Hydrodynamic Scaling of Viscosity and Viscoelasticity of Polymer Solutions, Including Chain Architecture and Solvent Quality Effects

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ABSTRACT: This paper examines the dependence of polymer solution viscosity η and higher viscoelastic parameters (e.g., $\dot{\gamma}_r$, J_e^0) on polymer concentration, molecular weight, chain architecture, and solvent quality. For solutions of linear chains, a transition from a solutionlike (stretched-exponential) to meltlike (power-law) dependence of η on c or M occurs at $c[\eta] \gg 1$, and sometimes $c[\eta] > 100$. The hydrodynamic scaling description of polymer transport coefficients remains applicable to concentrations far above the overlap concentration $c[\eta] \approx 1$. Star polymers remain in the solutionlike regime at c and M far above the c and M at which linear chains show a transition to meltlike behavior. Other viscoelastic parameters, notably $\dot{\gamma}_r$ and J_e^0, have the same c and M dependences (stretched exponential at lower (c, M), power law at larger (c, M)) that η does, with the same solutionlike–meltlike transition concentration for all three parameters. If η for a single polymer in a series of solvents is fit to $\exp(\alpha c^\nu)$, the several-fold variation in α at fixed M is almost entirely accounted for by the dependence of α on solvent quality, as expressed by the chain expansion parameter α_η. Experiment is consistent with the $\alpha \sim \alpha_\eta^3$ here shown to be predicted by the hydrodynamic scaling model (Phillies, G. D. J. *Macromolecules* **1987**, *20*, 558).

Introduction

The objective of this paper is to apply the hydrodynamic scaling analysis[1–5] of polymer dynamics to viscoelastic properties of polymer solutions. Properties treated here include the zero-shear viscosity η, characteristic shear rate $\dot{\gamma}_r$, and steady state compliance J_e^0. The dependence of these properties on system variables including polymer concentration c, molecular weight M, chain architecture (linear and star), and solvent quality is examined.

Results here represent substantial extensions of our previous work, which focused on the dependence of zero-frequency transport coefficients for linear chains in good solvents. In an earlier paper, Phillies and Peczak[2] analyzed studies of η,[6–10] sedimentation coefficient s,[11–21] and rotational diffusion coefficient D_r.[22–26] These data were shown to be accurately described by stretched exponentials in polymer concentration, namely

$$\eta = \eta_0 \exp(\alpha c^\nu) \qquad (1)$$

$$s = s_0 \exp(-\alpha c^\nu) \qquad (2)$$

and

$$D_r = D_{r0} \exp(-\alpha c^\nu) \qquad (3)$$

Here ν and α are a scaling exponent and scaling prefactor different for each system and property, s_0 and D_{r0} are zero-concentration limits of s and D_r, and η_0 is the solvent viscosity.

Equations 1–3 were inspired by the earlier observation that the polymer self-diffusion coefficient D_s and the diffusion coefficient D_p for mesoscopic probes in polymer solutions both[1,5] usually follow stretched exponentials

$$D = D_0 \exp(-\alpha c^\nu) \qquad (4)$$

in c. Equations 1–4 almost always describe data well throughout the dilute and semidilute regimes, including data that had previously been identified as following scaling (power-law) behavior in c.

In a few systems at very large η, Phillies and Peczak[2] noted that eq 1 was not followed well by a few data points; the highest viscosity data instead appeared to follow a power law in c. The possible significance of power-law behavior was clarified by more recent reanalysis of η and D_s in several systems having very large c and/or M. It was found[3] that measurements of η and D_s sometimes[27–30] but not always[31–33] show a transition at very large c and M from stretched-exponential to power-law dependences on concentration or molecular weight. To label these behaviors in a model-independent way, we[4] denoted the stretched-exponential (in c and M)

$$\eta = \eta_0 \exp(\alpha c^\nu M^\gamma) \qquad (5)$$

regime as "solutionlike", and the power-law (in c and M)

$$\eta = \bar{\eta} c^\nu M^\gamma \qquad (6)$$

regime as "meltlike". In almost all cases, data permitted determination of the c-dependence or the M-dependence of η, but not both at once in a single system. Measurements on hydroxypropylcellulose–water show[4] that in at least some systems the transition between solutionlike and meltlike behavior is extremely sharp, with no indication of a bridging or transition region.

When the solutionlike–meltlike transition was found[3] at all, it became apparent only for η/η_0 or $D_0/D \gg 10^3$. Reference 3 was unable, based on the data it reanalyzed,[27–33] to provide a more precise criterion for locating the solutionlike–meltlike boundary in an a priori way. For systems reconsidered in ref 3, a transition to meltlike behavior was only seen unambiguously if $M \geq 1 \times 10^6$.

We previously presented a derivation[34] of eq 4 and exhibited a no-free-parameter calculation[35,36] of the numerical value of the scaling prefactor α for polymer

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Table 1. Parameters for Fits of Measured Viscosities Below or Above the Transition Molecular Weight M_t to a Stretched Exponential (Eq 7) or Power Law (eq 8), Respectively, in Polymer Molecular Weight

system	c	η_0	β	γ	% RMSE[a]	$\bar{\eta}$	y	% RMSE[a]
polystyrene–DOP[37]	30	0.57	0.93	0.19	10	1.9×10^{-13}	3.2	11
	40	0.58	1.81	0.155	2	2.6×10^{-12}	3.23	16

[a] RMSE, root-mean-square fractional error in the data, expressed as a percent.

self-diffusion. These calculations were based on the predominance of hydrodynamic over topological (chain-crossing constraint) forces in polymer solutions. It is rationally possible to argue that hydrodynamic interactions are important for unentangled chains, but that when chains approach interpenetration (i.e., if $c[\eta] \geq 1$ or so), nonhydrodynamic entanglement interactions replace interchain hydrodynamic interactions as the dominant forces. By this argument, the hydrodynamic scaling model would perhaps be applicable in dilute solution but would cease to be applicable when the overlap concentration $c[\eta] \approx 1$ was approached. To test this rational argument, it is useful to delineate more precisely the phenomenological conditions under which a solutionlike–meltlike transition is found.

In the following, we first examine how literature data on the zero-shear viscosity, the characteristic shear rate for appreciable shear thinning, and the steady-state compliance are related to polymer concentration, molecular weight, and chain architecture. We analyzed η of linear chains, finding solutionlike behavior at smaller c and M and meltlike behavior at larger c and M. The differential effect of linear and star architecture on η is treated. Hydrodynamic scaling analysis is applied to time-dependent viscoelastic parameters $\dot{\gamma}_r$ and J_e^0. Finally, the effect of solvent quality on η of concentrated polymer solutions is noted. The internal consistency in the behavior of different transport coefficients is discussed.

Solutionlike–Meltlike Transition for Linear Chains

This section examines η in solutions of linear chains. The focus is on studies that extend systematically from dilute solution to very large concentrations or that extend at fixed elevated concentration from small to large polymer molecular weight. At sufficiently large $c[\eta]$, a solutionlike–meltlike transition is often but not always seen in these data sets. The objective of the following analysis is to locate the transition, when it occurs, and to identify variables correlated with the transition's location.

Gupta and Forsman[37] determined the zero-shear viscosity of linear polystyrenes in di-2-ethyl hexyl phthalate (DOP) at concentrations of 30 and 40% at 25 °C. As seen in Figure 1, their data are consistent with a solutionlike regime for $M < 1 \times 10^5$ Da and $\eta/\eta_0 < 1 \times 10^3$ or 1×10^4 (respectively, by concentration) and a meltlike regime at higher M. Parameters (Table 1) were obtained by nonlinear least-squares fits of

$$\eta = \eta_0 \exp(\beta M^{\gamma}) \tag{7}$$

and

$$\eta = \bar{\eta} M^{y} \tag{8}$$

to the data below or above the transition molecular weight, respectively. Solid lines in Figure 1 correspond to these fits. The rationale for the choice of transition molecular weight M_t is apparent from Figure 1; fits that assigned more or fewer points to the solutionlike or meltlike regimes have grossly worse mean-square errors in the fits than the 11–16% error of fits in Figure 1.

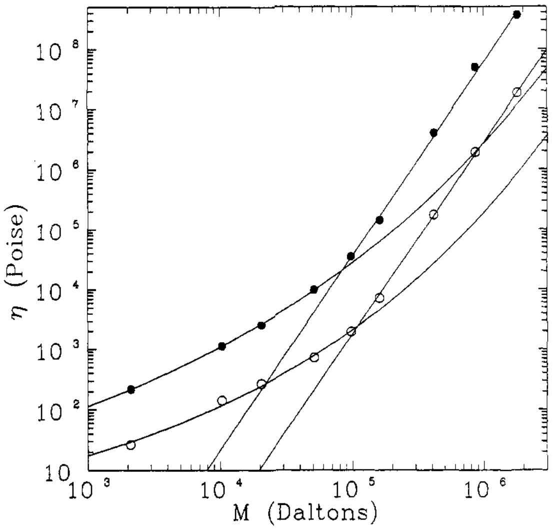

Figure 1. Viscosity[37] of polystyrenes in di-2-ethyl hexyl phthalate at concentrations of 30 (open circles) and 40% (closed circles). Fits (parameters in Table 1) are to stretched exponentials (smooth curves) and power laws (straight lines) in M.

Within the resolution of the data, the transition from one regime to the other is abrupt. There is no indication (note especially the 30% data) of a crossover region separating the two regimes. Each data point lies on or near to its associated line, to within the apparent scatter in the data points around the line in question. In contrast, if data points near the transition had lain on a smooth line that was clearly dissociated from both the power law and the stretched exponential, as was not the case here, there would have been a clear transition regime in the observed data. Furthermore, lines corresponding to eqs 7 and 8 cross each other but are not tangent at contact. The lack of tangency implies that the transition is continuous, but not analytic, i.e., $d\eta/dc$ is not apparently continuous at the transition.

How is the transition here related to the overlap concentration c^*? To pursue this question, an estimate of c^* is necessary. For polystyrene–DOP, c^* can be obtained from data of Colby et al.[27] Namely, for 925 000-Da linear polystyrene in DOP, Colby et al.[27] reported $[\eta]$ at 16.5 and 21.5 °C; extrapolation to the 25 °C of Gupta and Foresman's measurements indicates $[\eta] \approx 0.18$ L/g, so $c^* = 1/[\eta] \approx 5.6$ g/L. 25 °C is rather more remote from the θ temperature of polystyrene–DOP than is the 21.5 °C at which Colby et al.[27] reported $[\eta] \sim M^{0.549}$. Using an approximate $[\eta] \sim M^{0.6}$ for 25 °C, at the transition molecular weight 1×10^5 of Gupta and Forsman, $c^* \approx 20$ g/L. For Figure 1, at the location (c_t, M_t) marking the solutionlike–meltlike transition, the concentration c_t is thus $c_t[\eta] \equiv c/c^* \approx 15–20$ in dimensionless units.

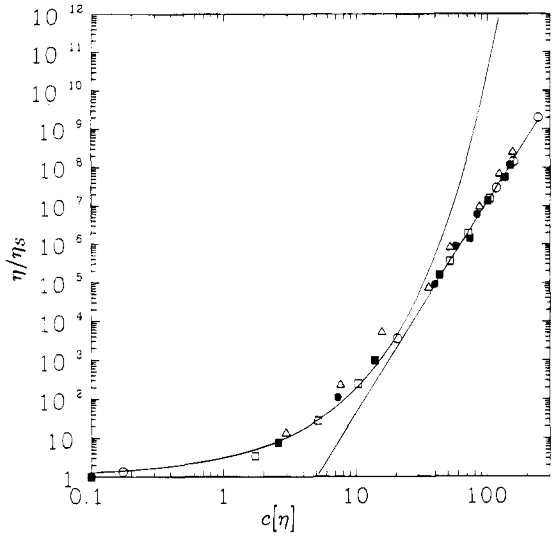

Figure 2. Viscosity[39] of polybutadiene–methylnaphthalene and fits to stretched exponentials (smooth curves) and power laws (straight lines). Samples had $M_w/M_n \leq 1.1$ and M of (a) 38 (○), (b) 76 (●), (c) 100 (□), (d) 150 (■), and (e) 240 (△) kDa.

Dreval et al.[38] reviewed η from a long series of references not readily available in the Western literature. We consider these seriatim:

Malkin et al.[39] studied polybutadiene (M of 38, 76, 100, 150, and 240 kDa; $M_w/M_n \leq 1.1$) in methylnaphthalene at 24 °C; the concentration range with concentration in dimensionless units was $0.1 \leq c[\eta] \leq 200$. The data and our fits appear in Figure 2; fitting parameters are in Table 2. As seen in the figure, η follows a stretched exponential in c (i.e., the samples are in the solutionlike regime) for $\eta/\eta_0 \leq 10^4$ and $c[\eta] \leq 25$. There is a clear transition from a stretched-exponential (smooth curve) to a power-law (straight line) dependence of η on c at $c[\eta] \approx 25$ and $\eta/\eta_0 \approx 10^4$. For the 240-kDa polymer, two points near $c[\eta] \approx 10$ do not agree well with either curve. For concentrations $c[\eta] > 25$ and $\eta/\eta_0 \geq 10^4$, meltlike behavior is evident. At the transition, the curve and line do not quite touch, but each data point is evidently associated with one line or the other. The gap between the lines is comparable in size to the scatter in the data; there is no clear sign of data points bridging between the lines.

We fit data for all M (including the $c = 0$, $\eta/\eta_0 = 1$ point) simultaneously to one of our two functional forms, eq 5 or 6, while forcing $\gamma = 0$. Fitting data on polymers having a variety of molecular weights, while using a single α, ν pair, is appropriate only if the dimensionless concentration units completely capture the molecular weight dependence of η. As argued by Dreval,[38] to good approximation, plotting data against $c[\eta]$ reduces η/η_0 to a single curve, implying that the capture is approximately complete and our procedure is appropriate. The procedure is evidently less satisfactory for the 240-kDa polybutadiene than for the lower-M materials.

Measurements on samples below the transition concentration c_t were fit to eq 5; measurements on samples above c_t were fit to eq 6. The resultant fitting parameters depend on c_t. To determine the best value of c_t, we fit data for $0 \leq c \leq c_t$ to eq 5 and data for $c_t \leq c \leq \infty$ to eq 6, while varying our choice of c_t. Increasing or reducing c_t from its optimal value rapidly increases the root-mean-square error in the fit to one or the other of the two equations. The optimal c_t is consistent with visual inspection of the figure. This general fitting process, including a systematic variation of c_t or M_t as appropriate to find its optimal value, was used throughout this paper. In the following, parameters are reported for the optimal c_t or M_t.

Mochalova et al.[40] reported η/η_0 against $c[\eta]$ for a series of polyisobutylenes ($3.8 \leq M \leq 3700$ kDa) in CCl_4 at 25 °C. Their data appear in Figure 3 with fit parameters in Table 2. Measurements on polymers of

Table 2. Parameters from Fits of Viscosities to a Stretched Exponential (Eq 5) or Power Law (Eq 6) in Polymer Concentration[a]

system	c_t[c]	η_0	α	ν	% RMSE[b]	$\bar{\eta}$	ν	% RMSE[b]
polybutadiene–[39]methylnaphthalene	25	1[d]	1.12	0.67	28	1.39×10^{-4}	5.5	32
polyisobutadiene–CCl_4[40]	35	1[d]	0.993	0.69	27	5.97×10^{-4}	5.20	39
polyisobutylene–[41–43]								
decalin	80	1[d]	1.36	0.56	33	1.9×10^{-8}	7.5	24
cyclohexane	80	1[d]	1.12	0.64	28	2.0×10^{-10}	8.4	15
CCl_4	>300	1[d]	2.06	0.46	49			
isooctane	>200	1[d]	2.51	0.45	28			
toluene	150	1[d]	2.66	0.45	50			
polystyrene–[41–43]								
ethylbenzene	≥60	1[d]	0.76	0.76	30			
3:1 ethylbenzene–decalin	≥50	1[d]	0.76	0.78	27			
1:1 ethylbenzene–decalin	≥50	1[d]	0.70	0.82	18			
1:3 ethylbenzene–decalin	≥40	1[d]	0.84	0.82	21			
decalin	≥20	1[d]	1.34	0.80	47			
CCl_4	≥50	1[d]	0.50	0.90	34			
ethyl acetate	≥25	1[d]	1.07	0.86	27			
benzene–[44]								
1240-kDa polystyrene	≥8–10 g/dL	5.6 mP	2.26	0.566	13			
4000-kDa polystyrene	≤3 g/dL	5.6 mP				10.9	4.43	1.6
cyclohexane–[44]								
310-kDa polyisoprene	≥10 g/dL	8.2 mP	1.69	0.63	8.3			
940-kDa polyisoprene	3–4 g/dL	8.2 mP	2.56	0.72	10	2.03	4.48	4.2
960-kDa polybutadiene	1.5–2 g/dL	8.2 mP	3.82	0.78	13	21.7	4.73	10
xanthan–0.1 M NaCl[45]	7	1[d]	0.97	0.83	6.7	5×10^{-2}	3.91	22
tetradecalin–[51]								
polyisoprene ($f = 2$)	<0.02 g/mL					3.35×10^{8}	4.86	11
polyisoprene ($f = 4$)	>0.33 g/mL	0.02	40.2	0.56	9			
polyisoprene ($f = 6$)	>0.33 g/mL	0.02	32.2	0.574	8			

[a] In both fits $\gamma = 0$ is forced to eliminated the dependence on M. [b] RMSE, root-mean-square fractional error in the data, expressed as a percent. [c] c_t in dimensionless units $c_t[\eta]$ unless elsewise specified. [d] Data and fit are to η/η_0, η_0 being the solvent viscosity.

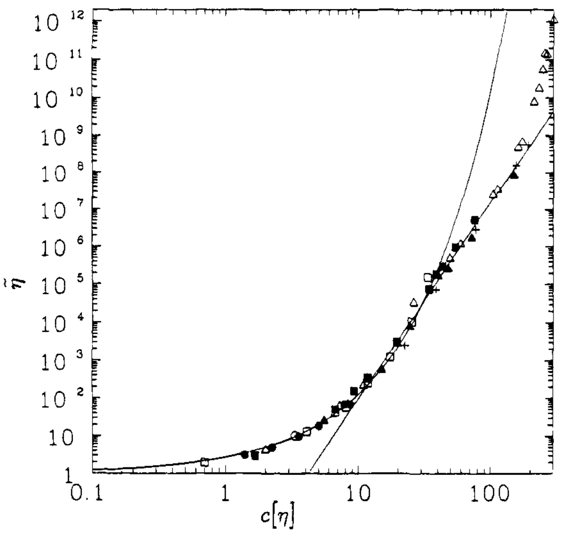

Figure 3. Viscosity[39] of polyisobutylenes in CCl_4 and fits to stretched exponentials (smooth curves) and power laws (straight lines). Samples had M of (a) 3.8 (○), (b) 21.4 (●), (c) 142 (□), (d) 760 (■), (e) 1200 (△), (f) 1800 (▲), and (g) 3700 kDa (+).

all M were fit simultaneously to eq 5 or 6 using the process described for Figure 2 with $\gamma = 0$ forced. As in Figure 2, concentration units are $c[\eta]$; the implications of these units are the same as in Figure 2.

There is a prominent solutionlike–meltlike transition in the data. Below $c[\eta] \approx 15$, η for all M follows eq 1; above $c[\eta] \approx 35$, η almost always follows eq 6. In the intermediate range $15 \le c[\eta] \le 35$, η is approximately consistent with either form. One could readily choose a transition concentration $c_t[\eta]$ such that the two forms have the same slope at the transition concentration, but the data do not force such a choice. An optimal choice of $c_t[\eta]$ is ≈ 35, i.e., $\eta/\eta_0 \approx 5 \times 10^4$. At very large $\eta/\eta_0 > 10^9$, results on the 1200-kDa polyisobutylene deviate upward from the power law form; these half-dozen points were not included in any fit. We lack a specific explanation for the behavior of these points. One might rationally propose the appearance of a further viscoelastic regime, above the power law regime, at these very large viscosities associated with the approach to the glass; with such limited data, it is difficult to rule out the possibility of experimental difficulties at large η. A similar upward deviation is seen in Figure 5 for a few points having $\eta > 10^8$.

Figure 4 presents η/η_0 of 1.2×10^6-Da polyisobutylene in decalin, cyclohexane, CCl_4, isooctane, and toluene at 25 °C, as measured by Tager et al.[41–43] For this system, the behavior of η/η_0 depends on the solvent. In decalin and cyclohexane, there is a solutionlike–meltlike transition near $c[\eta] \approx 80$ and $\eta/\eta_0 \approx 10^6$, with meltlike behavior at larger $c[\eta]$ and η/η_0. In CCl_4, isooctane, and toluene, the same polyisobutylene remains to reasonable approximation in the solutionlike regime up to the highest concentrations and viscosities studied ($c[\eta]$ up to 300, 200, or 150, respectively; η/η_0 up to $\sim 10^{12}$). Measurements on polyisobutylene in toluene and CCl_4 show oscillatory structure relative to the fit lines, with evident fluctuations in the sign of $d^2\eta/dc^2$. Unless η is remarkably more structured in these systems than in others, there needs to be some reservation about the accuracy of these data. Clearly neither $c[\eta]$ nor η/η_0 uniquely determines the location of the transition, which therefore must be affected by solvent quality or other system properties. Fitting parameters corresponding to Figure 4 appear in Table 2.

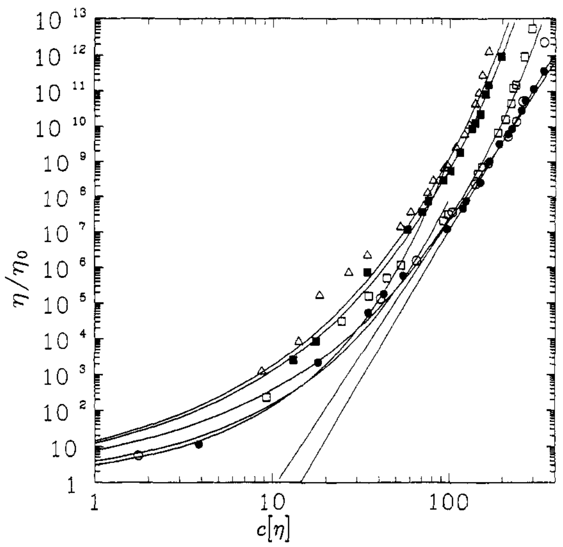

Figure 4. Viscosity[41–43] of 1.2×10^6-Da polyisobutylene in (a) decalin (○), (b) cyclohexane (●), (c) CCl_4 (□), (d) isooctane (■), and (e) toluene (△) and fits to stretched exponentials (smooth curves) and power laws (straight lines). A solutionlike–meltlike transition is only seen in decalin and cyclohexane.

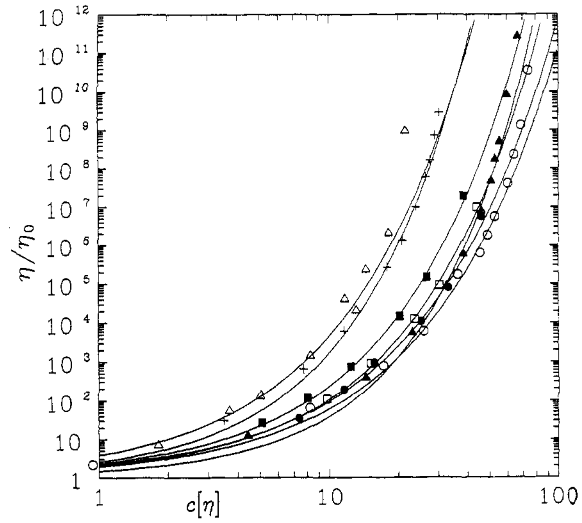

Figure 5. Viscosity[41–43] of 2.2×10^5-Da polystyrene in (a) ethylbenzene (○), (b) 3:1 ethylbenzene–decalin (●), (c) 1:1 ethylbenzene–decalin (□), (d) 1:3 ethylbenzene–decalin (■), (e) decalin (△), (f) CCl_4 (▲), and (g) ethyl acetate (+) and fits of each data set to a stretched exponential; the stretched exponential works well in each case for $\eta/\eta_0 < 10^8$.

Tager et al.[41–43] also presented η/η_0 for $\bar{M}_\eta = 2.2 \times 10^5$-Da polystyrene in a long series of solvents, including ethylbenzene, decalin, their mixtures, CCl_4, and ethyl acetate. Their data and stretched-exponential fits are shown in Figure 5 and Table 2. For $\eta/\eta_0 < 2 \times 10^8$, stretched exponentials fit the data reasonably well. With $\eta/\eta_0 > 2 \times 10^8$, measured viscosities deviate upward from stretched exponential forms. The higher viscosity data points appear to be consistent with a power-law dependence of η on $c[\eta]$, but with only one to three points per solvent in these apparent power-law regimes, fits to eq 8 are not totally convincing. For polystyrene in ethyl acetate, CCl_4, and ethylbenzene, these deviations from a stretched exponential, which could represent transitions to a higher concentration power-law regime, appear at $c_t[\eta]$ of 25, 50, and 60, respectively.

Raspaud et al.[44] reported η/η_0 of polystyrene–benzene, polyisoprene–cyclohexane, and polybutadiene–

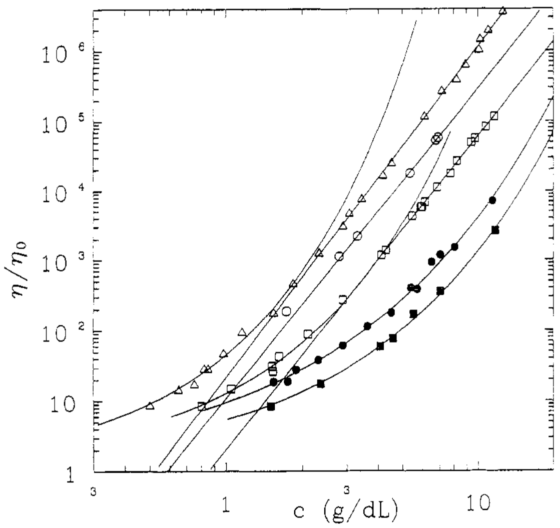

Figure 6. Viscosities of (a) 4000-kDa polystyrene–benzene (○), (b) 1240-kDa polystyrene–benzene (●), (c) 310-kDa polyisoprene–cyclohexane (■), (d) 940-kDa polyisoprene–cyclohexane (□), and (e) 960-kDa polybutadiene–cyclohexane (△), from results of Raspaud et al.[44] Smooth curves and straight lines are stretched exponentials and power laws, respectively; fitting parameters appear in Table 2. Some systems were only studied in one viscosity regime.

cyclohexane samples (total of five molecular weights) at concentrations of 5–126 g/L. They reported extensive data at 30 °C. Their measurements made over a range 7–50 °C confirm that the temperature dependence of the solution viscosity and terminal relaxation time are determined by the temperature dependence of solvent properties, consistent with the hydrodynamic scaling model, which attributes the concentration dependence of η to solvent–viscosity-mediated hydrodynamic interactions. The data are presented in Figure 6; fit parameters appear in Table 2. Of the five systems studied by Raspaud et al., two (polystyrene, M = 1240 kDa; polyisoprene, M = 310 kDa) were studied only in the solutionlike regime (perhaps up to the edge of the meltlike transition), one was studied almost entirely in the meltlike regime (polystyrene, M = 4000 kDa), and two (polyisoprene, M = 940 kDa; polybutadiene, M = 960 kDa) are represented by substantial data in both regimes. The transition concentrations $c_t[\eta]$ were > 20–30 for the first two systems and <20, ~15–20, and ~10, respectively, for the latter three systems. For the two systems in which both regimes are clearly identifiable, $\eta/\eta_0 \approx 1 \times 10^3$ at the transition. The stretched-exponential and power-law curves are very close to tangential, consistent with an analytic (continuous $d\eta/dc$) transition at $c_t[\eta]$. Raspaud et al.[44] identified a scaling (i.e., meltlike) regime in their data but did not provide a functional form for their lower concentration measurements.

Milas et al.[45] examined η and other viscoelastic properties of unpasteurized xanthan gum in native and renatured states. The gum had $M_w = 5.25 \times 10^6$; data cover $0.0125 \le c \le 5$ g/L in 0.1 M NaCl at 25 °C. Low-shear viscosities are presented as a function of $c[\eta]$ in Figure 7, with fitting parameters in Table 2. The solutionlike–meltlike transition apparent in the figure near $c_t[\eta] \approx 6$–8 or $\eta/\eta_0 \approx 1 \times 10^2$ was identified by Milas et al. and is noted here for comparison with their findings on shear thinning. Milas et al.[45] remarked that the specific viscosity goes over to power-law ($\eta_{sp} \sim c^{3.7}$) behavior above $c[\eta] \approx 8$ and that, at concentrations $c[\eta] <\approx 8$, η_{sp} is proportional to the Martin form, $\exp(k''c[\eta])$. At $c_t[\eta] \approx 8$, the stretched-exponential and power-law curves are very close to tangent.

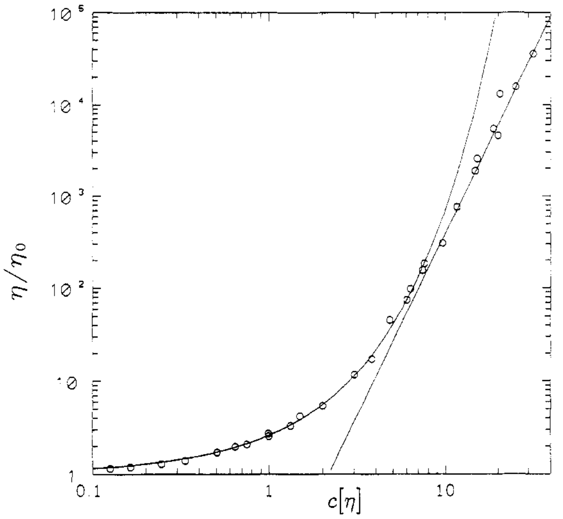

Figure 7. Viscosity[45] of 5.25-MDa xanthan as a function of concentration. Parameters for the displayed stretched-exponential and scaling-law fits appear in Table 2.

Effect of Chain Architecture

Some models[46,47] of polymer dynamics indicate that chain architecture (e.g., linear chain, star, ring) has an especially strong effect on the viscoelastic properties of polymer solutions. The effect of chain architecture on polymer self-diffusion was extensively examined, for example, by Lodge and collaborators,[48] who studied stars and linear chains in solutions of linear polymers. Lodge et al.[48] proposed that their results were "... consistent only with the reptation-based picture ..." of polymer dynamics. An alternative analysis[49] of the same measurements maintained that Lodge et al.'s data on polymer self-diffusion are also consistent with other pictures of polymer dynamics. This section examines the effect of chain architecture on the solution zero-shear viscosity by considering η for f-armed stars (a linear chain is, of course, a two-armed star).

Utracki and Roovers[50] reported η of two-, four-, and six-armed polystyrenes at a fixed c = 255 g/L in diethylbenzene at 30 °C. Figure 8 and Table 3 exhibit their results. At all molecular weights, η falls with increasing f, so that solutions of six-armed stars are less viscous than solutions of four-armed stars, which are in turn less viscous than are solutions of linear chains. For M as large as 675–1650 kDa and any f, η follows accurately a stretched exponential in M, eq 7, with no indication of a transition to power-law behavior. This lack of power-law behavior was in fact noted by Utracki and Roovers,[50] who remarked in their original paper "For polymer solutions ... it became exceedingly difficult to draw the two straight lines [corresponding to M^1 and $M^{3.4}$ behavior] on the logη vs. log$M$ plot, ..., as the exponent [of M] changes continuously with M".

In these data, it is noteworthy that at large M an order of magnitude change in η results from a 10% change in β and γ. It would then seem to be straightforward to determine β with good precision, if it were not for the difficulty that errors in determining β and γ are cross-correlated and (because of the nonlinearity of the exponentiated exponential) it is difficult to determine γ with good precision. Conversely, if small errors in calculating β and γ from a fundamental theory change the computed η substantially, then very accurate cal-

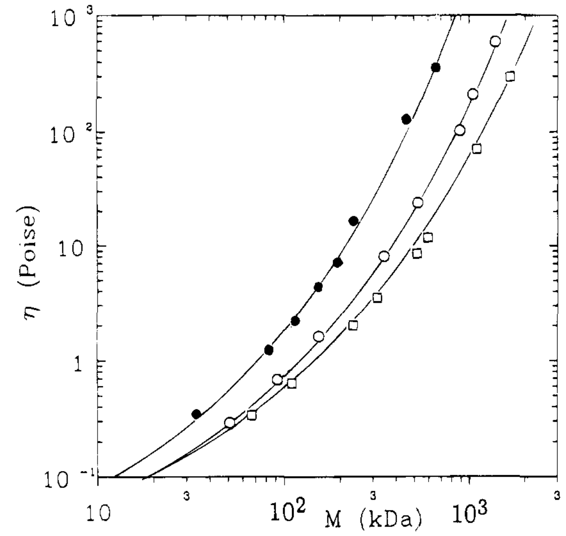

Figure 8. Viscosity[50] of (a) linear chain (●), (b) four-armed star (○), and (c) six-armed star (□) polystyrenes in diethylbenzene at the fixed polymer concentration of 255 g/L, showing solutionlike behavior at all polymer molecular weights.

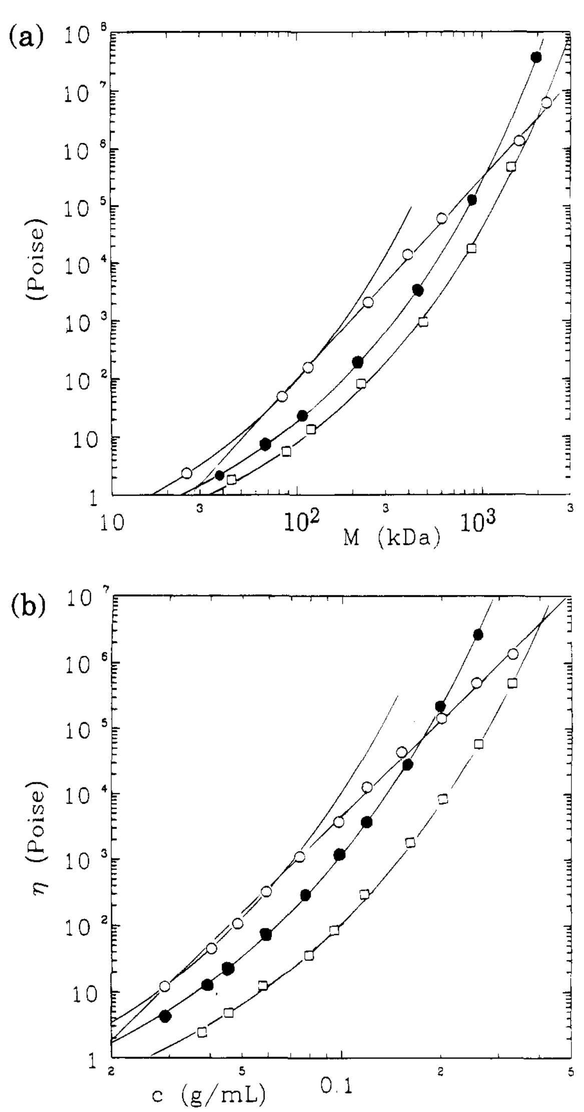

Figure 9. Viscosity[51] of polyisoprene–tetradecalin for linear chains (○), four-arm stars (●), and six-arm stars (□). (a) η against polymer molecular weight at $c = 330$ g/L; (b) η against polymer concentration for M of 1611 (linear chains), 1950 (four-arm stars), and 1446 kDa (six-arm stars). Straight lines and smooth curves represent fits to power laws and stretched exponentials, respectively, using parameters in Tables 2 and 3.

culations of β and γ will be required before absolute numerical values of η can be computed theoretically with tolerable accuracy.

The zero-shear viscosity and other viscoelastic parameters of polyisoprenes in tetradecane were also examined by Graessley et al.,[51] who studied chains and four- and six-armed stars having M_w as large as 2.2×10^6 Da at concentrations as large as 330 g/L, all at 25.5 °C. Figure 9 and Tables 2 and 3 present their data and an anlysis of η; other viscoelastic properties are treated in the following section.

In Figure 9a, η is given as a function of M at the highest concentration employed by Graessley et al.,[51] namely, 330 g/L. η for the linear polymers is in the meltlike regime, following a power law in M accurately, except at the lowest molecular weight examined (26 kDa), where η is larger than expected from the power-law line. This upward deviation from expectation at small M is consistent with a transition from meltlike to solutionlike behavior for linear chains as M is reduced. η for star polymers remains in the solutionlike (stretched-exponential) regime at all M, even at $\eta > 10^6$ P. In agreement with Utracki and Roover's[50] findings, at the lowest molecular weights studied here, η of the stars is less than η of the linear chains. Furthermore, at small M, η decreases monotonically with increasing f. However, once the linear-chain solutions enter the meltlike regime, their viscosities only increase as M^γ, where here $\gamma \approx 3.5$. For sufficiently large M, a stretched exponential in M will always outgrow a polynomial in M. As a result, as seen in Figure 9a, at the largest M studied, η of the four-armed stars (which remain in the solutionlike regime) has indeed become larger than η of the linear chains (which are in their meltlike regime).

Figure 9b shows η against c for the highest molecular weight chains and stars studied by Graessley et al.[51] M is in the range 1.44–1.95 MDa. Parts a and b of Figure 9 are compatible. From Figure 9a, at large fixed c and large M, η is in the meltlike regime for linear chains and in the solutionlike regime for star polymers. This meltlike–solutionlike behavior is repeated in Figure 9b.

Table 3. Parameters from Fits of Measured Viscosities to a Stretched Exponential (Eq 7) or Power Law (Eq 8) in Polymer Molecular Weight M for f-Armed Stars

system	M_t	η_0	β	γ	% RMSE[a]	$\bar{\eta}$	γ	% RMSE[a]
diethylbenzene–[50]								
polystyrene ($f = 2$)	>675 kDa	8.02×10^{-3}	1.02	0.36	12			
polystyrene ($f = 4$)	>1.4 MDa	8.02×10^{-3}	0.93	0.34	5.7			
polystyrene ($f = 6$)	1.65 MDa	8.25×10^{-3}	0.92	0.33	8			
tetradecalin–[51]								
polyisoprene ($f = 2$)	≤70 kDa	0.02	1.21	0.422	1.4	1.05×10^{-5}	3.49	13
polyisoprene ($f = 4$)	>1500 kDa	0.02	1.17	0.38	3			
polyisoprene ($f = 6$)	>2000 kDa	0.02	1.00	0.39	11			

[a] RMSE, root-mean-square fractional error in the data, expressed as a percent.

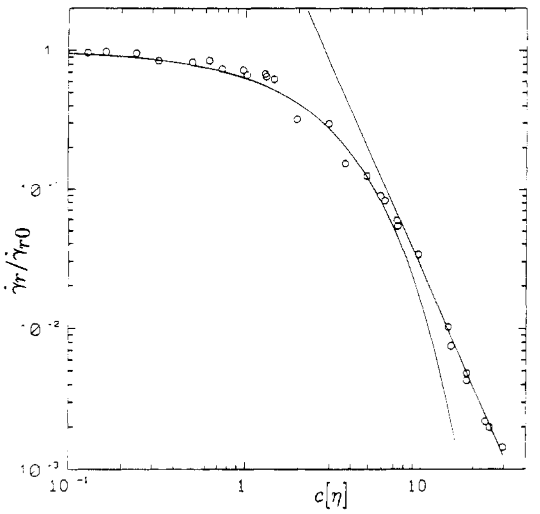

Figure 10. Normalized shear rate $\dot{\gamma}_r/\dot{\gamma}_{r0}$ for the Newtonian−pseudoplastic transition in xanthan−0.1 M NaCl, from measurements of Milas et al.,[45] together with fits to power-law and stretched-exponential behavior.

For linear chains of large M, η follows a power law in c except at the lowest c. For star polymers of large M, η follows a stretched exponential in c at all c. When linear chains and star polymers are both in the solutionlike regime, η of the star polymers is less than η of the chains. Except at the lowest concentrations, solutions seen here of linear chains are in the meltlike regime. The increase in η with increasing c or M is less for a solution in the meltlike regime than for a solution in the solutionlike regime. If sufficiently large c or M is attained, η of a solutionlike system will exceed η of a meltlike system, as seen in Figure 9.

Viscoelastic Parameters Beyond η

A prominent characteristic of many polymer solutions is their viscoelastic response—a dependence of viscosity and other parameters on frequency or shear rate. The parameters that characterize the viscoelastic response depend on underlying solution properties; e.g., c, M, and chain architecture. A complete model of solution dynamics will account for frequency- and shear-dependent as well as zero-frequency, zero-shear behavior. Here we explore the extent to which hydrodynamic scaling analysis describes the dependence of shear-rate and frequency-dependent viscoelastic parameters on polymer concentration and molecular weight.

Milas et al.[45] examined 5.25×10^6-Da xanthan in 0.1 M NaCl. They reported the required shear rate $\dot{\gamma}_r$ for the transition from Newtonian to pseudoplastic behavior; their $\dot{\gamma}_r$ is normalized by the shear rate $\dot{\gamma}_{r0} \approx 11 \pm 2$ s^{-1} required for non-Newtonian behavior in the limit $c \rightarrow 0$. Milas et al.'s data on native-state and renatured xanthan appear in Figure 10; fitting parameters are in Table 4. As seen in the figure, $\dot{\gamma}_r/\dot{\gamma}_{r0}$ shows meltlike behavior ($\eta \sim c^{-2.8}$ for $c[\eta] > 8$ and $\dot{\gamma}_r/\dot{\gamma}_{r0} < 0.06$), but is solutionlike at lower power concentrations and larger $\dot{\gamma}_r/\dot{\gamma}_{r0}$. The stretched-exponential and power-law curves are close to tangent at their point of contact. Milas et al. noted the higher concentration power-law behavior in their paper, but did not suggest a functional form for $\dot{\gamma}_r/\dot{\gamma}_{r0}$ in more dilute solutions. In these xanthan solutions, transitions from solutionlike to meltlike behavior by η and by $\dot{\gamma}_r$ happen at approximately the same concentration.

For linear and star polyisoprenes in tetradecalin at 25 °C, the study by Graessley et al.[51] described in the previous section reported not only the zero-shear viscosity but also a characteristic shear rate $\dot{\gamma}_r$ and steady-state compliance J_e^0. Graessley et al.[51] defined their $\dot{\gamma}_r$ to be the shear rate at which $\eta(\dot{\gamma})$ had declined to 80% of its zero-shear limit η. Graessley et al.[51] reported concentration dependences at large fixed M, and molecular weight dependences at large fixed c, as seen in Figure 11 and Tables 4 and 5.

Parts a and b of Figure 11 show how $\dot{\gamma}_r$ depends on c for chains of large M (1.4−2 MDa) and how $\dot{\gamma}_r$ depends on M in concentrated solution (0.33 g/mL). Under these conditions, polyisoprene linear polymers are almost entirely in the meltlike regime, with $\dot{\gamma}_r$ following power laws in both c and M, except perhaps at the lowest concentrations and molecular weights studied. At the same concentrations, for roughly the same molecular weights, solutions of polyisoprene stars are in the solutionlike regime, $\dot{\gamma}_r$ following stretched exponentials in both c and M. At small c and M, $\dot{\gamma}_r$ for chains is less than $\dot{\gamma}_r$ for stars. $\dot{\gamma}_r$ for chains has, however, a weaker functional dependence on c and M than does $\dot{\gamma}_r$ for stars, so at large c or M, $\dot{\gamma}_r$ for chains becomes larger than $\dot{\gamma}_r$ for stars.

Parts c and d of Figure 11 show the steady-state compliance J_e^0 at different c and M. The concentration dependence of J_e^0, Figure 11c, exactly parallels the concentration dependence of $\dot{\gamma}_r$, in that linear chains show meltlike behavior except at low c while solutions of star polymers remain in the solutionlike regime at all concentrations studied. The molecular weight dependence of J_e^0 also shows (Figure 11d) a pronounced difference between linear polymers and stars, though not the difference seen for other variables: J_e^0 of solutions of linear chains is very nearly independent of M, while J_e^0 of star polymer solutions increases as $M^{3/4}$ or so in the same molecular weight range.

Thus, both in xanthan−water and in polyisoprene−tetradecalin, the circumstances under which η shows solutionlike or meltlike behavior are precisely the same as the conditions under which $\dot{\gamma}_r$ shows solutionlike or meltlike behavior, respectively, and are precisely the

Table 4. Parameters from Fits of $\dot{\gamma}_r/\dot{\gamma}_{r0}$, $\dot{\gamma}_r$, or J_e^0 to a Stretched Exponential (Exp($-\alpha c^\nu$) or Power Law $\bar{\gamma} c^\nu$ in Concentration

system	parameter	c_t	α	ν	% RMSE[a]	$\bar{\gamma}$	ν	% RMSE[a]
xanthan−0.1 M NaCl[45]	$\dot{\gamma}_r$	8[b]	0.45	0.96	14	18.8	−2.84	9.6
tetradecalin−[51]								
polyisoprene ($f = 2$)	$\dot{\gamma}_r$	<0.04 g/mL				2.49×10^{-3}	−2.75	10
polyisoprene ($f = 4$)	$\dot{\gamma}_r$	≥0.3 g/mL	35.2	0.66	13			
polyisoprene ($f = 6$)	$\dot{\gamma}_r$	≥0.35 g/mL	27	0.69	8			
tetradecalin−[51]								
polyisoprene ($f = 2$)	J_e^0	0.07 g/mL	12.8	0.45	10	3.5×10^{-7}	−2.35	3.7
polyisoprene ($f = 4$)	J_e^0	>0.2 g/mL	5.6	0.65	14			
polyisoprene ($f = 6$)	J_e^0	>0.3 g/mL	5.8	0.84	12			

[a] RMSE, root-mean-square fractional error in the data, expressed as a percent. [b] c_t in dimensionless units $c_t[\eta]$ unless elsewise specified.

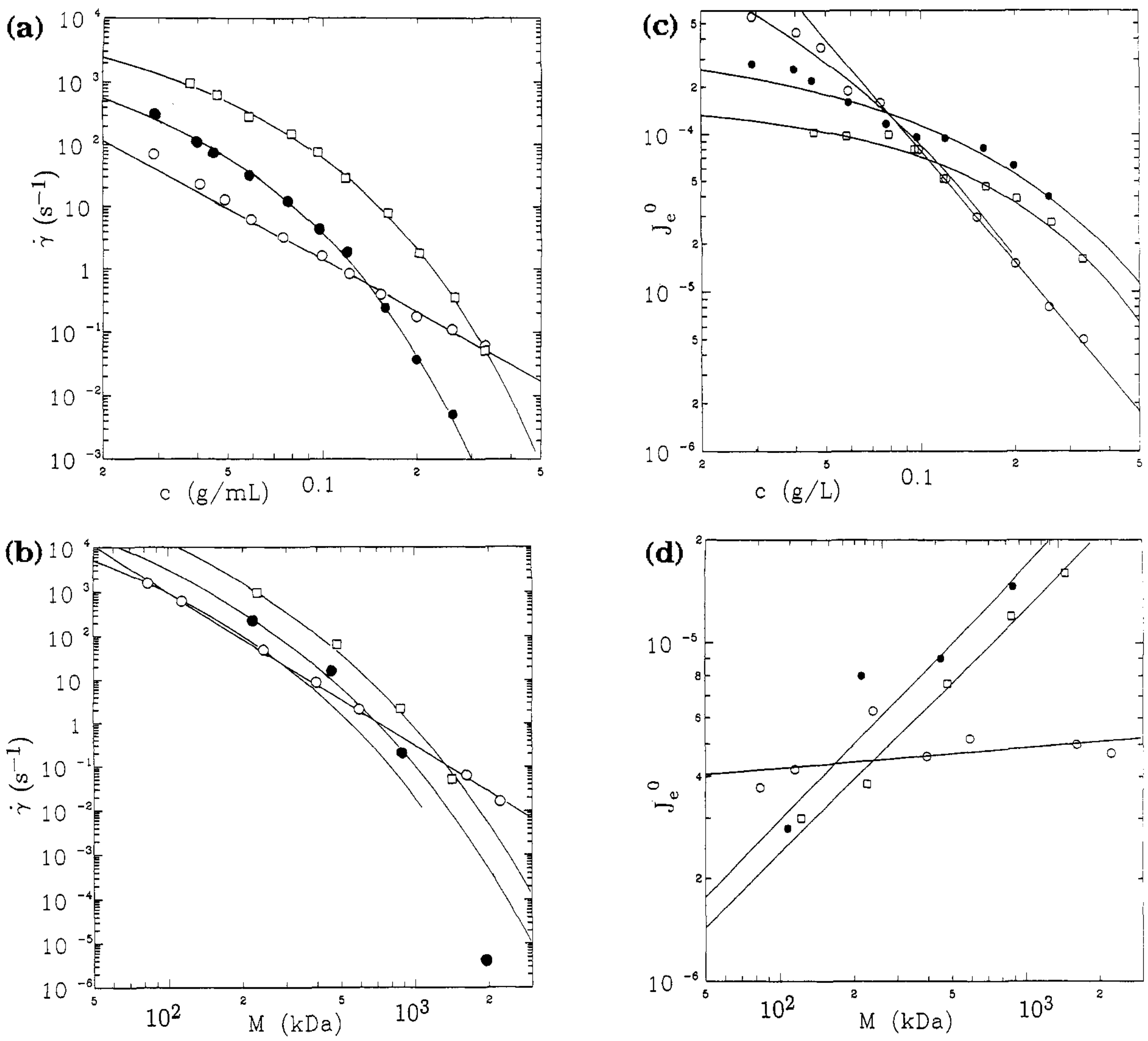

Figure 11. Viscoelastic parameters from Graessley et al.[51] in isoprene–tetradecalin as functions of concentration and molecular weight for linear chains (open circles), four-armed stars (filled circles), and six-armed stars (squares). (a, c) $\dot{\gamma}_r$ and J_e^0, respectively, against c for M of 1.61 ($f = 2$), 1.95 ($f = 4$), and 1.45 MDa ($f = 6$). (b, d) $\dot{\gamma}_r$ and J_e^0, respectively, against M for c of 0.33 g/cm^3. Straight lines, power-law behavior in the meltlike regime; smooth curves, stretched-exponential behavior in the solutionlike regime.

Table 5. Parameters from Fits of $\dot{\gamma}_r/\dot{\gamma}_{r0}$, or J_e^0 to a Stretched Exponential (Exp($-\alpha M^\nu$)) or Power Law $\bar{\gamma}M^\nu$ in Polymer Molecular Weight

system	parameter	M_t (kDa)	α	ν	% RMSE[a]	$\bar{\eta}$	ν	% RMSE[a]
tetradecalin–[51]								
polyisoprene ($f = 2$)	$\dot{\gamma}_r$	<100				9.35×10^9	−3.49	11.3
polyisoprene ($f = 4$)	$\dot{\gamma}_r$	>1500	0.28	0.56	14			
polyisoprene ($f = 6$)	$\dot{\gamma}_r$	>2000	0.25	0.56	6.1			
tetradecalin–[51]								
polyisoprene ($f = 2$)	J_e^0	≤100				3.2×10^{-6}	0.06	13
polyisoprene ($f = 4$)	J_e^0	<100				9.3×10^{-8}	0.75	18
polyisoprene ($f = 6$)	J_e^0	<100				8.5×10^{-8}	0.72	7.5

[a] RMSE, root-mean-square fractional error in the data, expressed as a percent.

same as the conditions under which the concentration dependence of J_e^0 shows solutionlike or meltlike behavior, respectively.

Solvent Quality Effects

The above results include several studies of a single polymer under different solvent conditions, notably results of Tager et al.[41–43] on a single polyisobutylene and a single polystyrene, each in a series of solvents. From Table 2, for each polymer–solvent pair studied by Tager et al. the hydrodynamic scaling form of eq 1 describes tolerably well the concentration dependence of η. However, in order to describe the measurements well, the scaling prefactor α must be varied from solvent to solvent by a factor of up to 2.5. The variation in α from sample to sample is not caused by the known[3] strong molecular weight dependence of α, because these results are on a single polymer sample with fixed M. This section presents an explanation for the observed variability of α.

The need to use different values of α to describe η of polymers of a given M has been observed before in a related context. Just as eq 1 describes well the concentration dependence of η of many polymers, so also does the corresponding eq 4 describe well the concentration dependence of D_s. If one fits eq 4 to data on a variety of polymers and plots the resultant α against M, one finds[52,53] $\alpha \sim M^1$ or so, in agreement with theory. However, if one focuses on results at a single M (cf. ref 53, Figure 6), one finds that one needs very different α values to describe D_s of different polymers having a single M. The ~4-fold variation in the α for D_s, at fixed M, is contrary to any expectation that α is determined by M and the chain thickness.

The derivation[35] of the hydrodynamic scaling form shows that the scaling prefactor α is actually determined by the radius R of the chain in solution, namely, $\alpha \sim R^4$ for translational self-diffusion, and

$$\alpha \sim R^3 \tag{9}$$

for rotational diffusion. As is well-known, under a wide variety of conditions R depends weakly on c. As seen[35] in the first-principles derivation of eq 9, in writing the stretched-exponential $\exp(-\alpha c^{\nu})$ this concentration dependence is factored out from α (which thereby becomes independent of c) and transferred to c^{ν}, the difference $\nu - 1$ being due to chain contraction. The motion of a polymer chain in a shear flow is predominantly rotational; the corresponding scaling prefactor for viscosity will follow eq 9 or (given the relationship between R and c^*) $\alpha \sim 1/c^*$.

The spatial extent of a polymer coil in solution is substantially dependent upon solvent quality, the radius of gyration R_g of a polymer chain in a good solvent being appreciably greater than R_g of the same chain in a Θ solvent. The variation in chain dimensions with solvent quality can be related to the intrinsic viscosity via an expansion parameter

$$\alpha_\eta^{\ 3} = [\eta]/[\eta]_\theta \tag{10}$$

where $[\eta]_\Theta$ is the intrinsic viscosity under Θ conditions. By definition $\alpha_\eta = 1$ at the Θ point. Combining eqs 9 and 10, the hydrodynamic scaling prediction for α_r is

$$\alpha_r \sim \alpha_\eta^{\ 3} \tag{11}$$

The hydrodynamic scaling model thus predicts that α depends on solvent quality. Results of Dreval et al.[38] allow a quantitative test of eq 11.

Dreval et al.[38] examined the concentration dependence of η, representing the viscosity as $\tilde{\eta} = (\eta - \eta_0)/(\eta_0 c[\eta])$. They plotted $\tilde{\eta}$ against reducing variables $c[\eta]$ and $K_M c[\eta]$. $c[\eta]$ was shown to be a good reducing variable for homologous polymers in a single solvent, collapsing $\tilde{\eta}$ for homologues of different M onto a single master curve. Data for the same polymer in different solvents lay along different curves.

Dreval et al.[38] then introduced a further reducing variable K_M, obtained by fitting the Martin equation

$$\tilde{\eta} = \exp(K'_M c[\eta]) \tag{12}$$

(with $K_M = K'_M/\ln(10)$) to the low-concentration part of the $\tilde{\eta}-c[\eta]$ plots.

By choosing an appropriate K_M for each polymer–solvent pair, Dreval et al.[38] found that $K_M c[\eta]$ collapsed $\tilde{\eta}$ for each of several polymer species (poly(dimethylsiloxane), polyisobutylene, polystyrene, poly(vinyl acetate), polyarylate) in a variety of solvents onto a single master curve. The molecular weight dependence of $\tilde{\eta}$ is accounted for by $[\eta]$, so the role of K_M is to account for the solvent quality dependence of $\tilde{\eta}$.

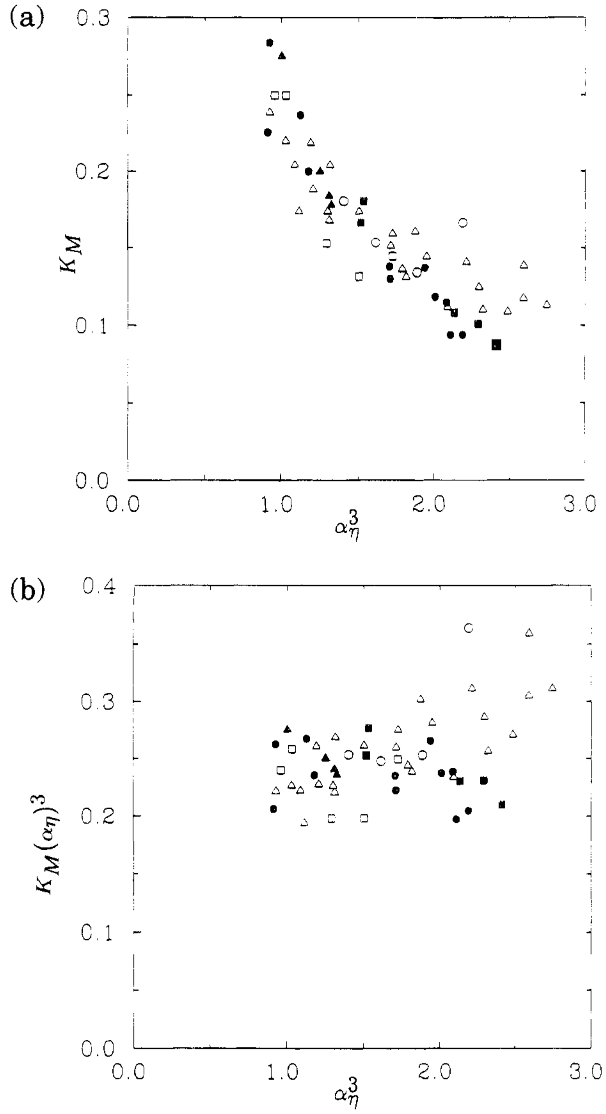

Figure 12. Dependence on α_η of the reducing parameter K_M of Dreval et al.[38] plotted as K_M and as $K_M\alpha_\eta^{\ 3}$, for viscosities of poly(dimethylsiloxanes) (○),[43] polyisobutylenes (●)[40-42] and (△),[55] polystyrenes (□)[41-43], and (△),[55] poly(vinyl acetates) (■),[54] and polyarylates (▲).[43]

Mathematically, a reducing variable acts to generate a master curve by suppressing a functional dependence on an independent variable. For example, suppose the concentration dependence of the viscosity may be written $\tilde{\eta} = f(Qc)$, in which all dependence of $\tilde{\eta}$ on α_η is contained in Qc, so that α_η does not appear separately as a variable. (Replacing $Qc \rightarrow Q'c[\eta]$ has no effect on the α_η dependence of f, if Q and Q' differ appropriately in their dependence on α_η.) If one plots $f(Qc)$ against c, while replacing the abscissa with a new variable $K_M \cdot Q'c[\eta]$, where K_M is chosen anew for each $Q'c[\eta]$ so that $K_M Q'c[\eta] \sim [\alpha_\eta]^0$, then the variations of $\tilde{\eta}$ and K_M with α_η will negate each other. Plots of $\tilde{\eta}$ against $K_M Q'c[\eta]$ for systems having different α_η will then superpose. Also, if $Qc \sim \alpha_\eta^{\ 3}$ as predicted above, then $K_M \sim [\alpha_\eta]^{-3}$.

Figure 12a, based on Dreval et al.,[38] gives K_M against $\alpha_\eta^{\ 3}$ for poly(dimethylsiloxane),[43] polyisobutylene,[41,42,40,55] polystyrene,[41,42,43,55] poly(vinyl acetate),[54] and polyarylate.[43] The 3-fold range of K_M seen here corresponds directly to the range of α seen in Table 2 for one polymer in multiple solvents. There is a strong inverse correlation between K_M and α_η. Figure 12b replaces K_M with $K_M\alpha_\eta^3$ as the ordinate. In contrast to K_M, $K_M\alpha_\eta^3$ is visibly very weakly dependent on α_η. That is, to first approximation $K_M\alpha_\eta^3$ is a reducing variable for K_M, indicating $K_M \sim \alpha_\eta^{-3}$ and confirming eq 11. For some polymers, $K_M\alpha_\eta^3$ climbs weakly with increasing α_η; in other polymers, $K_M\alpha_\eta^3$ decreases slowly with increasing α_η. These residual dependences of $K_M\alpha_\eta^3$ on α_η may reflect either limitations in the experimental data or actual chemical effects more subtle than those described by the expansion parameter.

Discussion

This paper has explored four substantial themes relevant to the polymer solution dynamics including the hydrodynamic scaling model, namely, (i) better localization of the solutionlike–meltlike transition in solution viscosity, (ii) effect of chain architecture, (iii) transitions in the behavior of viscoelastic parameters, notably $\dot{\gamma}_r$ and J_e^0, and (iv) influence of solvent quality on viscosity and its scaling parameters.

With respect to the solutionlike–meltlike transition in η, we examined a substantial body of literature, demonstrating that η systematically follows a stretched exponential in c and M at smaller c and M. In some but not all systems, at sufficiently large c and M the stretched exponential in c and M is replaced by scaling (power-law) behavior in the same variables. These results substantially reinforce conclusions by earlier studies[2,3] that relied on more restricted data bases.

There do not appear to be transition regimes, intermediate between stretched-exponential and scaling behavior, visible in the data. Each data point near the transition can be associated with one behavior or the other. In some cases, the stretched-exponential and power-law lines are very nearly tangent at the transition, implying that the transition is analytic in c and M. In a few cases, the stretched-exponential and power-law curve do not quite contact each other, or cross rather than being tangent, at the point of contact. In these cases, if the curves have been determined with sufficient accuracy, it is necessary (or, respectively, at least plausible) that a transition regime exists, but a strong case for its existence in the actual data cannot be made.

The location of the transition varies substantially from system to system. From Table 2, the solutionlike–meltlike transition is typically observed at $c_t[\eta] > 20$. In two cases[4,45] involving relatively rigid polysaccharides, the transition is found at a low concentration, $c_t[\eta] \approx 7$. In other cases, there is no transition even for $c_t[\eta] \gg 100$. In cases in which measurements were not made up to the melt, extension of measurements to larger c might reveal a transition not present in the reported data.

In terms of the viscosity increment, η/η_0 at the transition is in the range 5×10^2–5×10^4, extremes of the range of viscosities at which the transition occurs being shown by 960-kDa polybutadiene[44] in cyclohexane ($\eta/\eta_0 \approx 500$; $c_t[\eta] \approx 10$) and polyisobutylene[41-43] in decalin or cyclohexane ($\eta/\eta_0 \approx 10^6$, $c_t[\eta] \approx 80$). In some systems with no transition, the viscosity remains stretched exponential for $\eta/\eta_0 > 10^{12}$. In a few systems at $\eta/\eta_0 > 10^9$, there is an upward deviation of η from scaling behavior.

It could be argued that the hydrodynamic scaling/stretched-exponential description is perhaps valid in dilute solutions, in which hydrodynamic interactions are paramount, but cannot be valid in more concentrated solutions, in which chain overlap leads to the dominance of entanglement constraints over hydrodynamic forces. By this argument, hydrodynamic scaling is perhaps valid for $c[\eta] \ll 1$ but assuredly loses it validity near or above the overlap concentration $c[\eta] \approx 1$. This argument is conclusively rejected by experiment. In a long series of polymer solutions, hydrodynamic scaling provides an excellent description of the c and M dependence of η, in some cases even for concentrations $c[\eta] \gg 20$.

Raspaud et al.[44] proposed an alternative reducing variable, $C_e = MA_2/N_e^{0.76}$, for their viscosity measurements. The variable contains the second virial coefficient A_2 (a solution property) and the number of monomers N_e between entanglements in the melt (a melt property). C_e thus reflects the stiffness of the polymer chains. By writing their concentrations as C/C_e, Raspaud et al. were able to generate a single master curve for their results, their measurements at higher concentrations agreeing with a scaling law in c. In particular, all of their data agree (in reduced units) with a single lowest concentration $c/C_e \approx 1$ at which meltlike behavior appears. C_e depends on A_2; so in different solvents solutions of the same polymer have different c_t, at least if concentration is expressed in absolute (g/L) or natural ($c[\eta]$) units. For most of the systems studied here, we do not have the auxiliary measurements needed to test Raspaud et al.'s observation further.

With respect to the effect of chain architecture, we reexamined the literature[50,51] on viscosity of chain and star polymers in solution. At lower c and M, both linear and star polymers show solutionlike behavior for their viscosity; at larger c and M, η of linear polymers does go over to meltlike behavior, while η of star polymers remains solutionlike at all concentrations and molecular weights, even for η/η_0 as large as 10^9. These observations are consistent with models that afford linear chains modes of, or opportunities for, motion that are not as easily accessible to star polymers. In terms of such models, the appearance of the meltlike regime corresponds to the onset of entangled, e.g., Kolinski–Skolnick–Yaris[56] or reptational[46,47] dynamics. In some models one says that the frictional behavior of a branch point may be qualitatively different from the frictional behavior of a linear chain segment; in other models one says that linear chains can reptate but stars cannot. There are predictions[46] that the viscosity of star polymer melt depends exponentially on a power of M, in which case there is no logical necessity that star polymers have a solutionlike–meltlike transition for η at sufficiently large M as the melt regime is approached. In contrast, as argued above, the observation that linear chain melts have $\eta \sim M^\gamma$ while dilute solutions are in a stretched-exponential regime requires that a solutionlike–meltlike transition be observed with increasing c for linear chains having sufficiently large M.

With respect to other viscoelastic parameters, we have examined several studies of the concentration or molecular weight dependence of viscoelastic parameters beyond η, e.g., J_e^0 or $\dot{\gamma}_r$. Qualitatively speaking, η, $\dot{\gamma}_r$, and J_e^0 (in its c-dependence) all behave the same way. Where one parameter shows solutionlike behavior, all three parameters show solutionlike behavior. Where one parameter shows meltlike behavior, all three parameters show meltlike behavior. For xanthan–0.1 M NaCl,[45] in which both regimes are seen at different concentrations of the same material, the transition concentrations c_t for η and $\dot{\gamma}_r$ are the same to within experimental error.

With respect to solvent quality, we examined correlations between this parameter and hydrodynamic scaling parameters. If one assumes, e.g., viscosity, to have a stretched-exponential concentration dependence exp(αc^{ν}), and extracts α from studies on different materials, the observed variation in α from system to system is partially explained by the dependence of α on M. However, if one looks at different polymer–solvent pairs lying within a single narrow range of M, one finds that there is still a considerable variation in α. On applying a parameterization suggested by Dreval,[38] one finds that the variability from solvent to solvent in Dreval et al.'s parameter K_M—a parameter equivalent to α—at fixed M is accounted for by the variation in the expansion parameter α_η from solvent to solvent. The product $K_M(\alpha_\eta)^3$ is nearly independent of α_η, implying that $\alpha \sim \alpha_\eta{}^3$. The result $\alpha \sim \alpha_\eta{}^3$ is also a prediction (eq 11) of the hydrodynamic scaling model. This prediction of the hydrodynamic scaling model is here for the first time confirmed by experiment.

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References and Notes

(1) Phillies, G. D. J. *Macromolecules* **1986**, *19*, 2367.
(2) Phillies, G. D. J.; Peczak, P. *Macromolecules* **1988**, *21*, 214.
(3) Phillies, G. D. J. *J. Phys. Chem.* **1992**, *96*, 10061.
(4) Phillies, G. D. J.; Quinlan, C. Macromolecules **1995**, *28*, 160.
(5) Phillies, G. D. J.; Ullmann, G. S.; Ullmann, K.; Lin, T.-H. *J. Chem. Phys.* **1985**, *82*, 5242.
(6) Enomoto, H.; Einaga, Y.; Teramoto, A. *Macromolecules* **1978**, *11*, 894.
(7) Kajiura, H.; Ushiyama, Y.; Fujimoto, T.; Nagasawa, M. *Macromolecules* **1978**, *11*, 1984.
(8) Isono, Y.; Nagasawa, M. *Macromolecules* **1980**, *13*, 862.
(9) Takahashi, Y.; Isono, Y.; Noda, I.; Nagasawa, M. *Macromolecules* **1985**, *18*, 1002.
(10) Jamieson, A. M.; Telford, D. *Macromolecules* **1982**, *15*, 1329.
(11) Nystrom, B.; Roots, J. *J. Macromol. Sci. Rev. Macromol. Chem.* **1980**, *C19*, 35.
(12) Roots, J.; Nystrom, B. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 979.
(13) Roots, J.; Nystrom, B. *J. Chem. Soc., Faraday Trans. 1* **1981**, *77*, 947.
(14) Nystrom, B.; Bergman, R. *Eur. Polym. J.* **1978**, *14*, 431.
(15) Nystrom, B.; Roots, J.; Bergman, R. *Polymer* **1979**, *20*, 157.
(16) Nystrom, B.; Porsch, B.; Sundelof, L.-O. *Eur. Polym. J.* **1977**, *13*, 683.
(17) Nystrom, B.; Roots, J. *Eur. Polym. J.* **1978**, *14*, 551.
(18) Mijnlieff, P. F.; Jaspers, W. J. M. *Trans. Faraday Soc.* **1971**, *67*, 1837.
(19) Nystrom, B.; Sundelof, L.-O.; Bohdanecky, M.; Petrus, V. *J. Polym. Sci., Polym. Lett. Ed.* **1979**, *17*, 543.
(20) Nystrom, B.; Sundelof, L.-O. *Chem. Scr.* **1976**, *10*, 16.
(21) Nystrom, B.; Roots, J. *Makromol. Chem.* **1979**, *180*, 2419.
(22) Mori, Y.; Ookubo, N.; Hayakawa, R. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *20*, 2111.
(23) Teraoka, I.; Ookubo, N.; Hayakawa, R. *Phys. Rev. Lett.* **1985**, *55*, 2712.
(24) Maguire, J. F.; McTague, J. P.; Rondelez, F. *Phys. Rev. Lett.* **1980**, *45*, 1891.
(25) Statman, D.; Chu, B. *Macromolecules* **1984**, *17*, 1537.
(26) Zero, K. M.; Pecora, R. *Macromolecules* **1982**, *15*, 87.
(27) Colby, R. H.; Fetters, L. J.; Funk, W. G.; Graessley, W. W. *Macromolecules* **1991**, *24*, 3873.
(28) Lin, T.-H.; Phillies, G. D. J. *J. Colloid Interface Sci.* **1984**, *100*, 82.
(29) Nemoto, N.; Kojima, T.; Inoue, T.; Osaki, K. *Macromolecules* **1989**, *22*, 3793.
(30) Nemoto, N.; Kishine, M.; Inoue, T.; Osaki, K. *Macromolecules* **1991**, *24*, 1648.
(31) Onogi, S.; Masuda, T.; Miyanagi, N.; Kimura, S. *J. Polym. Sci. A2* **1967**, *5*, 899.
(32) Tead, S. F.; Kramer, E. J. *Macromolecules* **1988**, *21*, 1513.
(33) Daivis, P. J.; Pinder, D. N.; Callaghan, P. T. *Macromolecules* **1992**, *25*, 170.
(34) Phillies, G. D. J. *Macromolecules* **1987**, *20*, 558.
(35) Phillies, G. D. J. *Macromolecules* **1988**, *21*, 3101.
(36) Phillies, G. D. J.; Kirketelos, P. C. *J. Polym. Sci. B: Polym. Phys.* **1993**, *31*, 1785.
(37) Gupta, D.; Forsman, W. C. *Macromolecules* **1969**, *2*, 305.
(38) Dreval, V. E.; Malkin, A. Ya.; Botvinnik, G. O. *J. Polym. Sci., Polym. Phys. Ed.* **1973**, *2*, 1055.
(39) Malkin, A. Ya.; Blinova, N. K.; Vinogradov, G. V. Paper presented at the VI Symposium on Polymer Rheology, Moscow, 1971 (as cited in ref 38).
(40) Mochalova, O. A.; Slonim, I. Ya.; Dreval, V. E.; Yusupov, T. K.; Vzvadskaya, Z. P.; Tager, A. A. *Vysokomol. Soedin.* **1972**, *A14*, 1294 (as cited in ref 38).
(41) Tager, A. A.; Dreval, V. E. *Usp. Khim.* **1967**, *36*, 888 (as cited in ref 38).
(42) Tager, A. A.; Dreval, V. E. *Rheol. Acta* **1970**, *9*, 517 (as cited in ref 38).
(43) Tager, A. A.; Dreval, V. E.; Botvinnick, G. O.; Kenina, S. B.; Novitskaya, V. I.; Sidorova, L. K.; Usoltseva, T. A. *Vysokomol. Soedin.* **1972**, *A14*, 1294 (as cited in ref 38).
(44) Raspaud, E.; Lairez, D.; Adam, M. *Macromolecules* **1995**, *28*, 927.
(45) Milas, M.; Rinaudo, M.; Knipper, M.; Schuppiser, J. L. *Macromolecules* **1990**, *23*, 2506.
(46) de Gennes, P. G. *Scaling Concepts in Polymer Physics*, Cornell University Press: P., Ithaca, NY, 1979.
(47) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Clarendon Press: Oxford, UK, 1986.
(48) Wheeler, L. M.; Lodge, T. P. *Macromolecules* **1989**, *23*, 3409. Lodge, T. P.; Markland, P.; Wheeler, L. M. *Macromolecules* **1989**, *22*, 3409.
(49) Phillies, G. D. J. *Macromolecules* **1990**, *23*, 2742.
(50) Utracki, L. A.; Roovers, J. E. L. *Macromolecules* **1973**, *6*, 366.
(51) Graessley, W. W.; Masuda, T.; Roovers, J. E. L.; Hadjichristidis, N. *Macromolecules* **1976**, *9*, 127.
(52) Phillies, G. D. J. *J. Phys. Chem.* **1989**, *93*, 5029.
(53) Phillies, G. D. J. *Nucl. Phys. B* **1988**, *5A*, 214.
(54) Smirnova, Yu. P.; Dreval, V. E.; Azanova, A. I.; Tager, A. A. *Vysokomol. Soedin.* **1971**, *A13*, 2397 (as cited in ref 38).
(55) Bodhanecky, M. *Collect. Czech. Chem. Commun.* **1972**, *35*, 1970 (as cited in ref 38).
(56) Skolnick, J.; Yaris, R.; Kolinski, A. *J. Chem. Phys.* **1988**, *86*, 1407, 1418.

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