^{-3}	1.53	3.08×10^{-3}	6.92×10^{-2}
7.05×10^{-3}	2.45	4.62×10^{-3}	1.10×10^{-1}
1.06×10^{-2}	7.58	6.15×10^{-3}	1.78×10^{-1}
2.14×10^{-2}	9.0×10^1	9.23×10^{-3}	4.31×10^{-1}
3.08×10^{-2}	7.60×10^2	2.14×10^{-2}	7.06
8.06×10^{-2}	6.0×10^4	2.74×10^{-2}	2.08×10^1
1.57×10^{-1}	5.1×10^5	6.21×10^{-2}	1.13×10^3
3.06×10^{-1}	9.1×10^6	1.40×10^{-1}	5.0×10^4
5.23×10^{-1}	6.0×10^7	2.80×10^{-1}	1.0×10^6
1.00	4.5×10^8	4.88×10^{-1}	1.3×10^7
		1.00	4.5×10^8

[a] Values for $\phi < 0.02$ were calculated from the data on kinematic viscosity at 21.5 °C and adjusted to 25 °C by multiplying by $\eta_s(25)/\eta_s(21.5) = 0.81$. [b] Values for $\phi < 0.02$ were calculated from the data on kinematic viscosity at 25 °C.
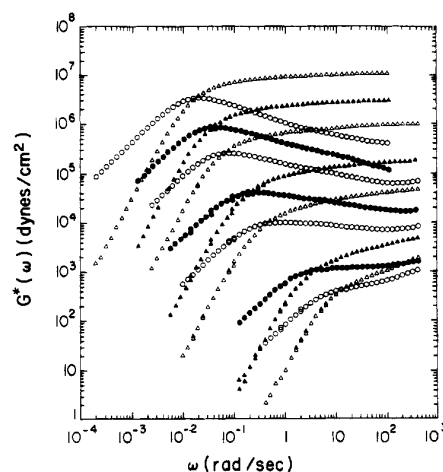
Figure 2. Complex modulus for DOP solutions at 25 °C. Triangles are the storage modulus, G'; circles are the loss modulus, G''. Concentrations are ϕ = 1, 0.523, 0.306, 0.157, 0.0806, 0.0308, and 0.0214.

Zero shear viscosity was determined from the loss modulus data at low frequencies:

$$\eta = \lim_{\omega \to 0} \frac{G''(\omega)}{\omega} \qquad (3)$$

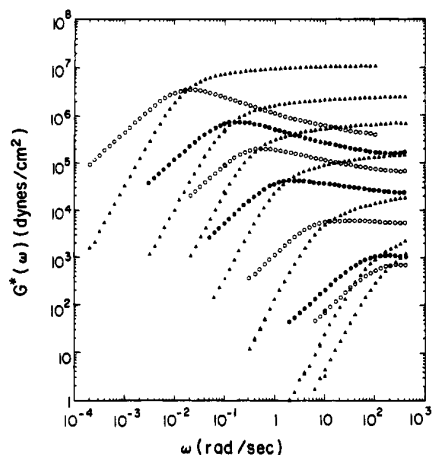Some values obtained in this way for dioctyl phthalate are given

Figure 3. Complex modulus for PHO solutions at 25 °C. Same symbols as Figure 2. Concentrations are ϕ = 1, 0.488, 0.280, 0.140, 0.0621, 0.0274, and 0.0214.

Table VI
Viscosity of Polybutadiene Solutions at Various Temperatures

ϕ	T, °C	η, P
	Dioctyl Phthalate	
2.14×10^{-2}	25	9.0×10^{1}
	48	2.4×10^{1}
	72	9.1
3.08×10^{-2}	25	7.60×10^{2}
	48	2.16×10^{2}
	72	8.16×10^{1}
8.06×10^{-2}	25	6.0×10^{4}
	72	7.5×10^{3}
1.57×10^{-1}	25	5.1×10^{5}
	48	1.8×10^{5}
	72	7.4×10^{4}
	Phenyloctane	
2.14×10^{-2}	-27	4.47×10^{1}
	-1	1.51×10^{1}
	25	7.06
2.74×10^{-2}	-27	1.45×10^{2}
	-1	4.6×10^{1}
	25	2.08×10^{1}
6.21×10^{-2}	-27	9.4×10^{3}
	-1	2.7×10^{3}
	25	1.13×10^{3}
1.40×10^{-1}	-27	4.7×10^{5}
	-1	1.26×10^{5}
	25	5.0×10^{4}
2.80×10^{-1}	-27	8.9×10^{6}
	-1	2.5×10^{6}
	25	1.0×10^{6}

in Table IV. Results for the solutions at 25 °C are given in Table V and at other temperatures (48 and 72 °C for the dioctyl phthalate solutions and -27 and -1 °C for the phenyloctane solutions) in Table VI. Measurements at temperatures much below 25 °C were anomalous for the dioctyl phthalate solutions, presumably because of phase separation. Figure 4 shows the results of a temperature sweep from +19 to -3 °C at ω = 5 rad/s for ϕ = 0.0806. Rather than G' and G'' both rising slowly as the temperature decreases, the anticipated result for a solution that does not phase separate, both moduli fall rather rapidly near 10 °C and then assume nearly constant values below this range. We take this to be another indication that 25 °C is "not far" from the Θ condition for polybutadiene–dioctyl phthalate solutions.

Recoverable shear compliance was determined from the storage modulus data at low frequencies:

$$J^{\circ}_{e} = \frac{1}{\eta^{2}} \lim_{\omega \to 0} \frac{G'(\omega)}{\omega^{2}} \tag{4}$$

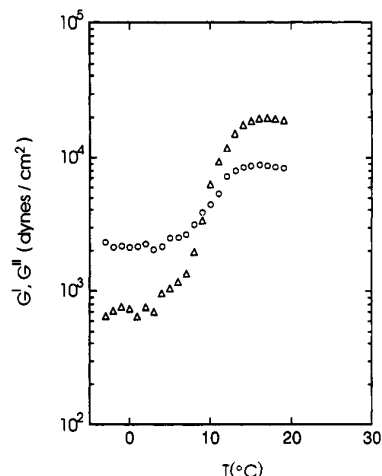The loss modulus maximum G''_{m}, a parameter closely related to

Figure 4. Descending temperature sweep for a DOP solution with ϕ = 0.0806. ω = 5 rad/s. Triangles are the storage modulus, G'; circles are the loss modulus, G''. A 15-min thermal equilibration was used at each temperature.

Table VII
Recoverable Compliance and Loss Modulus Maximum of Polybutadiene Solutions at 25 °C

solvent	ϕ	G''_{m}, dyn cm^{-2}	J°_{e}, cm^{2} dyn^{-1}	$J^{\circ}_{e}G''_{m}$
dioctyl phthalate	0.0214		1.2×10^{-3}	
	0.0308	1.2×10^{3} ^{a}	5.2×10^{-4}	0.62
	0.0806	1.09×10^{4}	5.5×10^{-5}	0.60
	0.157	4.1×10^{4}	1.3×10^{-5}	0.53
	0.306	2.57×10^{5}	2.3×10^{-6}	0.59
	0.523	8.97×10^{6}	6.3×10^{-7}	0.57
phenyloctane	0.0214		1.1×10^{-3}	
	0.0274	1.1×10^{3} ^{a}	5.6×10^{-4}	0.62
	0.0621	5.71×10^{3}	1.0×10^{-4}	0.57
	0.140	3.99×10^{4}	1.4×10^{-5}	0.56
	0.280	2.07×10^{5}	2.7×10^{-6}	0.56
	0.488	8.02×10^{5}	7.5×10^{-7}	0.60
none	1.000	3.55×10^{6}	1.6×10^{-7}	0.57

^{a} Estimated for these solutions as G'' where G' and G'' cross (see Figures 2 and 3).

the plateau modulus, was also recorded. Values of J°_{e} and G''_{m} are given in Table VII.

Analysis of Viscosity Results

Thermodynamic effects on dilute solution properties are of course well-known and understood.[2] The viscosity scales with solvent viscosity and depends on the intrinsic viscosity of the polymer:

$$\eta(\phi) = \eta_{s}[1 + [\eta]\rho\phi + k_{H}([\eta]\rho\phi)^{2} + ...] \tag{5}$$

where ρ is the polymer density (assuming no volume change on mixing) and k_{H} is the Huggins coefficient. The intrinsic viscosity depends in turn on chain dimensions ($[\eta] \propto R^{3}/M$, where R is the coil radius) and thus on polymer–solvent thermodynamics through the excluded volume interaction. Intrinsic viscosity is larger in good solvents and relatively insensitive to temperature. Smaller and temperature-dependent values of $[\eta]$ typify near-Θ conditions. The results in phenyloctane and dioctyl phthalate (Table II) are consistent with those expectations. The molecular weight exponents (eq 1 and 2) are also consistent, although they do depart somewhat from the values of 0.764 for the good solvent limit ($R \propto M^{0.588}$ (ref 3)) and 0.5 for the Θ condition.

Thermodynamic interactions appear to play very little role in dynamical behavior at the other extreme of dense (highly concentrated) solutions. Chain dimensions are near their unperturbed values for all solvents (see ref 4),

Table VIII
Scaling Predictions of the Exponent for the Concentration
Dependence of Viscosity

	Θ	good	DOP	PHO
single-parameter scaling with $\eta \sim M^3$	6.0	3.9	5.6	4.5
single-parameter scaling with $\eta \sim M^{3.4}$	6.8	4.5	6.3	5.1
two-parameter scaling with $\eta \sim M^3$	4.7	3.9	4.4	4.3
two-parameter scaling with $\eta \sim M^{3.4}$	5.2	4.5	4.9	4.9

so the static structure of the solution should be insensitive to solvent choice. The viscosity for highly entangled linear chains in this range scales with the undiluted polymer viscosity η_p and can be written as

$$\eta(\phi) = \eta_p \frac{\zeta_0(\phi)}{\zeta_0(1)} \phi^y \tag{6}$$

where $\zeta_0(\phi)$ and $\zeta_0(1)$ are the respective monomeric friction coefficients for the polymer in solution and the undiluted state. The concentration exponent y is closely related to the molecular weight exponent for undiluted polymer

$$\eta_p \propto M^b \tag{7}$$

with $b \le y \le b + 0.6$ encompassing the experimental results.[5-7] The values of $\zeta_0(1)/\zeta_0(\phi)$ are viewed as strictly dynamical and can be obtained, at least in principle, from the diffusion rate of small probe molecules[8,9] or by applying the free volume theory to measurements of the temperature dependence of viscosity.[5]

The upper limit of the dilute range is the overlap concentration, which can be estimated as[10]

$$\phi^* = ([\eta]\rho)^{-1} \tag{8}$$

For this sample of polybutadiene, $\phi^* = 0.0069$ in dioctyl phthalate and $\phi^* = 0.0025$ in phenyloctane. The lower limit of the dense range, where chain dimensions become insensitive to solvent power, is independent of chain length and has been estimated to be $0.1 < \phi^{\dagger} < 0.2$ for typical good solvent-polymer combinations.[4] We estimate $\phi^{\dagger} \cong 0.1$ for our phenyloctane solutions from the reciprocal of $[\eta]^{\dagger}$, the value of the intrinsic viscosity, where the Mark-Houwink-Sakurada relation in phenyloctane (eq 1) intersects that of a Θ solvent[4] (see Appendix). The semidilute range is between ϕ^* and $\phi^{\dagger}$. Intrachain hydrodynamic and thermodynamic interactions become progressively screened with increasing concentration in this range, and the solution viscosity crosses over from the solvent viscosity scaling of dilute solutions (eq 5) to the polymer viscosity scaling of dense solutions (eq 6).

de Gennes[11,12] has assumed a single parameter scaling in the semidilute range and predicts a power law dependence for the solution viscosity:

$$\eta(\phi) = \eta_s(\phi/\phi^*)^x \tag{9}$$

An expression for the concentration exponent x is obtained by requiring agreement with the molecular weight dependence in the concentrated regime (eq 7). This leads to $x = b/\beta$, where β is the Mark-Houwink exponent ($[\eta] \propto M^\beta$).

A different scaling idea, based on two parameters, has been proposed.[13] The result for the viscosity is

$$\eta = \eta_s(a/\xi)^2(M/M_e)^b \tag{10}$$

where M_e is the entanglement molecular weight, a is the
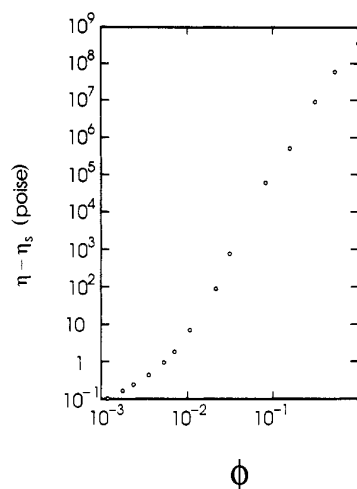
Figure 5. Concentration dependence of viscosity for DOP solutions at 25 °C.

entanglement tube diameter, and ξ is the screening length. In the good solvent limit, a and ξ have the same concentration dependence, and the single-parameter de Gennes results are recovered. In a Θ solvent $a \propto \phi^{-2/3}$ and $\xi \propto \phi^{-1}$, which leads to predictions for the viscosity that are quite different from the de Gennes predictions.

The crossover between the good solvent limit and the Θ point is not fully understood theoretically. Here we assume that the Mark-Houwink exponent β changes continuously from 0.5 to 0.764 as the quality of solvent is varied from the Θ to the good solvent limit. This is consistent with the vast amount of literature data (see, for example, Figure 12 in the Appendix), which indicate that a continuously varying exponent is more appropriate than the crossover anticipated from scaling and renormalization group calculations,[12] where the only true power laws would have universal exponents of 0.5 and 0.764. This crossover assumption influences the scaling predictions of the concentration dependence of viscosity in semidilute solution through the molecular weight dependence of the overlap concentration in eq 9 ($\phi^* \propto M^{-\beta}$) and the concentration dependence of the screening length in eq 10 ($\xi \propto \phi^{(\beta+1)/3\beta}$). There are no theoretical predictions yet for the crossover of the concentration dependence of the tube diameter, required for the two-parameter scaling prediction. Here we assume the tube diameter has the same concentration dependence as the closest limiting case.[14]

The scaling predictions for the exponent x ($\eta \propto \phi^x$) are summarized in Table VIII for the Θ solvent limit, the good solvent limit, and the two solvents used in this study.[14] Note that the two-parameter scaling theory (with the assumed crossover) does not anticipate much difference between the two solvents in the concentration dependence of viscosity, despite the rather large differences in coil expansion for dilute solutions (see Table II and the Appendix).

Viscosity at 25 °C for the solutions in dioctyl phthalate and phenyloctane (Table V) is plotted over the full range of concentrations as $\eta(\phi) - \eta_s$ in Figures 5 and 6. The following sections describe the free volume adjustment and the behavior of the resulting iso-free-volume viscosities.

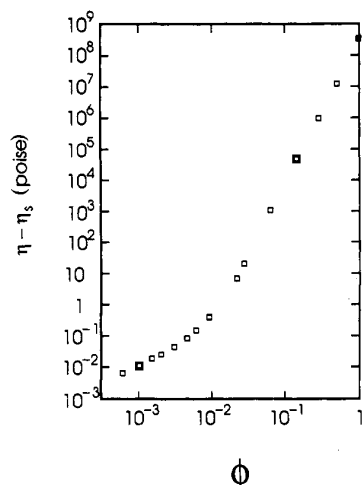**A. Free Volume Adjustments.** The temperature dependence of viscosity for the pure components and

Figure 6. Concentration dependence of viscosity for PHO solutions at 25 °C.

Table IX
WLF Coefficients and Free Volume Parameters for Pure Components and Selected Solutions

	ϕ	C_1	C_2, K	f_0/B	$10^4\alpha_f/B$, K^{-1}
dioctyl phthalate	0	3.34	131	0.131	9.9
	0.0214	3.41	114	0.127	11.1
	0.0308	3.76	135	0.115	8.6
	0.157	4.12	184	0.105	5.7
phenyloctane	0	1.39	146	0.312	21.0
	0.0214	1.94	177	0.224	12.7
	0.0274	1.98	174	0.219	12.6
	0.0621	2.46	191	0.177	9.2
	0.140	2.42	182	0.179	9.9
	0.280	2.58	193	0.168	8.7
polybutadiene[a]	1.0	3.48	163	0.125	7.7

[a] Result for a high molecular weight sample of similar microstructure, reported in ref 1.

selected solutions was fitted with the WLF equation:[15]

$$\log \frac{\eta(T)}{\eta(T_0)} = -\frac{C_1(T - T_0)}{C_2 + T - T_0} \qquad (11)$$

A reference temperature T_0 of 25 °C was used in all cases. Values of C_1 and C_2 were established with the data in Tables IV and VI and then used to calculate the free volume parameters:[15]

$$f_0/B = (2.303C_1)^{-1} \qquad (12)$$

$$\alpha_f/B = (2.303C_1C_2)^{-1} \qquad (13)$$

where f_0 is the fractional free volume at the reference temperature, α_f is the thermal expansion factor for free volume, and B is a constant of order unity. Lacking a better alternative, we assume B to be the same for the undiluted polymer and all solutions. The results are given in Table IX.

The fractional free volumes of dioctyl phthalate and polybutadiene at 25 °C are nearly the same, $f_0/B = 0.131$ and 0.125, respectively, the slightly larger thermal expansion coefficient for dioctyl phthalate (Table I) apparently offsetting its slightly higher glass transition temperature. The values for their solutions are not greatly different, as seen in Figure 7. We assume that the fractional free volume, and therefore the monomeric friction coefficient, is essentially independent of concentration for the dioctyl phthalate solutions.

There is a substantial variation of f_0/B with concentration in the phenyloctane solutions (Figure 7). Beginning
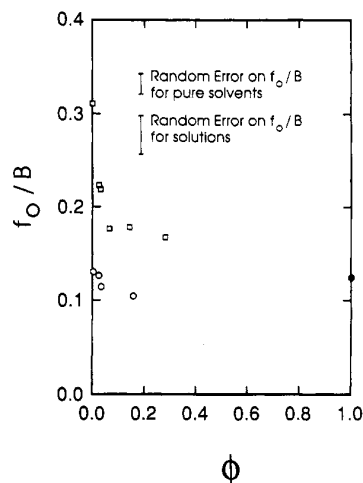

Figure 7. Free volume of solutions at 25 °C obtained from the temperature dependence of viscosity (see text). Circles are DOP solutions; squares are PHO solutions. Error bars are based on ±1 K uncertainty in temperature.

Table X
Free Volume Adjustment Factors Used for the Viscosities of Phenyloctane Solutions

ϕ	$\zeta_0(1)/\zeta_0(\phi)$	ϕ	$\zeta_0(1)/\zeta_0(\phi)$
<0.01	13.0	0.140	10.0
0.0214	12.5	0.280	7.6
0.0274	12.4	0.488	4.8
0.0621	11.7	1.0	1.0

from the very large value for pure phenyloctane, f_0/B falls rapidly over the first few percent of polymer concentration but then changes much more gradually over the remainder. The data are unfortuantely quite limited, but a linear variation beyond $\phi \sim 0.05$ would appear reasonable:

$$f_0/B = 0.184(1 - \phi) + 0.125\phi \qquad (14)$$

We have been unable to account for the apparently rapid change in f_0/B with concentration below $\phi \sim 0.03$: for good solvents $\eta - \eta_s$ would be expected to scale with temperature like η_s alone in this range of concentrations (eqs 6 and 9). Similar behavior of f_0/B has recently been reported by Fujita and Einaga.[16] Perhaps it is somehow related to the progressive unshielding of hydrodynamic interactions in the semidilute range[8] but then it should also have been seen in the dioctyl phthalate solutions. In any case, we have ignored the f_0/B values obtained for ϕ < 0.03 in the free volume adjustment procedure, described below, and use eq 14 at all concentrations.

According to the free volume theory,[15] the fractional free volume and the monomeric friction coefficient are related by

$$\zeta_0 \propto \exp(B/f) \qquad (15)$$

The factor needed to adjust the phenyloctane solution viscosities to the same monomeric friction coefficient as undiluted polybutadiene at 25 °C is therefore

$$\frac{\zeta_0(1)}{\zeta_0(\phi)} = \exp\left[\frac{B}{f_0(1)} - \frac{B}{f_0(\phi)}\right] \qquad (16)$$

where $f_0(\phi)/B$ is given by eq 14 and $f_0(1)/B = 0.125$. Values of $\zeta_0(1)/\zeta_0(\phi)$ used for the various concentrations of polybutadiene in phenyloctane at 25 °C are listed in Table X.

B. Comparison of Viscosities at Constant Monomeric Friction. The polymeric contribution to viscosity,
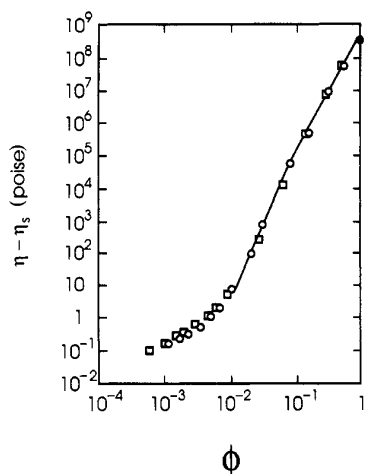
Figure 8. Viscosity of solutions at the free volume of pure polymer at 25 °C (f_o/B = 0.125). Circles are DOP solutions; squares are PHO solutions. Solid lines are eqs 17 and 18 (in text).

Figure 9. Loss modulus of undiluted polymer. Solid curve is a high-frequency extrapolation described in the text (eq 21).

adjusted to the free volume of undiluted polybutadiene at 25 °C, is plotted in Figure 8 as a function of concentration in the two solvents (no adjustment for dioctyl phthalate solutions, adjustments for phenyloctane with the factors in Table X). Adjustment is of course inappropriate in dilute solutions, where $\eta - \eta_s$ is scaled by η_s, and it is at least questionable in the semidilute range, where η_s is still presumed to be the correct scaling (see eqs 9 and 10). However, the adjustment is nearly a constant factor below $\phi \sim 0.1$ anyway, so its effect on any concentration power laws should be relatively unimportant.

Whether adjusted for free volume or not, values of $\eta - \eta_s$ at the lowest concentrations approach direct proportionality to ϕ in both solvents but are displaced from one another because η_s and [η] are different. Interestingly, the adjusted results very quickly become similar for the two solvents at higher concentrations, and above 1% polymer their viscosity–concentration relationships are indistinguishable.

The behavior at high concentrations is described quite well by the same power law for both solvents:

$$\eta = 5.3 \times 10^8 \phi^{3.6} \quad \text{(P)} \qquad (17)$$

which was obtained by a least-squares fit to the dioctyl phthalate data above ϕ = 0.1. This equation, shown by the upper solid line in Figure 8, is also reasonably consistent with the adjusted phenyloctane data above ϕ = 0.1.

The viscosity decreases more rapidly with dilution for concentrations below $\phi \sim 0.1$. The adjusted data in the range 0.01 < ϕ < 0.10 can also be fitted fairly well by a single power law, but with a larger exponent than in eq 17. The lower solid line drawn in Figure 8 corresponds to

$$\eta = 7.6 \times 10^9 \phi^{4.7} \quad \text{(P)} \qquad (18)$$

The unadjusted phenyloctane data for the same range give essentially the same power law exponent but a different prefactor.

$$\eta = 7.9 \times 10^8 \phi^{4.8} \quad \text{(P)} \qquad (19)$$

Departures from these expressions and differences between iso-free-volume viscosities in the two solvents commence with further dilution in the same range of concentrations, $\phi \sim 0.01$, as noted earlier.
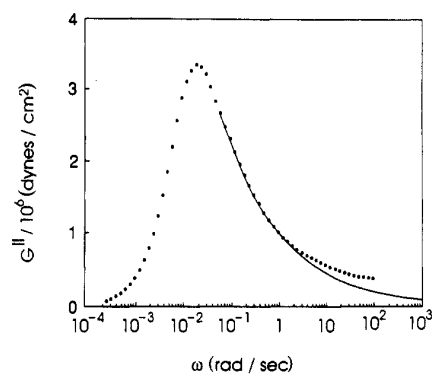
Analysis of Elastic Properties

The plateau modulus for the undiluted polymer was determined from the area under the terminal loss peak:[15]

$$G^\circ_N = \frac{2}{\pi} \int_{-\infty}^{\infty} G''(\omega) \, d \ln \omega \qquad (20)$$

The data at 25 °C are plotted in Figure 9. The terminal response was separated from the transition response by fitting $G''(\omega)$ for $3\omega_m \leq \omega \leq 75\omega_m$ to a power law

$$G'' = 4.2 \times 10^6 (\omega/\omega_m)^{-0.345} \qquad (21)$$

and then extrapolating to higher frequencies. The area under the solid curve in Figure 9 then provides the plateau modulus for polybutadiene, G°_N = 1.15 × 10⁷ dyn/cm². This value agrees with the result obtained by Raju et al.[17] for a polybutadiene of somewhat lower molecular weight, using a different extrapolation procedure. The same authors noted that G''_m is in fact directly proportional to G°_N for nearly monodisperse linear polymers of many species. For the sample here

$$G^\circ_N = 3.24 G''_m \qquad (22)$$

in which the proportionality constant is somewhat different from the earlier value[17] of 3.56. The entanglement molecular weight

$$M_e \equiv \rho \phi RT/G^\circ_N \qquad (23)$$

is 1900 for undiluted polybutadiene at 25 °C.

The product of G°_N and J°_e is a measure of the breadth of the terminal relaxation spectrum[10] and a strong function of sample polydispersity for linear polymers. With J°_e for the undiluted polymer (Table VII)

$$J^\circ_e G^\circ_N = 1.8 \qquad (24)$$

which is consistent with the expected near monodispersity of the sample. Likewise, from the above

$$J^\circ_e G''_m = 0.57 \qquad (25)$$

Values of $J^\circ_e G''_m$ for the solutions are listed in Table VII. They strongly suggest that the breadth of the terminal spectrum is unchanged by dilution, a result noted in earlier work as well.[17]

Values of G''_m and J°_e are shown in Figure 10 as functions of concentration in phenyloctane and dioctyl phthalate. Their concentration dependences are well described by power laws that are essentially the same in both solvents:

$$G''_m = 3.5_5 \times 10^6 \phi^{2.29} \qquad (26)$$

$$J^\circ_e = 1.6 \times 10^{-7} \phi^{-2.31} \qquad (27)$$

We conclude that the plateau modulus of the solutions is
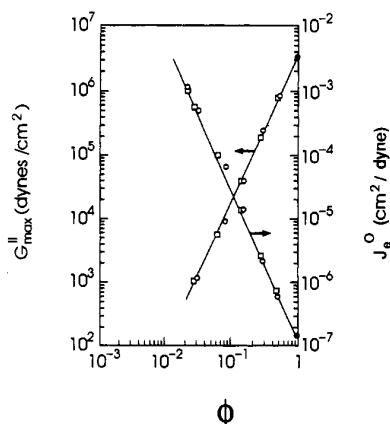
Figure 10. Concentration dependence of the loss modulus maximum and the recoverable compliance for solutions. Circles are DOP solutions; squares are PHO solutions. Lines are power laws described in the text (eqs 26 and 27).

independent of solvent power and proportional to $\phi^{2.3}$ from the undiluted state down to $\phi \sim 0.02$. The entanglement molecular weight (eq 23) is also independent of solvent power:

$$M_e = 1900\phi^{-1.3} \qquad (28)$$

Discussion

A. Viscosity. Beyond about 1% polymer we find two power law regimes of concentration dependence for the viscosity, one from $\phi \sim 0.01$ to 0.10 (eqs 18 and 19) and the other from ~ 0.10 to 1.0 (eq 17). That result is seen more directly with the dioctyl phthalate solutions, where free volume adjustment is unnecessary, but it also shows up in the adjusted viscosities in phenyloctane (see Figure 8).

For concentrated solutions at constant free volume, the viscosity has been found to vary according to[5]

$$\eta(\phi) = K_0\phi M[M/M_c(\phi)]^{2.4} \qquad M > M_c(\phi) \qquad (29)$$

where K_0 depends on the polymer species and the reference state and $M_c(\phi)$ is the characteristic molecular weight for the onset of entanglement effects in the viscosity. For undiluted polybutadiene of this microstructure,[1] $M_c = 6380$. If $M_c(\phi) = M_c/\phi$, as reported in many earlier studies[5,10] then ϕ_c, the characteristic concentration, would be $6.38 \times 10^3/9.25 \times 10^5 = 0.0069$ for this polymer. That value seems plausible since it is near the break in the viscosity–concentration relationship in the two solvents (Figures 5 and 6). On the other hand, if M_c has the same concentration dependence as M_e, as is commonly assumed, then $\phi_c = (6.38 \times 10^3/9.25 \times 10^5)^{1/1.3} = 0.022$, based on the exponent in eq 28. This value of ϕ_c, however, seems too large, again judged by the data in Figures 5 and 6. Moreover, the observed concentration exponent of 3.6 (eq 17) agrees somewhat better with 3.4 than 4.1, the values obtained from eq 29 using $M_c \propto \phi^{-1}$ and $\phi^{-1.3}$, respectively. It would seem, therefore, that M_c/M_e is not independent of the polymer concentration.

This appears to conflict with earlier work on polybutadiene solutions,[6] in which the iso-free-volume viscosity was found to be proportional to $\phi^{4.0}$ above $\sim 2\%$ polymer. The molecular weights were smaller in that study, however, so perhaps the change in exponent near $\phi = 0.1$, as noted here, would have been less obvious. Indeed, if we simply force a single power law through all data from $\phi = 0.01$ to 1.0 we obtain $\eta \propto \phi^{4.1}$, giving a poorer overall fit, of course,

but an exponent near the earlier value.[6] Thus, the earlier conclusion that $M_c(\phi)$ is directly proportional to $M_e(\phi)$ may not be valid.

Early scaling ideas[12] assumed that entanglement would occur where the coils start to overlap (i.e., $\phi_c \cong \phi^*$). Indeed, this is very nearly the case for our dioctyl phthalate solutions, as $\phi^* = 0.0069$ and $\phi_c \cong 0.01$. However, the phenyloctane solutions have $\phi^* = 0.0025$, which is much smaller than ϕ_c. This simply means that the tube diameter is larger than the screening length, giving a regime of concentration that is semidilute but not entangled.[4] As expected from the two-parameter scaling theory,[13] the width of the semidilute unentangled regime increases with solvent quality because the ratio of lengths a/ξ increases.

Between 1% and 10% polymer, which we take to be the entangled semidilute range, the concentration exponent is ~ 4.7 in both solvents (eqs 18 and 19), whether or not free volume adjustments are made. As seen in Table VIII, the magnitude of this exponent, as well as the observed independence of solvent power, is predicted by the two-parameter scaling theory of Colby and Rubinstein.[13] The actual coincidence of exponents is fortuitous, however. Neither solvent here corresponds to one of the limiting cases of solvent quality. At the Θ condition and the good solvent limit, the predicted concentration exponents for viscosity are quite different (see Table VIII), with the Θ solvent giving a considerably stronger concentration dependence in the semidilute regime.

The fact that Θ solvents show a stronger concentration dependence of viscosity than good solvents is evident in many studies in the literature.[18-26] By way of example, we consider the data of Adam and Delsanti[22,23] for polystyrene in a good solvent (benzene) and at the Θ condition (cyclohexane at 35 °C). The good solvent data obeyed the de Gennes scaling prediction, as the viscosity data for different molecular weights reduced to a common power law (with $x = 4.1$) when plotted against ϕ/ϕ^*. The Θ solvent data clearly did not obey the single-parameter scaling but are quite consistent with the two-parameter scaling idea:[13] the viscosity data for different molecular weights collapse onto a common power law when plotted as $\eta/M^{2/3}$ versus ϕ/ϕ^*. The concentration exponent for that case is $x = 5.1$, which is clearly larger than for good solvent and in excellent agreement with the two-parameter scaling prediction (see Table VIII).

B. Elastic Response. Results for the elastic properties are relatively unambiguous, at least in the sense that they are not subject to the uncertainties of a free volume adjustment. Both G''_m and J°_e are independent of thermodynamic interactions (Figure 10), and each is well described by a single power law in concentration from $\sim 2\%$ polymer to the undiluted state (eqs 26 and 27). The concentration exponent, 2.3 ± 0.1 for G''_m and $(J^\circ_e)^{-1}$, is consistent with an earlier value of 2.25, obtained in several other solvents for $\phi > 0.1$.[17] There is no suggestion of a change in exponent near $\phi = 0.1$, such as found in the viscosity data.

Thermodynamic effects should vanish at high concentrations, so the agreement between data obtained for concentrated solutions in dioctyl phthalate and phenyloctane is not surprising. According to the simplest arguments, based on the concentration of binary chain contacts,[10] $G^\circ_N \propto \phi^2$ is expected at high concentrations, and an exponent near 2.0 is indeed found for polystyrene ($G''_m \propto \phi^{2.09}$ (ref 27) and $(J^\circ_e)^{-1} \propto \phi^{2.13}$ (ref 28); see ref 30). Why the exponent is larger for polybutadiene, and for other polymers as well,[17] remains a puzzle. The plateau modulus was not measured directly, however, so the

possibility of some systematic error must be considered. The exponent obtained from $G''_m(\phi)$ relies on the assumption of direct proportionality between $G°_N$ and G''_m, and $G''_m/G°_N$ could conceivably vary with concentration. The data at high frequencies ($\omega > \omega_m$) are too limited to apply eq 20 and thus test the $G°_N \propto G''_m$ assumption for the solutions. There is a similar uncertainty about the exponent from $J°_e(\phi)$, since the terminal spectrum breadth $G°_N J°_e$ could conceivably vary with concentration. Indeed, the fluctuation theory of Doi[29] actually predicts the terminal spectrum breadth to increase as concentration is lowered but in such a way that the product $J°_e G''_m$ remains constant. Thus the observed concentration exponents for G''_m and $(J°_e)^{-1}$ may overestimate the true exponent for $G°_N$. Aside from these concerns, however, the concentration exponent for elastic response does appear to differ somewhat with polymer species, and this difference seems unrelated to the thermodynamic interactions between solvent and polymer. Perhaps it somehow depends on the absolute magnitude of $G°_N$, as discussed previously.[30]

The two-parameter scaling theory[13] predicts a power law in concentration for $G°_N$ in the semidilute range:

$$G°_N \simeq kT/a^2\xi \propto \phi^\alpha \tag{30}$$

However, the predictions for the exponent α, 2.31 in the good solvent limit ($a \propto \xi \propto \phi^{(\beta+1)/3\beta}$, with $\beta = 0.764$)[3,11] and 2.33 at the Θ condition ($a \propto \phi^{-2/3}$ and $\xi \propto \phi^{-1}$),[13] are too close to be distinguished in our experiments. Indeed, $G''_m/\phi^{2.31}$ and $J°_e\phi^{2.29}$ show essentially random scatter with no suggestion of systematic departures in either solvent, even at the lowest concentrations. The modulus for semidilute solutions of polystyrene, the only other polymer studied extensively, is generally consistent with the polybutadiene results. Adam and Delsanti[22,23] determined a modulus, probably akin to $(J°_e)^{-1}$, from stress relaxation following steady shearing flow in a good solvent (benzene) and at the Θ condition (cyclohexane at 35 °C). The values were independent of molecular weight and similar in magnitude for the two solvents over the experimental range of 1.5–9% polymer. A single power law with a concentration exponent of ~2.4 would comfortably accommodate the results in both solvents. Osaki et al.[31] found $G°_N \propto \phi^{2.4}$ from 2% to 8% polystyrene in a good solvent (Arochlor 1248) and similar values over the same range in a near-Θ solvent (dioctyl phthalate).[32] They also pointed out that their correlation extrapolated to a value of $G°_N$ for undiluted polystyrene that was too large, implying a weaker dependence on concentration in the concentrated regime. That is indeed consistent with the smaller exponent ($G''_m \propto \phi^{2.09}$) found for polystyrene solutions above ~10% concentration.[30] Thus, in contrast with the polybutadiene results reported here, there may be a slight difference in concentration exponent between the semidilute and concentrated range for polystyrene. The only indication of thermodynamic effects on the modulus are the results of Takahashi et al.[33] They found clearly different power laws for polystyrene in the semidilute range, $(J°_e)^{-1} \propto \phi^{2.1}$ in a good solvent and $(J°_e)^{-1} \propto \phi^{2.3}$ in a near-Θ solvent. Aside from those data, there is no evidence that solution thermodynamics has a bearing on elastic behavior in any regime other than dilute solution.

Table XI
Intrinsic Viscosity for Polybutadiene Sample C25
(M = 548 000) in Selected Solvents at 25 °C

solvent	[η], dL/g	$V_s{}^b$
dioxane[a]	1.47	85.5
tetrahydrofuran	4.41	81.4
cyclohexane	3.85	108.5
methylnaphthalene	3.61	142.1
phenyloctane	3.04	222
phenyltetrahydronaphthalene	2.68	230
squalene	2.31	479

[a] Calculated value at the Θ condition ($\Theta = 26.5$ °C in dioxane) for this molecular weight.[34] [b] Molar volume of the solvent, mL/(g mol).
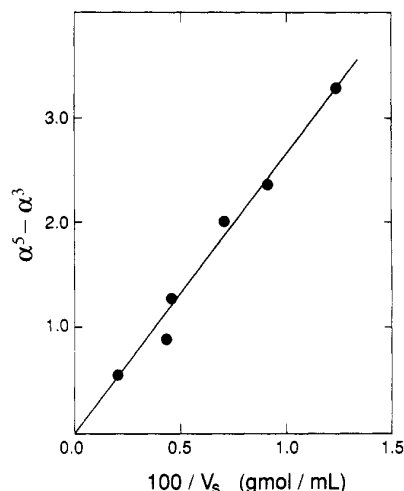
Figure 11. Coil expansion of polybutadiene (M = 548 000) in various solvents at 25 °C. Results are plotted in the form suggested by eq A1.

Appendix: Solvent Selection and Dilute Solution Viscometry

Intrinsic viscosity measurements were used to select the thermodynamically good solvent for the study. The ratio $[\eta]/[\eta]_\Theta$ reflects the expansion of coil dimensions in dilute solution and thus provides a simple measure of the excluded volume interaction. Values of $[\eta]$ in several solvents for one polybutadiene sample,[1] with $M = 5.48 \times 10^5$, are given in Table XI. Dioxane is a Θ solvent at 26.5 °C,[34] and tetrahydrofuran and cyclohexane are typical good solvents but much too volatile for our purposes. The remaining solvents are hydrocarbons of higher molecular weight, listed in order of decreasing volatility. Molecular volume V_s increases down the list, and $[\eta]$ decreases.

The latter observation may not be entirely coincidental, since it turns out to be roughly consistent with expectations based on excluded volume theory. Thus, for example, Flory's expression for the expansion factor $\alpha = R_G/(R_G)_\Theta \sim [[\eta]/[\eta]_\Theta]^{1/3}$ can be written as[35]

$$\alpha^5 - \alpha^3 = AM^{1/2}/V_s \tag{A1}$$

where A would be a constant for a series of solvents having the same thermodynamic interaction parameter χ with the polymer segments. Accordingly, $\alpha^5 - \alpha^3$ for the polymer should be inversely proportional to V_s. This is tested in Figure 11, using $\alpha^3 = [\eta]/[\eta]_\Theta$ and $[\eta]_\Theta$ for dioxane at ~26.5 °C. There is some scatter, as might be expected from the assumptions embodied in eq A1, but the data are nevertheless fitted reasonably well by a straight line through the origin. Since molar volume and volatility are closely

Table XII
Results of Dilute Solution Viscometry for Polybutadiene in Phenyloctane and Dioctyl Phthalate[a]

sample	$10^{-4}M$	$[\eta]$, dL/g	k_H
	Phenyloctane at 25 °C		
B1	7.09	0.80	0.44
B2	13.0	1.24	0.45
C25	54.8	3.04	0.40
B4	92.5	4.51	0.46
	Dioctyl Phthalate at 21.5 °C		
CDS-30	4.6	0.320	0.40
B1	7.09	0.418	0.44
B2	13.0	0.583	0.62
B3	35.5	1.036	0.73
C25	54.8	1.320	0.72
B4	92.5	1.619	0.77
	Dioctyl Phthalate at 16.5 °C		
CDS-30	4.6	0.308	0.42
B1	7.09	0.405	0.40
B2	13.0	0.587	0.49
B3	35.5	1.000	0.75
C25	54.8	1.227	0.81
B4	92.5	1.47	0.95

[a] Molecular and microstructural data for the samples are given in more detail in ref 1. Vinyl contents range from 7 to 10%, and $\bar{M}_w/\bar{M}_n$ is less than 1.1 in all cases.

related properties for hydrocarbon liquids, we abandoned the search for better candidates and settled upon phenyloctane as the best compromise of low volatility and large coil expansion.

Several low-vinyl polybutadienes, prepared by anionic polymerization, were used to establish Mark–Houwink–Sakurada equations for solutions in phenyloctane and dioctyl phthalate. The molecular characteristics of these samples are given elsewhere.[1] The solvents were sparged with nitrogen to remove volatile impurities but were otherwise used as received. Elimination of the sparging step for dioctyl phthalate, which served to dry the solvent, led to erratic results. Flow times were determined in Ubbelohde viscometers, equipped with automatic timers. Serial dilution was used to obtain relative viscosities for several concentrations in the dilute range. Measurements were made at 25 °C for the phenyloctane solutions and at 21.5 °C and 16.5 °C for the dioctyl phthalate solutions. The resulting values of intrinsic viscosity and Huggins coefficient are given in Table XII.

Intrinsic viscosity versus molecular weight is shown in Figure 12 for the three data sets. The resulting Mark–Houwink–Sakurada equations, $[\eta] = KM^\alpha$, are given as eqs 1 and 2 of the text for polybutadiene in phenyloctane at 25 °C and in dioctyl phthalate at 21.5 °C, respectively. The expression for dioctyl phthalate solutions at 16.5 °C is

$$[\eta] = 1.11 \times 10^{-3}M^{0.529} \quad (\text{dL g}^{-1}) \qquad (A2)$$

in which the exponent suggests that the Θ condition is only a few degrees below this temperature.

The Burchard–Stockmayer–Fixman extrapolation procedure[36,37] was used to estimate K_Θ, the prefactor at true Θ, for polybutadiene in dioctyl phthalate. The results were $K_\Theta = 1.50 \times 10^{-3}$ dL g^{-1} from the data at 16.5 °C and $K_\Theta = 1.51 \times 10^{-3}$ dL g^{-1} from the data at 21.5 °C. These values were used to calculate the characteristic ratio C_∞ for polybutadiene at the Θ condition in dioctyl phthalate.[38] The result, $C_\infty = 4.6 \pm 0.2$, is considerably smaller than the values obtained from data in dioxane solutions[34,39] at the Θ condition, $C_\infty = 5.5 \pm 0.2$, and the value in the melt state, $C_\infty = 5.6 \pm 0.3$, obtained by neutron scattering.[40,41] The potential for specific solvent effects on "un-
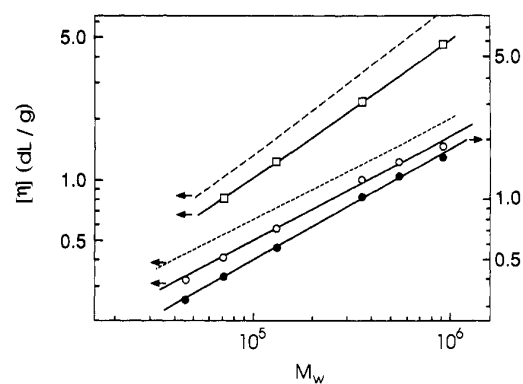
Figure 12. Intrinsic viscosity for polybutadiene solutions. Squares are PHO solutions at 25.0 °C; filled circles are DOP solutions at 21.5 °C; open circles are DOP solutions at 16.5 °C. Solid lines are eqs. 1, 2, and A2 in the text. The dotted line is for dioxane solutions at $\Theta = 26.5$ °C.[34] Dashed line is for tetrahydrofuran solutions at 25.0 °C.[1]

perturbed" dimensions is well recognized, and the existence of such effects has been amply demonstrated in the case of polystyrene.[42–44] Polybutadiene would appear to be unusually susceptible in this regard.

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