Concentrated entangled and semidilute entangled polystyrene solutions and the second normal stress difference

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Steady shear flow values of the normal stress ratio $\Psi = -N_2/N_1$ are compared for monodisperse polystyrene solutions in the concentrated entangled and semidilute entangled regimes. In both regimes, the zero shear rate limiting values are the same: $\Psi_0 = 0.275 \pm 0.005$. Surprisingly, the molecular weight required for full entanglement (on the basis of Ψ_0) scales with concentration as $C^{-1.5 \pm 0.1}$, rather than C^{-1} as commonly supposed. The value of Ψ_0 is insensitive to fractional free volume and to solvent affinity for polystyrene, even at semidilute concentrations. However, Ψ depends on the shear rate, with shear-thinning behaviour in all solvents. Shear thinning of Ψ has not been widely reported, probably because of the 'edge fracture' flow instability in rotational rheometers. In concentrated solutions or melts, edge fracture usually occurs before Ψ shear thins by a significant amount.

(Keywords: polymer solutions; rheology; entanglements)

INTRODUCTION

Considerable success has been achieved in predicting the rheological behaviour of entangled, undiluted amorphous polymers using the reptation model[1–6]. However, the conditions under which this model applies to solutions of entangled polymers remain uncertain[7,8]. This paper is a rheological comparison of two polystyrene (PS) concentration regimes for which the reptation model is believed to apply: the concentrated entangled regime and the semidilute entangled regime. The approximate locations of these two concentration regimes are shown in *Figure 1*, along with three other regimes identified by Graessley[9]. These five concentration regimes are distinguished on the basis of both dynamic and thermodynamic considerations, as discussed in the next section. In an earlier study from this laboratory[10], the zero shear limit of $\Psi = -N_2/N_1$ was reported for three of the five PS concentration regimes, and the measured values are given in *Figure 1*. The current paper is a continuation of this earlier study, with Ψ_0 values reported for the two remaining concentration regimes. In all cases, nearly monodisperse polystyrene samples have been employed. The value of Ψ_0 provides a sensitive test on molecular constitutive models of polymer flow[11].

In our earlier work[10], Ψ_0 was reported as 0.20 ± 0.01 for semidilute entangled PS solutions. However, here we report that the true value of Ψ_0 is significantly higher (0.275 ± 0.005), because the solutions studied previously were not fully entangled on the basis of Ψ_0. We investigated the number of entanglements required for Ψ_0 to have its fully entangled value, and discovered that the required degree of entanglement is surprisingly large for semidilute polystyrenes.

The reptation prediction is that Ψ_0 is the same for both semidilute and concentrated entangled solutions. The predicted value of Ψ_0 is either 2/7 or 1/7, depending on whether or not one makes a mathematical approximation known as the independent alignment assumption[12]. Ψ_0 has apparently not been previously measured for nearly monodisperse, semidilute entangled PS solutions. However, Ψ_0 has been measured for concentrated entangled, monodisperse PS solutions by Osaki and coworkers[12] using optical techniques and by Ramachandran and coworkers[13] using the same technique as employed here. Osaki and coworkers reported that Ψ_0 lies slightly above 1/7, whereas Ramachandran and coworkers reported that $\Psi_0 = 0.287 \pm 0.003$. The latter result is close to the value reported here. Therefore we confirm the reptation prediction that Ψ_0 is the same for semidilute and concentrated entangled solutions.

The reptation model also predicts that Ψ has a shear-thinning dependence on the shear rate[5], but there are no reports confirming this prediction for steady shear flows of concentrated entangled solutions or melts. In fact, in the study discussed above, Ramachandran and coworkers[13] reported that Ψ was independent of the shear rate. Here we look for evidence of shear thinning in the same system studied earlier by Ramachandran and coworkers, and qualitatively confirm the predicted shear rate dependence. We attempt to explain the experimental reasons why various researchers have failed to observe shear thinning of Ψ in rotational rheometers. Rough guidelines are presented for choosing monodisperse PS solutions which are experimentally convenient for examining the shear thinning of Ψ and

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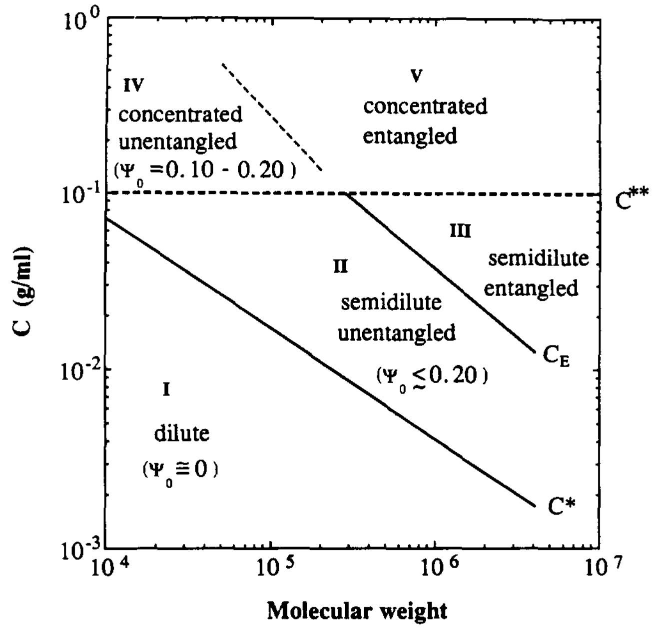

Figure 1 Approximate locations of the polystyrene concentration regimes, with measured values[10] of the normal stress ratio Ψ_0 in parentheses

for measuring the zero shear rate limit of Ψ. Such solutions must be chosen very carefully.

THEORETICAL BACKGROUND–CONCENTRATION REGIMES

The pseudo-phase diagram for polystyrene shown in *Figure 1* is based on the analysis of Graessley[9], and contains five concentration regimes distinguished by both dynamics and thermodynamics. The dynamic consideration is the degree of chain entanglement, and the thermodynamic consideration is the degree of chain swelling due to excluded volume forces. According to calculations based on the 'blob' model[14], excluded volume forces should be almost completely screened by segments from neighbouring chains for concentrations C greater than about 10 wt% polystyrene[9]. Therefore in *Figure 1* the horizontal line at $C = 10$ wt% represents an approximate dividing line between concentrated and non-concentrated polystyrene solutions. Above this line, the size of polymer coils should be independent of the solvent used to prepare the solution. The degree of chain entanglement, unlike the excluded volume screening, depends on polymer molecular weight as well as concentration. Solutions above and to the right of the curve labelled C_E in *Figure 1* should be sufficiently entangled for the reptation model to possibly apply. The precise location of this curve depends on which rheological property is used to probe the degree of chain entanglement, and the curve shown in *Figure 1* was calculated with viscosity data[15]. Finally, the curve labelled C^* represents the coil overlap concentration for PS in a good solvent as a function of molecular weight[14]. These three curves comprise the boundaries of the five concentration regimes identified by Graessley, though of course we should speak of boundary regions rather than boundary curves.

Glass transition temperatures should be much higher for solutions in *Figure 1* with high polystyrene content, and these solutions would need to be investigated at elevated temperatures experimentally. However, in keeping with the accepted ideas on polymer dynamics[16], *Figure 1* has been constructed assuming that concentration regime locations are unaffected by variations in temperature or fractional free volume. Such variations are only expected to affect necessary timescales of measurement, and are not expected to affect the ratio of the two normal stress differences (Ψ). This expectation will be tested in the results to follow. The reptation model has its best chance of working in the concentrated entangled regime, because the solutions in this regime are the most similar to the undiluted samples for which the model was originally developed. The semidilute entangled regime differs in that excluded volume forces and intrachain hydrodynamic interactions are not completely screened, but these differences are not expected to change qualitatively the rheological behaviour, at least according to the reptation picture. The semidilute entangled regime has not been widely studied in the literature, possibly because it can only be accessed by using PS molecules large enough to entangle at low volume fractions. For example, *Figure 1* suggests that the semidilute entangled regime is only accessible using PS molecules with molecular weights in excess of 1×10^5. If the curve labelled C_E in *Figure 1* had been calculated using Ψ_0 data rather than viscosity data, then it would show that even larger molecular weights are required to access the semidilute entangled regime.

MATERIALS

Table 1 lists four monodisperse polystyrene (PS) standards purchased from the Pressure Chemical Company, Pittsburgh, PA. Nominal molecular weights were verified by intrinsic viscosity measurements in toluene at 35°C using the Mark–Houwink–Sakurada relation[17]. The lowest molecular weight standard is the same sample studied some eight years ago by Ramachandran and coworkers[13]. According to intrinsic viscosity measurements, no detectable degradation of this polymer has occurred since the time of purchase. Most of the polymer solutions studied here and in the earlier work by Ramachandran and coworkers were prepared with n-butylbenzene (b.p. = 183°C) as the solvent, purchased from the Phillips Petroleum Company, Bartlesville, OK. The Mark–Houwink–Sakurada equation for PS in n-butylbenzene has not been reported, but we estimate the exponent as 0.61 ± 0.01 at 25°C. This estimate was obtained by measuring the intrinsic viscosity values in n-butylbenzene for three of the molecular weight standards in *Table 1*. This exponent indicates that n-butylbenzene is a 'good' solvent for PS at room temperature. For some solutions, dioctyl phthalate (DOP, b.p. = 384°C) or tricresyl phosphate

Table 1 Polystyrene materials

Sample	Manufacturer	M_v[a]	M_w/M_n
PS600	Pressure Chemical	581 000	1.00
PS1800[b]	Pressure Chemical	1 800 000 (nominal)	1.06
PS2000	Pressure Chemical	1 970 000	<1.3
PS4000	Pressure Chemical	4 000 000	1.06

[a] As determined from intrinsic viscosity measurements in toluene at 35°C using the Mark–Houwink–Sakurada relation[17]

[b] Previously studied by Magda and coworkers[10]

Table 2 Characteristics of the polystyrene solutions

Polymer concentration C ($\mathrm{kg\,m^{-3}}$)	Polymer molecular weight M	Solvent	Mean relaxation time λ (s) at 25°C
255[a]	581 000	n-Butylbenzene	0.0250
188	581 000	n-Butylbenzene	0.00718
160	581 000	n-Butylbenzene	0.00410
177[a]	1 970 000	n-Butylbenzene	0.260
133[a]	1 970 000	n-Butylbenzene	0.0930
115[a]	1 970 000	n-Butylbenzene	0.0610
96.6[a]	1 970 000	n-Butylbenzene	0.0339
75.0[a]	1 970 000	n-Butylbenzene	0.0150
52.3	1 970 000	n-Butylbenzene	0.00525
58.9[b]	1 800 000	Dioctyl phthalate	1.10[c]
68.6[b]	1 920 000	Tricresyl phosphate	0.828
87.6[a]	4 000 000	n-Butylbenzene	0.294
69.4[a]	4 000 000	n-Butylbenzene	0.146
40.9[a]	4 000 000	n-Butylbenzene	0.0281
30.3	4 000 000	n-Butylbenzene	0.0133
22.9[a,b]	>17 000 000	Tricresyl phosphate	>41

[a] Fully entangled on the basis of equation (5)
[b] Previously studied by Magda and coworkers[10]
[c] Measured near the theta temperature (22°C)

(TCP, b.p. = 275°C) was used as the solvent. TCP is also reported to be a good solvent for PS at room temperature, based on viscometry data at a single molecular weight[18]. In contrast, the theta temperature for PS in DOP is only 3°C below room temperature[19], and thus DOP has a much lower affinity for PS than the other solvents used. *Table 2* lists the solutions that were studied, including three solutions previously investigated by Magda and coworkers[10]. Note that the table includes both semidilute ($C < 100\ \mathrm{kg\,m^{-3}}$) and concentrated solutions. Polystyrene only requires about two weeks to dissolve in n-butylbenzene at room temperature, an observation which reflects both the low viscosity of the solvent ($\eta \approx 1$ mPa s) and its affinity for PS. By contrast, DOP and TCP have much higher viscosities ($\eta \approx 65$ mPa s for both) and give solutions with much larger monomeric friction coefficients. Consequently, DOP and TCP solutions are much more difficult to mix completely. Because limited amounts of PS were available, in some cases polymer was re-used after rheological measurement, with methanol used to precipitate the polymer from solution. Intrinsic viscosity measurements were performed to check for possible degradation of the sample after precipitation.

RHEOMETRY

Christiansen and Miller[20] pioneered the use of flush-mounted local pressure transducers for the measurement of N_2 in cone-and-plate shearing flows. The same technique was used by Ramachandran and coworkers[13,21] in their studies of polystyrene solutions, and we used essentially the same technique here. The pressure transducers measure the radial dependence of a total stress tensor component (Π_{22}) during flow, from which N_2 can be calculated using the fundamental equation[22]

$$\Pi_{22} - P_0 = -(N_1 + 2N_2)\ln(r/R) - N_2 \qquad (1)$$

Here Π_{22} is the normal component of the total stress tensor in the velocity gradient direction (negative for a tensile stress), P_0 is atmospheric pressure, r is the radial spherical coordinate and R is the radius of the cone-and-plate rheometer. According to equation (1), measured values of $\Pi_{22} - P_0$ on a semilogarithmic plot should exhibit a linear dependence on the radial coordinate. This prediction is verified in *Figure 2*, which contains typical 'pressure profiles' measured in our laboratory for representative PS solutions. Values shown were measured with a Weissenberg R-17 rheogoniometer modified for N_2 measurement. The cone radius was 37 mm, the cone angle was 0.038 radians and the sample temperature was maintained at 25.0±0.1°C with a circulating water bath. Unless otherwise noted, all reported N_2 values in this paper were measured using the same rheometer geometry at the same temperature. The measured pressure profiles are linear as expected, a result which provides a consistency check on the technique. N_2 can be calculated by either extrapolating the pressure profile to the rim, or by estimating the slope of the pressure profile and making an independent measurement of N_1 (see equation (1)). Both methods gave similar results for all the PS solutions studied. Inertia corrections to the pressure profile were applied when needed at high shear rates using the method of Walters[23]. Details of the construction and calibration of the apparatus are given elsewhere[24].

As with all rotational rheometers, the upper shear rate limit for a polymeric sample is often determined by the occurrence of an elastic instability at the air interface known as 'edge fracture'[25,26]. It has been shown both theoretically[27] and experimentally[28] that edge fracture occurs whenever the magnitude of N_2 exceeds a critical value which depends on the surface tension and cone geometry. The critical N_2 value is approximately given by

$$-N_{2,\mathrm{crit}} = K\gamma/H \qquad (2)$$

Here H is the rheometer gap at the rim, γ is the surface tension and K is a dimensionless empirical constant which is about 5 for the rheometer geometry employed here. Equation (2) implies that there are strong limitations on the samples that can be reasonably studied in rotational rheometers. In the next section it is shown that

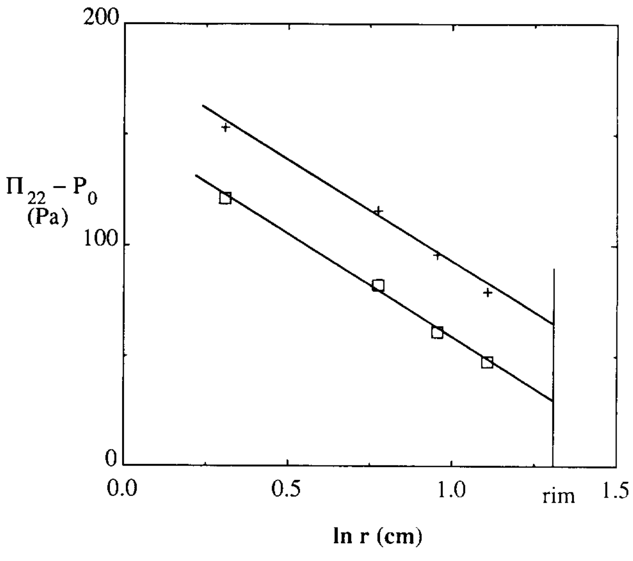

Figure 2 Stress profiles during flow for PS2000 in n-butylbenzene for the following conditions: (□) concentration = 52 $\mathrm{kg\,m^{-3}}$, shear rate = 196 $\mathrm{s^{-1}}$; (+) concentration = 115 $\mathrm{kg\,m^{-3}}$, shear rate = 7.8 $\mathrm{s^{-1}}$

concentrated entangled solutions and entangled polymer melts will exceed the critical N_2 value at relatively low dimensionless shear rates *Wi*. Here *Wi*, the Weissenberg number, is defined as the product of the shear rate with the average polymer relaxation time. Non-linear viscoelastic phenomena such as shear thinning[11] are expected to occur when *Wi* exceeds about 1. Because of edge fracture, many non-linear phenomena can only be studied by avoiding melts and concentrated solutions, or by employing special rheometers for which edge effects are minimal, such as the sliding plate rheometer[26]. We chose semidilute entangled solutions for the detailed study of shear-thinning phenomena. For concentrated entangled solutions of the type previously studied by Ramachandran and coworkers[13,21], we will show that the critical N_2 value is exceeded before $\Psi = -N_2/N_1$ shear thins by a significant amount.

RESULTS

Linear viscoelastic measurements and the onset of full entanglement

At low values of the Weissenberg number in the linear viscoelastic regime, it was possible to measure all three shear flow material functions for all but the last solution in *Table 2*. The three linear viscoelastic shear flow properties are the zero shear rate limiting values of the viscosity (η), the first normal stress difference coefficient (Ψ_1) and the normal stress ratio (Ψ). The first two of these quantities can be used to calculate the average polymer relaxation time (λ), defined as[16]

$$\lambda = \Psi_{1,0}/2\eta_0 \qquad (3)$$

In equation (3) and elsewhere, zero shear rate limiting values are denoted by zero subscripts or superscripts. *Table 2* shows that λ (measured at 25°C) varies by over four orders of magnitude among the various PS solutions studied. The reptation prediction for λ is given by[16]

$$\lambda = (C_1/RT)\zeta M^{3.5}/M_e^{1.5} \qquad (4)$$

Here C_1 is constant for a given species, R is the gas constant, T is the temperature, M is the molecular weight, ζ is the monomeric friction coefficient and M_e is a function of concentration known as the average molecular weight between entanglements. In *Table 2*, the ninth and tenth solutions from the top have similar values of C and M, and yet λ is some two orders of magnitude smaller for the ninth solution. According to equation (4), this must occur because ζ is much smaller for PS solutions prepared with n-butylbenzene than with DOP or TCP at the same concentration. Values of ζ are correlated with fractional free volumes or glass transition temperatures of polymer solutions[16]. Therefore, by comparing rheological measurements for the ninth and tenth solutions in *Table 2*, we can test the prediction that Ψ_0 is independent of the fractional free volume.

According to the reptation picture[6], rheological behaviour is primarily determined by the number of entanglements per chain, $N_e = M/M_e$. Above a certain characteristic molecular weight which depends on concentration, N_e is sufficiently large for reptation predictions to be obeyed and the solution is said to be 'fully entangled'. However, the value of the characteristic molecular weight depends on which rheological property is compared to the reptation predictions[16]. For PS solutions, the characteristic molecular weight for the steady-state recoverable compliance (M_J) is larger than the characteristic molecular weight for the viscosity (M_η) at every concentration[6]. Nonetheless, the ratio M_J/M_η is expected to be independent of concentration. M_J and M_η are well known to depend on the inverse first power of the concentration in the concentrated entangled regime, but the exponent is less certain for the semidilute regime[9]. Experimental measurements on entangled PS solutions over a wide concentration range by Noda and coworkers[15] suggest that M_J is given by

$$C^{1.02}M_J = 1.4 \times 10^8 \qquad (5)$$

where C is the polymer concentration in kg m^{-3}. Ten of the 16 solutions studied here have molecular weights in excess of M_J when calculated with equation (5), and these solutions are identified in *Table 2*. *Figure 3* is a logarithmic plot of the steady-state recoverable compliance ($Je^0 = \Psi_{1,0}/2\eta_0^2$) against polymer concentration for all the PS solutions studied. Data for essentially all of the solutions fall on a single line of slope -2.2, which summarizes the earlier results of Noda and coworkers[15]. Je^0 appears to be independent of molecular weight, and the slope is reasonably close to the reptation prediction, provided that one assumes $M_e \propto C^{-1.2}$. Thus, on the basis of the recoverable compliance, essentially all of the solutions in *Table 2* are fully entangled or close to it. As noted in an earlier publication[29], the transition from semidilute ($C < 100$ kg m^{-3}) to concentrated has no discernible effect on Je^0. Furthermore, the few data points shown for DOP and TCP solutions suggest that solvent power also has no discernible influence on Je^0, even in the semidilute regime where excluded volume forces should be present.

Given that the viscosity and the recoverable compliance imply different characteristic molecular weights for full entanglement, it is perhaps not too surprising that a third value of the characteristic molecular weight (M_Ψ) is suggested by measured values of the normal stress ratio Ψ_0. For each concentration, M_Ψ is defined as the molecular weight above which Ψ_0 has its fully entangled value. Here it should be recalled that the reptation prediction for the fully entangled value of Ψ_0 is either

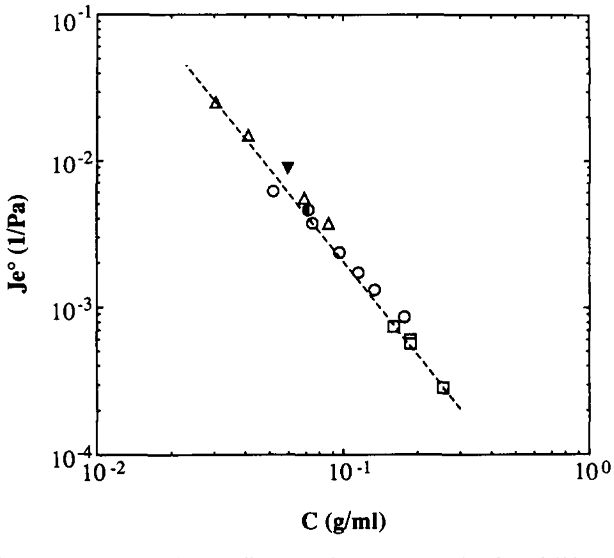

Figure 3 Recoverable compliance against concentration for PS600 (□), PS1800 (▼), PS2000 (○) and PS4000 (△). Open symbols indicate n-butylbenzene solutions, half-filled symbols indicate TCP solutions and filled symbols indicate DOP solutions

2/7 or 1/7, depending on whether or not the independent alignment assumption is made. Furthermore, Ψ_0 is expected to be much smaller (nearly zero) for dilute unentangled solutions[30]. In *Figure 4a*, Ψ_0 is plotted against CM/M_c, where M_c is the characteristic molecular weight for the viscosity in undiluted molten polystyrene ($M_c = 33\,000$). The abscissa should be proportional to the number of entanglements per chain N_e, provided that both M_η and M_c scale as C^{-1}, as expected to be the case for concentrated entangled solutions[16]. Nonetheless, this scaling clearly fails to collapse the data for the three different molecular weights studied. Some of the solutions with higher molecular weight solutes appear to be fully entangled on the basis of equation (5) or *Figure 3*, and yet have Ψ_0 values below the fully entangled limit in *Figure 4a*. However, the fully entangled limit does appear to be the same for all three molecular weights: $\Psi_0 = 0.275 \pm 0.005$. The highest molecular weight sample (4×10^6) reaches this limit at a concentration below $100\,\text{kg m}^{-3}$. Therefore the fully entangled value of Ψ_0 is the same for semidilute and concentrated PS solutions.

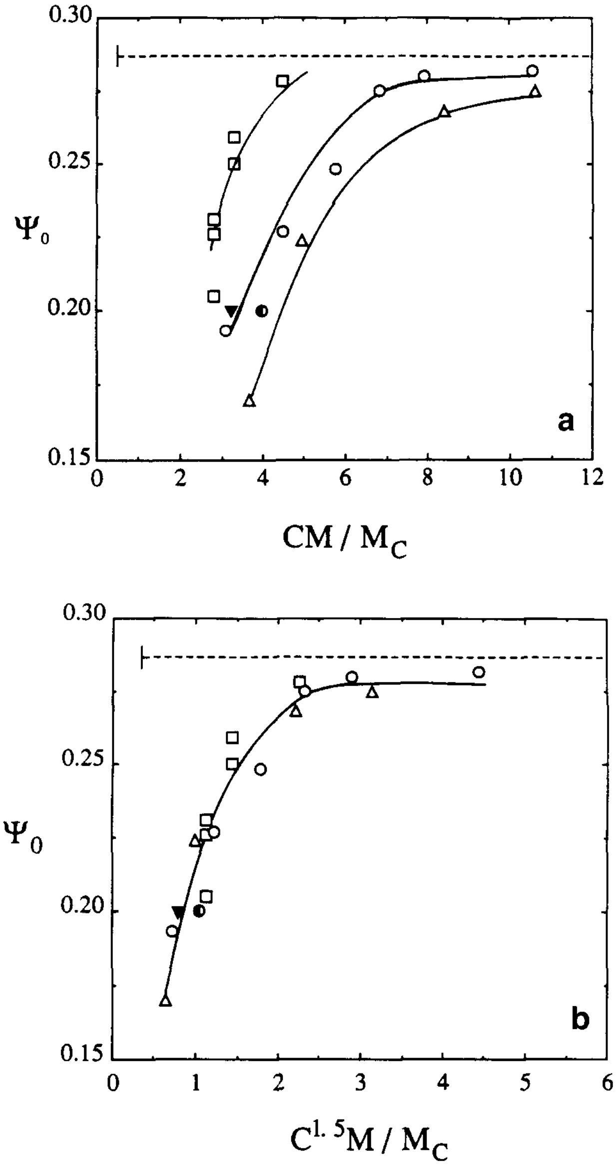

Figure 4 Zero shear rate limiting values of the normal stress ratio Ψ_0. The symbols have the same meanings as in *Figure 3*, and the dashed line summarizes the data of Ramachandran and coworkers[13]. In part (a) an abscissa is used which should be proportional to the number of entanglements per chain in concentrated solutions. In part (b) the abscissa is based on a new scaling parameter proposed in the text for semidilute concentrations

The systematic dependence on molecular weight observed in *Figure 4a* suggests that polymer concentration has a stronger influence on entanglement than molecular weight, so in *Figure 4b* the data are replotted against $C^{1.5}M/M_c$. The new scaling succeeds in collapsing all of the data onto a single curve, including data for solutions with large differences in the monomeric friction coefficient (TCP *versus* n-butylbenzene). Solvent power also appears to have little effect on Ψ_0, even at semidilute concentrations. For a given molecular weight, Ψ_0 gradually approaches the fully entangled limit as C increases, so it is difficult to locate precisely the onset of full entanglement on the basis of Ψ_0. Nonetheless, the data in *Figure 4* suggest the following estimate for the characteristic molecular weight M_Ψ ($70\,\text{kg m}^{-3} < C < 250\,\text{kg m}^{-3}$)

$$M_\Psi C^{1.5 \pm 0.1} = 2.5 \times 10^9 \qquad (6)$$

Surprisingly, the concentration dependences of the characteristic molecular weights M_J (equation (5)) and M_Ψ (equation (6)) differ. An analogous conclusion has already been reported for polybutadiene solutions by Colby and coworkers[29], who found that the characteristic molecular weights for the viscosity and the recoverable compliance have different concentration dependences. Here the ratio M_Ψ/M_J is much larger than one at low concentrations, especially if one can assume that equation (6) continues to be valid at concentrations below $70\,\text{kg m}^{-3}$. As a specific example, consider the last solution listed in *Table 2*, a solution described in an earlier publication[10] as a semidilute entangled solution of an ultrahigh molecular weight polymer. Equation (6) suggests that this solution is not fully entangled, even though conventional calculations[16] based on $M_e \propto C^{-1}$ suggest that the number of entanglements per chain should be in excess of 20! Ψ has already been reported as being surprisingly small for this solution[10], but unfortunately Ψ_0 could not be measured owing to shear-thinning effects.

Also shown in *Figure 4b* are earlier results by Ramachandran and coworkers[13,21] for monodisperse PS solutions in n-butylbenzene, measured using the same rheometer with different pressure transducers. Most of the polymers investigated in this earlier work were relatively low in molecular weight ($M < 1 \times 10^6$), and thus polymer concentrations were correspondingly larger, rarely at semidilute levels. Our work is in very good agreement with this earlier work at high levels of entanglement: $\Psi_0 = 0.287 \pm 0.003$ *versus* 0.275 ± 0.005. The highest polymer concentration studied by Ramachandran[21] was $550\,\text{kg m}^{-3}$ at a PS molecular weight of 2×10^5. For fully entangled solutions, the lowest concentration studied here was about $70\,\text{kg m}^{-3}$ at a PS molecular weight of 4×10^6. If we can combine the results of both studies, then Ψ_0 is independent of concentration over a concentration range which is at least as wide as 70–$550\,\text{kg m}^{-3}$ polymer, provided that the molecular weight is large enough for full entanglement. Since the glass transition temperature probably increases strongly with polystyrene content, Ψ_0 is also insensitive to the fractional free volume. The results of Ramachandran[21] are also consistent with our conclusions here that Ψ_0 is independent of the solvent power and the monomer friction coefficient. However, we are in strong disagreement with the results of Ramachandran and coworkers[13,21] at low values of the abscissa in *Figure 4a*, because Ψ_0 values from this earlier work show no discernible dependence on the degree of entanglement. Such a result is hard to comprehend, given that Ψ_0 is predicted to be nearly zero for dilute unentangled polymer solutions[30], a result which has been experimentally verified[10]. In other PS studies, Osaki and coworkers[12] used optical techniques to measure Ψ_0 for a monodisperse PS solution during stress relaxation after a linear-step shear strain. According to equation (6), these solutions were fully entangled, and yet Ψ_0 was reported to be just above 1/7, smaller than the value reported here. We may also compare with a few published measurements of Ψ_0 for other polymers. Meissner and coworkers[31] measured $\Psi_0=0.24\pm0.02$ for undiluted, molten, entangled polyethylene using a cone-and-plate rheometer which also implies N_2 from the measured pressure distribution during flow. Kannan and Kornfield[32] used optical techniques to measure Ψ_0 for undiluted, molten, entangled polyisoprene during sinusoidal shearing and found $\Psi_0=0.26\pm0.07$. In our laboratory, with the same instrument used in this work, we have measured $\Psi_0=0.21\pm0.01$ for fully entangled polyisoprene solutions[33]. Therefore most, if not all, of the available measurements on monodisperse polymers give Ψ_0 values which are larger than the reptation prediction without the independent alignment approximation (1/7).

Non-linear measurements and experimental guidelines

The normal stress ratio Ψ is often assumed[34] or reported[13,35] to be independent of the shear rate, despite predictions to the contrary by both the reptation model and the Curtiss–Bird model[5,36,37]. In an earlier study from this laboratory[10], shear thinning of Ψ was demonstrated for PS solutions in DOP and in TCP. However, the conclusions of this earlier study appeared at the time to be inconsistent with the findings of Ramachandran and coworkers[13,21], who reported that Ψ was independent of the shear rate for monodisperse PS solutions in n-butylbenzene. *Figure 5* is a plot of Ψ against *Wi* for semidilute solutions of PS in n-butylbenzene at various concentrations, but with a single molecular weight of polymer (4×10^6). All of the solutions are fully entangled on the basis of Je^0, but only two of the solutions shown are fully entangled on the basis of Ψ_0. In contrast to previously published results for this system[13], Ψ is most definitely a decreasing function of shear rate in *Figure 5*. The apparent discrepancy between the two laboratories is resolved by noting that Ramachandran and coworkers[13,21] did not study any semidilute solutions. In *Figure 5*, the terminal Weissenberg number of each curve systematically decreases with increasing polymer concentration due to the occurrence of edge fracture when $-N_2$ reaches about 100 Pa (see equation (2)). When the polymer concentration is high enough to screen excluded volume forces ($C\geqslant100\,\mathrm{kg\,m^{-3}}$), the n-butylbenzene solutions fracture before *Wi* reaches even 2. Therefore, concentrated entangled solutions or melts are unsuitable for studying the non-linear behaviour of Ψ. One must choose semidilute solutions in order to delay fracture to sufficiently large *Wi*.

Though molecular theory is qualitatively correct in its prediction that Ψ shear thins, the amount of shear thinning is greatly overestimated by the reptation model.

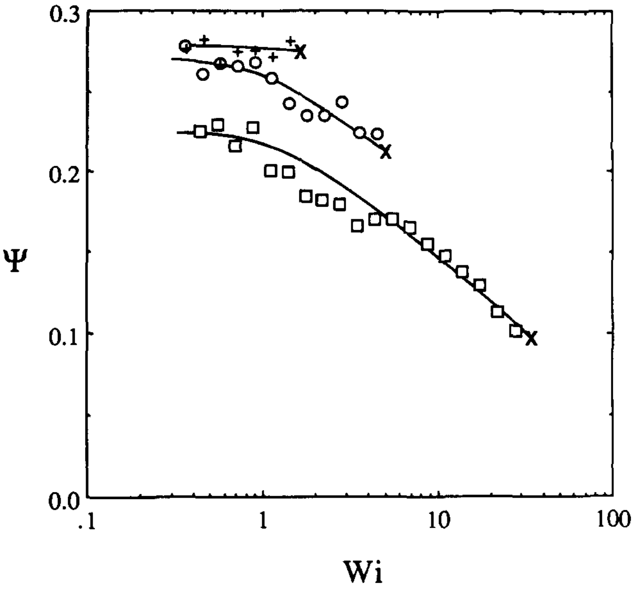

Figure 5 Dependence of the normal stress ratio Ψ on the dimensionless shear rate *Wi* for solutions of PS4000 in n-butylbenzene at the following concentrations: (+) $88\,\mathrm{kg\,m^{-3}}$; (○) $69\,\mathrm{kg\,m^{-3}}$; (□) $41\,\mathrm{kg\,m^{-3}}$. For each curve, the symbol X denotes the onset of the edge fracture instability

The reptation prediction[10] is that Ψ begins to decrease when the Weissenberg number *Wi* exceeds 0.5, and that Ψ/Ψ_0 is less than 0.20 for $Wi=10$. In *Figure 5*, Ψ thins to about 90% of its zero shear rate value at $Wi\approx2$. This is a slower rate of thinning than has been observed with PS in other solvents. For PS in DOP or TCP[10,38], $\Psi/\Psi_0=0.9$ at $Wi\approx1$. Of the three solvents, n-butylbenzene is the only one for which the Mark–Houwink–Sakurada exponent is known to have a good-solvent value. By contrast, DOP is a marginal solvent for PS, and thus PS/DOP solutions exhibit flow-induced concentration fluctuations[38]. These fluctuations may be partly responsible for the shear rate dependence of Ψ observed for the DOP solution.

The behaviour shown in *Figure 5* implies that it is very difficult to use a single entangled polymer solution to study both the linear and non-linear behaviour of Ψ in a rotational rheometer. The difficulty arises from the competing requirements of avoiding shear thinning in the linear regime and avoiding fracture in the non-linear regime. For an entangled solution, N_1 values can only be measured when they lie in a range from about 30 to 500 Pa. The lower limit is set by the transducer sensitivity – few commercially available rheometers can measure N_1 values below 30 Pa. The upper limit has been estimated by assuming $\Psi\approx0.2$, in which case $-N_2$ will exceed the critical value for fracture when N_1 reaches about 500 Pa. The upper limit could perhaps be increased by a factor of five by changing the fixture geometry, but then N_2 would be difficult to measure. As a very rough approximation, the reptation model can be used as a guide for monodisperse entangled solutions[16]

$$N_1\approx v_e kTWi^2 \tag{7}$$

Here v_e ($=C/M_e$) is the number density of entangled network strands, a function of polymer concentration but not molecular weight. If M_e scales as C^{-1}, as expected for concentrated entangled solutions, then v_e should increase roughly quadratically with C. In order to

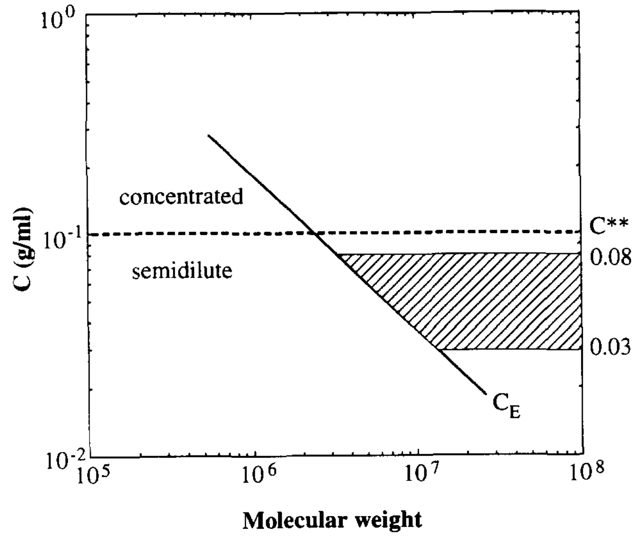

Figure 6 Experimental guidelines for the study of Ψ for fully entangled polystyrene solutions in rotational rheometers. The shaded area is recommended for investigating both linear and non-linear behaviour

measure linear viscoelastic properties, we require $Wi<0.4$ and $N_1>30$ Pa, which places a lower limit on ν_e or C according to equation (7). Empirically, we find that the lower limit is $C \geqslant 30\,\mathrm{kg\,m^{-3}}$ for PS solutions. In order to observe significant shear thinning of Ψ, we require $Wi>3$ (see *Figure 5*) and $N_1<500$ Pa, which places an upper limit on ν_e or C according to equation (7). Empirically, for PS solutions we find that the upper limit is given by $C \leqslant 80\,\mathrm{kg\,m^{-3}}$. The optimum conditions for Ψ measurement are thus given by the shaded region in *Figure 6*. This region is bounded by curves corresponding to the requirements that Ψ_0 be at its fully entangled value (equation (6)), that the linear regime be accessible ($C \geqslant 30\,\mathrm{kg\,m^{-3}}$), and that the non-linear regime be accessible ($C \leqslant 80\,\mathrm{kg\,m^{-3}}$). Obviously, most PS solutions will not satisfy all of these requirements. The optimum regime is even smaller than shown in *Figure 6*, because it is also bounded on the right by a maximum allowable molecular weight. If M is very much greater than 4×10^6, the relaxation time λ becomes so large (equation (4)) that transducer baseline drift becomes a problem. This problem can be mitigated to some extent by reducing ζ, the monomer friction coefficient. This can be done by either increasing the temperature or changing the solvent.

CONCLUSIONS

The reptation model has been shown to be quite successful in describing the elastic behaviour of entangled polystyrene solutions, even when the polymer concentration is as low as $\sim 70\,\mathrm{kg\,m^{-3}}$. The normal stress ratio Ψ is a shear-thinning function of shear rate, and its zero shear rate limit (Ψ_0) is the same for semidilute and concentrated entangled solutions. On the basis of a smaller amount of data, it also appears that Ψ_0 is independent of the segmental friction coefficient and thermodynamic interactions, even at semidilute concentrations. These conclusions can all be counted as qualitative successes of the reptation model. Quantitatively, the model is in error on the value of Ψ_0. We measure $\Psi_0=0.275\pm0.005$, similar to the value reported earlier for PS solutions by Ramachandran and coworkers[13]. The reptation prediction is smaller, $\Psi_0=1/7$, unless the model is solved with the independent alignment approximation, giving $\Psi_0=2/7$. Other laboratories have also measured Ψ_0 values greater than 1/7, such as Meissner and coworkers[31] looking at polyethylene, and Kannan and Kornfield[32] looking at polyisoprene. Ironically, the approximate version of the reptation model is in better accord with the experimental results for Ψ_0.

The transition from the semidilute to the concentrated regime has surprisingly little effect on rheological properties, provided that the system is fully entangled. Colby and coworkers[29] have shown for polybutadiene solutions that the transition changes the concentration exponent of the viscosity, but has no effect on the recoverable compliance Je^0. We have shown for PS solutions that the transition also has no effect on the normal stress ratio Ψ_0.

Colby and coworkers[29] also suggest that the concentration dependences of the characteristic molecular weights M_e and M_c may be different. We were led to a similar conclusion with regard to the characteristic molecular weights for the onset of entanglement effects on the recoverable compliance and the normal stress ratio (M_J and M_Ψ, respectively). Whereas M_J was already known to have an inverse dependence on concentration[15], we have found that $M_\Psi \propto C^{-1.5}$. As a consequence, M_Ψ is very large for semidilute solutions, much larger than the characteristic molecular weight for the viscosity or the recoverable compliance.

Osaki and coworkers[12] have shown that the normal stress ratio Ψ is a decreasing function of strain for concentrated entangled PS solutions in non-linear-step strain experiments. We have shown that the fully entangled value of Ψ decreases as a function of strain rate for semidilute solutions. Others[13,21] may have missed this result because they chose to study concentrated entangled solutions that fracture in rotational rheometers before Ψ shear thins. Also, the presence of significant polydispersity in samples studied by other groups[35] may have been responsible for reducing the level of shear thinning. Perhaps it should also be pointed out that the results presented here do not necessarily imply that entangled PS solutions do not climb rods[39]. The criterion[40] for rod climbing in the regime of low rod rotation speeds is $\Psi<0.25$. Owing to shear thinning, our data suggest that this inequality is satisfied at moderate shear rates or moderate rod rotation speeds.

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REFERENCES

1 de Gennes, P. G. *J. Chem. Phys.* 1971, **55**, 572
2 Doi, M. and Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* 1978, **74**, 1789
3 Doi, M. and Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* 1978, **74**, 1802
4 Doi, M. and Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* 1978, **74**, 1818

5 Doi, M. and Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* 1979, **75**, 38
6 Graessley, W. W. in 'Polymers in Solution' (Ed. W. C. Forsman), Plenum, New York, 1986
7 Lodge, T. P. and Wheeler, L. M. *Macromolecules* 1989, **22**, 3399
8 Douglas, J. F. and Hubbard, J. B. *Macromolecules* 1991, **24**, 3163
9 Graessley, W. W. *Polymer* 1980, **21**, 258
10 Magda, J. J., Lee, C. S., Muller, S. J. and Larson, R. G. *Macromolecules* 1993, **26**, 1696
11 Larson, R. G. 'Constitutive Equations for Polymer Melts and Solutions', Butterworths, Boston, 1988
12 Osaki, K., Kimura, S. and Kurata, M. *J. Polym. Sci., Polym. Phys. Edn* 1981, **19**, 517
13 Ramachandran, S., Gao, H. W. and Christiansen, E. B. *Macromolecules* 1985, **18**, 695
14 de Gennes, P. G. 'Scaling Concepts in Polymer Physics', Cornell University Press, Ithaca, NY, 1979
15 Takahashi, Y., Noda, I. and Nagasawa, M. *Macromolecules* 1985, **18**, 2220
16 Ferry, J. D. 'Viscoelastic Properties of Polymers', 3rd Edn, Wiley, New York, 1980
17 Kurata, M. and Tsunashima, Y. in 'Polymer Handbook' (Eds J. Brandrup and E. H. Immergut), 3rd Edn, Wiley, New York, 1989
18 Riande, E., Markovitz, H., Plazek, D. J. and Raghupathi, N. *J. Polym. Sci., Symp.* 1975, **50**, 405
19 Berry, G. C. *J. Chem. Phys.* 1967, **46**, 1338
20 Miller, M. J. and Christiansen, E. B. *AIChE J.* 1972, **18**, 600
21 Ramachandran, S. PhD thesis, University of Utah, 1988
22 Bird, R. B., Armstrong, R. C. and Hassager, O. 'Dynamics of Polymeric Liquids', 2nd Edn, Vol. 1, Wiley, New York, 1987
23 Walters, K. 'Rheometry', Chapman and Hall, London, 1975
24 Baek, S. G. PhD thesis, University of Utah, 1991
25 Hutton, J. F. *Nature* 1963, **200**, 646
26 Dealy, J. M. and Wissbrun, K. F. 'Melt Rheology and its Role in Plastics Processing', Van Nostrand Reinhold, New York, 1990
27 Tanner, R. I. and Keentok, M. *J. Rheol.* 1983, **27**, 47
28 Lee, C. S., Tripp, B. C. and Magda, J. J. *Rheol. Acta* 1992, **31**, 306
29 Colby, R. H., Fetters, L. J., Funk, W. G. and Graessley, W. W. *Macromolecules* 1991, **24**, 3873
30 Baldwin, P. R. and Helfand, E. *Phys. Rev. A* 1990, **41**, 6772
31 Meissner, J., Garbella, R. W. and Hostettler, J. *J. Rheol.* 1989, **33**, 843
32 Kannan, R. M. and Kornfield, J. A. *Rheol. Acta* 1992, **31**, 535
33 Lee, C. S., Magda, J. J., DeVries, K. L. and Mays, J. W. *Macromolecules* 1992, **25**, 4744
34 Ohl, N. and Gleissle, W. *Rheol. Acta* 1992, **31**, 294
35 Keentok, M. and Tanner, R. I. *J. Rheol.* 1982, **26**, 301
36 Curtiss, C. F. and Bird, R. B. *J. Chem. Phys.* 1981, **74**, 2016
37 Curtiss, C. F. and Bird, R. B. *J. Chem. Phys.* 1981, **74**, 2026
38 Moldenaers, P., Yanase, H., Mewis, J., Fuller, G. G., Lee, C. S. and Magda, J. J. *Rheol. Acta* 1993, **32**, 1
39 Lodge, A. S., Schieber, J. D. and Bird, R. B. *J. Chem. Phys.* 1988, **88**, 4001
40 Beavers, G. S. and Joseph, D. D. *J. Fluid Mech.* 1975, **69**, 475