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Rheology, Flow Instabilities, and Shear-Induced Diffusion in Polystyrene Solutions

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ABSTRACT: All three viscometric functions, namely the shear viscosity and the first and second normal stress coefficients, are measured for several solutions made from nearly monodisperse polystyrenes. The molecular weights and concentrations of the solution components were chosen so that molecular theories could be tested in three different regimes: dilute, semidilute entangled, and concentrated unentangled. We find for dilute solutions that the dependence of the first normal stress difference on dimensionless shear rate, or Weissenberg number Wi, is similar to the prediction of beads-and-springs theories and that Ψ, the negative of the ratio of the second to the first normal stress difference, is near zero, as predicted. For semidilute solutions, Ψ decreases with increased Wi in qualitative agreement with the Doi–Edwards theory for entangled solutions. Surprisingly, Ψ for the unentangled concentrated solutions is 0.10–0.20, in strong disagreement with the Rouse theory, which predicts $\Psi = 0$. In many of these solutions at suitable Wi and temperature, we observe three different kinds of time-dependent phenomena. The first of these phenomena bears the earmarks of an elastic secondary flow and occurs at large Wi for Ψ near zero, in agreement with theory. The second phenomenon, a second overshoot in normal stress, is consistent with shear-induced phase separation. And the third, a very gradual decrease in normal stress, is as yet unexplained.

I. Introduction

Thorough studies have been made of the nonlinear shear-flow rheological properties of well-characterized, nearly mondisperse, *concentrated* solutions and melts of flexible polymers;[1-3] but the same cannot be said for *dilute and semidilute* solutions. The main reason is that the low viscosities and short relaxation times of most dilute and semidilute solutions make them poorly suited for the cone-and-plate rheometers that have proved so useful for obtaining nonlinear steady and transient data for the more sluggish concentrated solutions and melts. Some dilute and semidilute solutions are suitable for study in cone-and-plate instruments, however, namely those for which the polymer molecular weight is high and/or the solvent is viscous, so that even isolated unentangled coils are slow to relax.[1] For sufficiently sluggish solutions, the shear rates required to produce measurable nonlinear effects, including normal stress differences, are low enough to avoid complications of inertial forces. Inertia can alter stresses, generate secondary flows, or even expel the sample from the rheometer. Sluggish solutions avoid these problems and are also advantageous in that their slow response to start-up or cessation of shearing can be tracked readily, yielding valuable rheological information.

Perhaps the most viscous of the dilute solutions studied so far are the "Boger fluids".[4-9] These are composed of a trace of an ultrahigh-molecular-weight polymer dissolved in a very viscous solvent. Often the solvent itself is a long oligomer or a low-molecular-weight polymer, whose relaxation spectrum is widely separated from that of the solute, so that at low shear rates such a solvent behaves as a Newtonian liquid. Boger fluids have been made with relaxation times as long as 50 s,[7] which is an amazingly long time for a single isolated molecule to require for relaxation. While shear stresses and first normal stress differences as functions of shear rate have been measured for several Boger fluids, such data have not been especially useful for testing molecular theories, in part because the polymers used were generally polydisperse in molecular weight.

Even before the identification of Boger fluids, early workers had studied dilute and semidilute polymer solutions that were sluggish enough to measure birefringence, normal stresses, and time-dependent nonlinear stresses.[10-13] In many of these early studies, and in more recent experiments,[7,14-17] peculiar time-dependent shear and normal stresses were reported, including shear thickening, erratic or chaotic time-dependence of the stresses, large differences in stresses from one run to the next, and strong prehistory effects that persisted much longer than could be explained by ordinary molecular relaxation processes. Often these rheological effects were accompanied by increased fluid turbidity, phase separation, or "gelation", which suggested that flow had somehow altered the state of mixing between solvent and polymer. Low-concentration solutions that are sluggish enough to lend themselves to rheological characterization are often "bad actors" in that the above phenomena occur and make the rheological measurements difficult or impossible to interpret. Since sluggish dilute solutions usually contain polymers of high molecular weight and solvents that are viscous and thus composed of relatively large molecules, entropies of mixing tend to be low in such fluids. Thus repulsive forces between unlike solute and solvent molecules can more easily render the thermodynamic stability of these mixtures marginal, and the balance between mixing and demixing is then more readily tipped by flow-induced mechanical stresses. Hence shear flows of sluggish

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low-concentration polymer solutions often cannot be understood in terms of molecular viscoelasticity alone.

In the last few years, however, fundamental theoretical and experimental advances have led to improved understanding of the complex phenomena that occur in these solutions.[17] It has been learned that dilute and semidilute polymer solutions in cone-and-plate and circular Couette shearing flows can experience elastically-driven hydrodynamic instabilities to secondary flow[7,8,18,19] and shear-induced diffusive effects, including shear-enhanced concentration fluctuations,[20] and shear-induced polymer migration.[21,22] Theories for these phenomena have been developed that are in semiquantitative agreement with observations on some well-characterized fluids.[8,18,23,24] With further progress in our understanding, it may be soon be possible to understand many of the peculiar rheological phenomena observed in sluggish dilute and semidilute polymer solutions.

In this article, we present cone-and-plate shearing-flow studies of a series of sluggish dilute and semidilute polymer solutions. The solutions are all composed of nearly monodisperse polystyrenes mixed with simple solvents, either dioctyl phthalate (DOP) or tricresyl phosphate (TCP). DOP is a Θ solvent for polystyrene at 22 °C, and TCP swells polystyrene at room temperature.[25,26] To make the dilute solutions sluggish enough for cone-and-plate rheometry, we have developed viscous binary solvents, made of 28% by weight low-molecular-weight polystyrene (LMPS), dissolved in either DOP or TCP. The molecular weight of this low-molecular-weight polystyrene "cosolvent" is low enough (M_w = 47 500) that it is unentangled even at a concentration of 28%. Thus these viscous binary solutions can serve as solvents for a high-molecular-weight ($M_w = 2 \times 10^7$) polystyrene, HMPS. Adding a trace amount (a few tenths of a percent) of HMPS produces a dilute, yet sluggish, solution. Semidilute ternary solutions are also made by adding 1 or 2% HMPS polystyrene to the binary solvents.

Because of entanglements among high-molecular-weight chains, semidilute solutions are much more sluggish than dilute solutions. Thus semidilute *binary* solutions made by mixing 2% HMPS polystyrene in pure DOP or TCP were viscous enough for rheological study without the low-molecular-weight polystyrene cosolvent. To check concentration and molecular weight dependencies of rheological properties, we also studied 6% solutions of "medium"-molecular-weight ($M_w \approx 2 \times 10^6$) polystyrenes, MMPS1 and MMPS2, in pure TCP and DOP.

As we report here, most of these polymer solutions, like many other sluggish dilute and semidilute solutions, show "peculiar" time-dependent rheological phenomena. However, at low shear rates, at high temperatures, or early after start-up of shearing, we find only "ordinary" time dependencies. Thus, we present our results in two sections. In the first section, we present the measurements for which peculiar time dependencies were not observed; these results are compared to the predictions of molecular theory for dilute and entangled polymer solutions. In the second section, the peculiar time-dependent rheological phenomena observed at higher rates are described and compared to similar phenomena observed for other, often less well characterized fluids.

II. Background

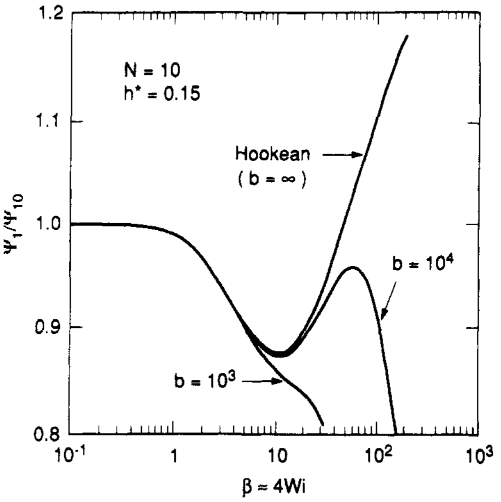

Figure 1. Dependence of the first normal stress coefficient Ψ_1 on dimensionless shear rate β predicted by the beads-and-springs theory with hydrodynamic interaction and finite extensibility for nine springs with hydrodynamic-interaction parameter, h^*, equal to 0.15 and various values of the finite-extensibility parameter, b (adapted from Kishbaugh and McHugh[32]).

We shall compare our rheological measurements with molecular theories for dilute and entangled polymer solutions. Dilute and semidilute unentangled solutions are distinguished by the criterion[1,27] that

$$cM \ll \rho M_c \tag{1}$$

The opposite inequality holds for semidilute entangled solutions. Here ρ is the polymer melt density, M_c is the critical molecular weight for entanglement in the melt ($M_c \approx 35\,000$ for polystyrene[2]), and c is the mass concentration of polymer in the solution. While the rheology of dilute solutions is dominated by the behavior of isolated polymer coils, semidilute entangled behavior is significantly influenced by polymer–polymer entanglement.[1] The crossover from dilute to semidilute rheology is not sharp, and solutions with concentrations near the crossover condition can be expected to display characteristics intermediate to those of very dilute and well-entangled solutions. A further transition from semidilute to concentrated solution behavior occurs when the mass fraction of polymer becomes large, e.g. greater than 10%.[27]

Molecular "beads-and-springs" theories for dilute polymer solutions predict that the shear viscosity η should depend on the shear rate.[28–32] but only weakly, especially if the solvent contribution, η_s, which is assumed to be Newtonian, is not subtracted from the total viscosity. The first normal stress coefficient Ψ_1, which has no solvent contribution, is predicted to show a shear-rate dependence similar to, but more pronounced than, that of the viscosity, though still not nearly as much shear-rate dependence as in an entangled solution. The prediction of Ψ_1 from bead-and-spring theories has an interesting shear-rate dependence, shown in Figure 1.[32] The parameter b in this figure describes the extensibility of the springs used to model the polymer chain; it is proportional to molecular weight and inversely proportional to the number of springs used to model the chain. A chain containing nine springs, which is used in the calculations of Figure 1, models the high-molecular-weight polystyrene studied here ($M_w = 20 \times 10^6$), if each spring corresponds to a molecular weight of about $M_s = 2.2 \times 10^6$. From its definition,[32] the parameter b should equal 3 $M_s/(M_0 C_\infty)$, where M_0 is the molecular weight of the styrene repeat unit, M_0 = 104, and C_∞ is Flory's characteristic ratio, which is about equal to 10 for polystyrene.[33] Thus, b is approximately 6000. In Figure 1, *Wi*, the Weissenberg number, is the shear rate times an "effective" relaxation time, which is defined by $\lambda_{\text{eff}} \equiv \Psi_{1,0}/2\eta_{p,0}$, where η_p is the polymer contribution to the viscosity,

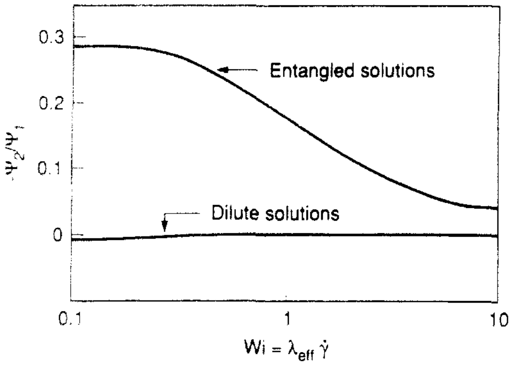

Figure 2. Prediction of $\Psi \equiv -\Psi_2/\Psi_1$ from beads-and-springs models for dilute solutions and from the Doi–Edwards model for entangled polymer solutions.

$\eta_p = \eta - \eta_s$, and the subscript "0" denotes a zero-shear-rate property.

According to Figure 1, as the shear rate increases, Ψ_1 is predicted to show a decrease, followed by an increase, and then a final decrease in value. The first decrease and the subsequent upturn are a consequence of changes in hydrodynamic interactions between different parts of a polymer molecule that occur when the molecule is deformed in the low field.[31] The final decrease in Ψ_1 at a large shear rate occurs when the shear rate is large enough to stretch the polymer molecules close to their maximum possible extension;[32] it is thus sensitive to the value of b. Estimating from the curves of Figure 1, Ψ_1 for a dilute Θ solution with $b \approx 6000$ has a local minimum at about $Wi = 2.5$ and a local maximum at $Wi \approx 10$. Ψ_1 at the local minimum is about 12% lower than $\Psi_{1,0}$, and Ψ_1 at the local maximum is about 4% lower than $\Psi_{1,0}$. This unusual shear-rate dependence of Ψ_1 predicted for dilute solutions differs drastically from that for entangled solutions; the latter are predicted to show strong, monotonic, shear thinning in Ψ_1.[1] While strong shear thinning has been abundantly verified for entangled solutions, until now, no data for *monodisperse* dilute polymer solutions have been available to compare to the predictions for dilute solutions.

Molecular theories also predict drastic differences between dilute and entangled solutions in the shear-rate dependence of the second normal coefficient. Figure 2 shows the ratio $-\Psi_2/\Psi_1$ as a function of Weissenberg number, predicted by a beads-and-springs model for a dilute Θ solution[31,32] and by the Doi–Edwards equation for entangled solutions.[34] For dilute solutions, Ψ_2/Ψ_1 at low Weissenberg number is predicted to be small, around 0.01, and positive and to decrease virtually to zero, as Wi increases above unity. For entangled solutions, Ψ_2/Ψ_1 is also predicted by the Doi–Edwards equation to be small in magnitude at large Wi but to be *negative* and to become much larger in magnitude as Wi approaches zero. The zero-shear-rate value of Ψ_2/Ψ_1 for well-entangled solutions is predicted to approach $-2/7$ at low Weissenberg number. However, this low-shear-rate value of Ψ_2/Ψ_1 changes to $-1/7$ when a mathematical approximation, the independent alignment approximation, invoked in the original Doi–Edwards theory, is relaxed.[35]

No profound rheological changes are predicted to occur at the transition from semidilute to concentrated solutions,[1,27] because the most significant factor affecting the rheology is the presence or absence of entanglements, not the concentration per se. In fact, highly concentrated solutions of low-molecular-weight (and hence unentangled) polymers, such as our binary solvents PS/DOP and PS/TCP, are predicted by the Rouse theory to behave like dilute solutions, in that the viscosity and normal stress coefficients should not show much shear thinning, until the limit of molecular extensibility is reached, and the ratio Ψ_2/Ψ_1 should be zero.[2,27,36] We can check these predictions by shearing our binary solvents at shear rates high enough to obtain measurable normal stress coefficients.

In general, the ratio Ψ_2/Ψ_1 is especially sensitive to constitutive theories.[1] Measurement of this ratio should therefore provide an important check on molecular models. Rarely, if ever, however, has Ψ_2 been measured accurately enough on materials well enough characterized to provide data useful for quantitative or even qualitative evaluation of molecular theories. Here, however, we shall present measurements of *all three* viscometric functions, including $\Psi_2(\dot{\gamma})$, for dilute semidilute entangled, and concentrated (but unentangled) solutions of nearly monodisperse polystyrenes. We shall compare these measurements with the above theoretical predictions.

Measurements of Ψ_2 are useful not only for checking the validity of molecular constitutive theories but also for examining the conditions for onset of a viscoelastically-driven instability that can occur in cone-and-plate and circular Couette flow.[37] Linear stability theories have predicted that a negative value of Ψ_2 strongly stabilizes the flow against such instabilities.[18,19,38] Thus, if these theories are accurate, flow instabilities should occur only when Ψ_2 is measured to be near zero or positive. Strong evidence for these instabilities have been found in several viscous dilute and semidilute solutions;[37] in some cases the existence of these instabilities was confirmed by direct visualization of the secondary flow.[8] The rheological signature of this instability in a cone-and-plate flow is an abrupt rise in both η and Ψ_1 upon onset of the instability. The critical Weissenberg number for the elastic instability is typically found to be within a factor of 2 of the predicted value, *assuming that Ψ_2 is zero.* Measurements reported here allow this assumption to be tested.

When semidilute solutions near a Θ point, such as polystyrene in DOP, are sheared, enhanced light scattering (or turbidity) is observed.[16,20,39] A recent theory of Helfand and Fredrickson[24] and extensions of this theory[40] have been shown to predict semiquantitatively these shear-enhanced scattering phenomena when $Wi \leq 1$.[20] For higher Wi, the scattering becomes much more intense, and rheological properties can show peculiar time-dependent phenomena.[17] For some solutions,[13] and even for a blend of two polymer melts,[41] there is a shear-rate regime in which the shear stress and the first normal stress difference each show a *second overshoot* after hundreds of strain units of shearing have been imposed. This second overshoot, unlike the first overshoot, cannot be explained by ordinary molecular viscoelasticity. It has been shown to be accompanied by *shear-induced demixing* or *phase separation.*[13,41] For the polymer blend, microscopy and fluorescence studies showed that the polymer–polymer demixing occurred during the second overshoot.[41] We shall here show that a second overshoot also occurs when polystyrene/DOP solutions are sheared and provide strong evidence that it is associated with polymer/solvent demixing.

It has also been shown theoretically[21] and experimentally[22] that in shearing flows in which pressure gradients are produced, such as viscoelastic cone-and-plate flows, polymer migration over macroscopic distances can occur, if shearing is prolonged for hours or longer. In a cone-and-plate flow of a viscoelastic solution, pressure gradients are produced both in the radial direction and across the gap.[3] Hence migration in either, or both, of these directions can, in principle, occur. We look for evidence of such migration in our shear-flow studies.

Table I
Solution Components

components	designation	M_W	M_W/M_N
dioctyl phthalate	DOP	391	
tricresyl phosphate	TCP	368	
polystyrene	LMPS	4.75×10^4	1.06
polystyrene	MMPS1	1.8×10^6	1.06
polystyrene	MMPS2	1.92×10^6	1.30
polystyrene	HMPS	2.0×10^7	1.30

Table II
Binary Solvents (Concentrated Unentangled Solutions)

designation	polymeric component (wt %)	small-molecule component (wt%)
PS/DOP	LMPS (28)	DOP (72)
PS/TCP	LMPS (28)	TCP (72)

Table III
Dilute Solutions in a Binary Solvent

designation	long polymer (wt %)	solvent
T.1	HMPS (0.1)	LMPS/DOP
T.2	HMPS (0.2)	LMPS/DOP
T.4	HMPS (0.4)	LMPS/DOP
T.6	HMPS (0.6)	LMPS/DOP
T.TCP.1	HMPS (0.1)	LMPS/TCP

III. Materials

Table I lists the characteristics of the components used to construct the polymer solutions studied here. Solvents were purchased from Aldrich and used as received. Four different polystyrenes with nominal molecular weights listed in Table I were purchased from Pressure Chemical Co., Pittsburgh, PA. The sample with highest molecular weight has an intrinsic viscosity of 17.2 dL/g in toluene at 35 °C, as measured in a Canon four-bulb viscometer with a wall shear stress of 0.1 Pa. From the appropriate Mark–Houwink relation,[42] this implies $M_v \approx 17 \times 10^6$, which compares favorably with the nominal molecular weight of 20×10^6. Because DOP and TCP both have a much higher viscosity than toluene, it was not possible to measure the intrinsic viscosity in either DOP or TCP, because of an unfavorable tradeoff between long capillary flow times and shear thinning.

Ternary and binary polymer solutions were prepared through the use of a volatile intermediate solvent, carbon disulfide. First, binary solvent mixtures (solutions PS/DOP and PS/TCP, Table II) were made from the lowest molecular weight polymer and one of the nonvolatile solvents. A measured amount of the LMPS was dissolved in carbon disulfide, and then the appropriate amount of either DOP or TCP was added. The carbon disulfide was allowed to evaporate from the mixture by leaving it at room temperature and pressures for 3 days and then placing it under vacuum at 30 °C for a period of 6–8 weeks. Beyond this period of time, there were no observable changes in the sample weight and removal of the carbon disulfide from the sample was considered to be complete. The binary solvent mixtures may be characterized as unentangled concentrated solutions with large viscosities. In the shear-rate range of interest for Boger fluids, the binary solvents exhibit little elasticity or shear thinning. The ternary solutions were prepared by an analogous procedure; a measured amount of the HMPS was dissolved in carbon disulfide, then the appropriate amount of the binary solvent was added, and the carbon disulfide was removed as above. Table III and the first two entries of Table IV give the concentrations of the seven ternary solutions prepared in this fashion. The first four solutions are quite similar to polystyrene Boger fluids which have already been studied in the literature.[18] In particular, these are moderately dilute solutions with large elasticity and little shear thinning. By contrast, the two ternary solutions in Table IV may be characterized as semidilute entangled solutions, because these solutions are very shear thinning and have a much higher solute concentration. This type of fluid has not been widely studied before. Finally, to investigate the possibility of ternary thermodynamic effects, four entangled binary polymer solutions were also prepared (the last four entries of Table IV).

Table IV
Semidilute Solutions

designation	long polymer (wt %)	solvent
T1	HMPS (1)	LMPS/DOP
T2	HMPS (2)	LMPS/DOP
H2DOP	HMPS (2)	DOP
H2TCP	HMPS (2)	TCP
M6DOP[a]	MMPS1 (6)	DOP
M6TCP	MMPS2 (6)	TCP

[a] Prepared by Professor G. G. Fuller, Stanford University.

IV. Rheometry

Shear-flow rheological properties to be investigated are defined as follows:[3]

$$\eta = \tau_{12}/\dot{\gamma} \tag{2}$$

$$\Psi_1 = (\tau_{11} - \tau_{22})/\dot{\gamma}^2 = N_1/\dot{\gamma}^2 \tag{3}$$

$$\Psi_2 = (\tau_{22} - \tau_{33})/\dot{\gamma}^2 = N_2/\dot{\gamma}^2 \tag{4}$$

$$\Psi = -\Psi_2/\Psi_1 \tag{5}$$

where $\dot{\gamma}$ is the shear rate and the τ_{ij} are deviatoric components of the stress tensor. A zero subscript or superscript on any of these properties denotes the zero-shear-rate limit. The measurements of η, N_1, and N_2 were performed using a Weissenberg R-17 Rheogoniometer with cone-and-plate fixtures of diameter 74 mm and a cone angle of 0.065 or 0.035 rads. The rheometer temperature was controlled within 0.2 deg with a water bath. η and N_1 values were obtained in the standard fashion[3] from measurements of the total torque and total vertical force on the cone during steady shear flow. Furthermore, the rheometer has been modified to allow accurate N_2 measurements by the placement of miniature pressure transducers at various radial locations along the rheometer plate.[43] The pressure transducers can be used to measure the radial dependence of Π_{22}, the normal component of the total stress tensor in the velocity gradient direction. According to a rigorous radial momentum balance given in standard rheometry textbooks,[3] the measured stress profile should obey

$$-\Pi_{22} - P_0 = 2N_1(\Psi - 0.5)\ln(r/R) + N_1\Psi \tag{6}$$

Here r is the spherical radial coordinate, R is the cone radius, and P_0 is atmospheric pressure. According to eq 6, a semilogarithmic plot of $-\Pi_{22} - P_0$ vs r should yield a straight line, the slope of which can be used to calculate Ψ. Thus the technique does *not* directly yield N_2, but rather the ratio of normal stress differences, Ψ. This distinction is significant when N_1 greatly exceeds N_2 in magnitude, in which case N_2 is difficult to distinguish from zero. Additional experimental details of the measurement technique and its application are given in refs 39 and 43–45.

V. Steady Shear Flow Material Functions

For all of the solutions, it was possible to avoid anomalous time-dependent behavior and to measure steady flow properties by either raising the temperature, lowering the shear rate, or performing measurements

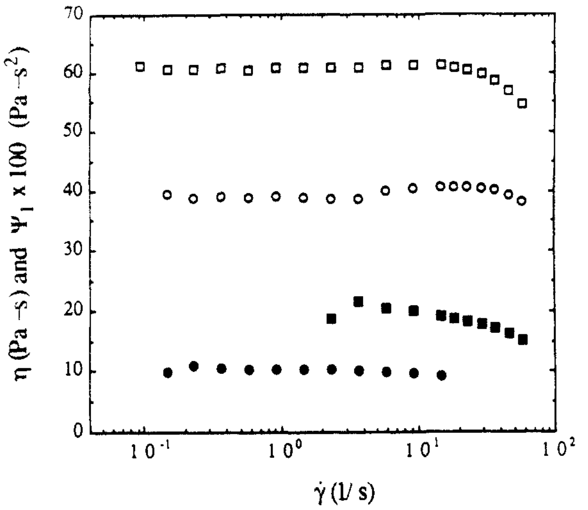

Figure 3. Viscosity (η) and the first normal stress difference coefficient (Ψ_1) vs shear rate for 28% binary solutions PS/DOP (circles) and PS/TCP (squares). The open and filled symbols denote η and Ψ_1, respectively. To clarify the comparison, measured Ψ_1 values have been multiplied by 100.

before the onset of possible flow demixing. The values of the material functions measured in this fashion are discussed in this section. Most experiments were performed at 25 °C; other temperatures are noted in the figure captions. In the next section, possible relationships are explored between the onset of time-dependent behavior and the values of the material functions.

A. Viscosity and First Normal Stress Difference. 1. Binary Solvents. Two solutions were constructed to serve as viscous solvents for the Boger fluids: binary solvent PS/DOP and binary solvent PS/TCP in Table II. The product of the molecular weight and concentration of polystyrene in these solutions is low enough to satisfy eq 1; hence these solutions should be Rouse-like in their rheological properties. Since the Rouse regime is characterized by moderate shear thinning and low elasticity,[2] these two solutions may plausibly be envisioned as very viscous Newtonian solvents. As expected, in Figure 3 the viscosities of these fluids are non shear thinning in the shear-rate range of interest for Boger fluids: $\dot{\gamma} < 20\ \mathrm{s}^{-1}$. Normal stresses are much smaller than shear stresses for the binary solvents in this shear-rate range but are nonetheless measurable. Thus also shown in Figure 3 is Ψ_1, shifted upward by a factor of 100. Like η, Ψ_1 is relatively insensitive to shear rate. Both η and Ψ_1 are larger for PS/TCP than for PS/DOP, a result which presumably reflects the better quality of TCP as a solvent for polystyrene than DOP.

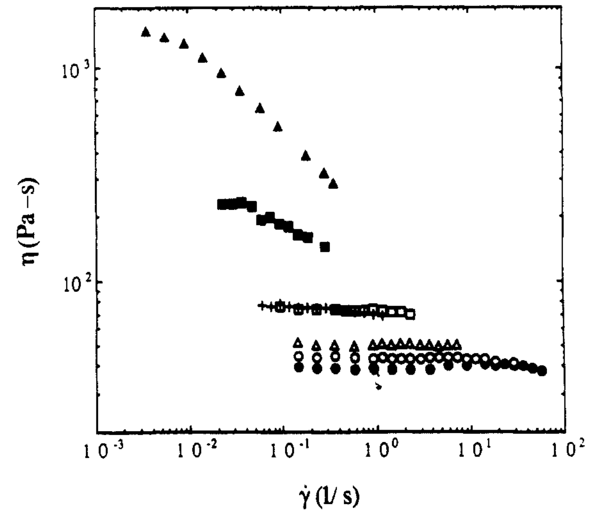

Figure 4. η vs shear rate for solutions of high-molecular-weight (2×10^7) polystyrene in a binary PS/DOP solvent. The symbols indicate solutions PS/DOP (●), T.1 (○), T.2 (△), T.4 (□), T.6 (+), T1 (■), and T2 (▲).

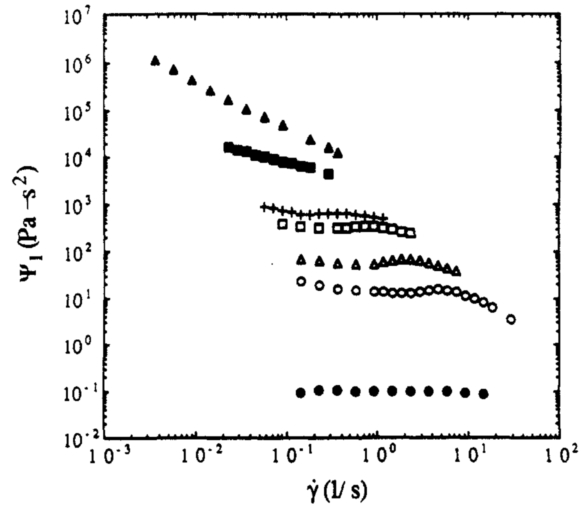

Figure 5. Ψ_1 vs shear rate for solutions of high-molecular-weight (2×10^7) polystyrene in a binary PS/DOP solvent. The symbols have the same meaning as in Figure 4.

2. Dilute Solutions. By adding a trace of ultrahigh-molecular-weight polymer (HMPS) to these binary solvents, Ψ_1 can be increased by 2 orders of magnitude while only slightly increasing the solution viscosity. This is of course the concept behind the formulation of Boger fluids. Four unentangled Boger fluids were formulated with HMPS solute concentrations in the range 1000–6000 ppm (Table III). Viscosities and first normal stress coefficients for these fluids at a slightly different temperature were also reported in an earlier publication.[18] It should be pointed out that the assessment of these fluids as "unentangled" is based on the observed rheological behavior, and not on molecular concepts. Because of the extraordinarily high molecular weight of the solute, two of these Boger fluids do *not* obey the inequality expressed in eq 1. Figures 4 and 5 show η and Ψ_1, respectively, for these four dilute ternary solutions, for the semidilute ternary solutions T1 and T2, and for the binary solvent PS/DOP. Note from Figure 5 that for each of the four dilute solutions, $\Psi_1(\dot{\gamma})$ has a local minimum and a local maximum, similar to that predicted by the dilute-solution molecular theory in Figure 1. This similarity between theory and experiment is unlikely to be a fortuitous artifact caused by the binary solvent, since a similar shape of $\Psi_1(\dot{\gamma})$ has been found for Boger fluids in which the solvent is a single component.[44,46] To facilitate comparison between theory and experiment, Figure 6 replots the Ψ_1 data for the dilute solutions against an approximate Weissenberg number, $Wi = \dot{\gamma}\lambda_{\mathrm{eff}}$. Here $\lambda_{\mathrm{eff}} \equiv \Psi_{1,\mathrm{min}}/2\eta_{\mathrm{p},0}$, where $\Psi_{1,\mathrm{min}}$ is the local minimum value of Ψ_1. Note that for the most dilute solution at least, the values of Wi at which the local minima and maxima occur are in good qualitative agreement with the theoretical predictions for $b = 10\,000$, as are the measured magnitudes of the local minima and maxima. For our solutions, we estimated earlier that b should be roughly 6000.

The agreement between theory and experiment is expected to be only qualitative, for several reasons. In particular, the theory applies to Θ solutions, but for the experimental solutions, the solution viscosities suggest that the solvent quality may be effectively *worse* than Θ. Using the data in Figures 3 and 4, the intrinsic viscosity of the ultrahigh-molecular-weight polystyrene *in the DOP binary*

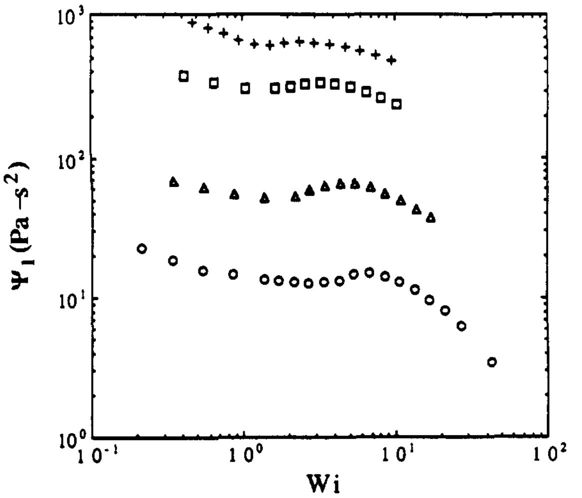

Figure 6. Ψ_1 data for the four dilute solutions of Figure 5 replotted versus an approximation to the Weissenberg number.

solvent can be estimated using

$$[\eta] \approx (\eta_0 - \eta_s)/(c\eta_s) \qquad (7)$$

Here η_0 is the Boger fluid viscosity, η_s is the binary solvent viscosity, and c is the HMPS solute concentration. The intrinsic viscosity thus calculated with eq 7 ($\approx$1 dL/g) is *below the* Θ *value* for polystyrene of molecular weight 20 million (4 dL/g).[42] This suggests that the polymer coils are smaller in size than they would be in a Θ solvent. Since DOP is slightly better than a Θ solvent at the experimental temperature and polystyrene is, of course, a good solvent for itself, one might naively expect a mixture of LMPS polystyrene and DOP to have an effective solvent quality somewhere between the two components and hence for the mixture to be better in quality for polystyrene than DOP by itself. This does not seem to be the case. Monte Carlo simulations of isolated polymer chains in binary solvents of unequal quality[47] have shown, in fact, that the polymer does shrink in size to a dimension smaller than would be the case in either of the two pure solvents. This counterintuitive result is obtained because the polymer chain selectively attracts the preferred solvent of the two to itself, so that the polymer coil is surrounded by a medium rich in the preferred solvent. By shrinking its size, the polymer can reduce the amount of preferred solvent it must attract, and this is favored entropically.[47]

There might, however, be other causes for the apparently low intrinsic viscosity of these solutions. The anomaly can perhaps be attributed to the difficulty in determining the polymer contribution to the viscosity at zero shear rate, in a solution for which the solvent contribution dominates. In Figure 4, η_0 appears to be almost identical for two solutions with differing solute concentrations, T.4 and T.6. However, at shear rates lower than those shown in Figure 4, the viscosity of solution T.6 exceeds that of solution T.4.[18] Alternatively, perhaps a small residue of the volatile intermediate solvent was present in the Boger fluids but not in the binary solvent. Such factors might possibly explain the surprisingly low value of $[\eta]$. Nonetheless, the coil overlap concentration $c^* = 1/[\eta]$ should be about 2500 ppm for HMPS in a Θ solvent.[27,42] Therefore, the absence of shear thinning in Figure 5 for solution T.4 (C = 4000 ppm) supports the idea that HMPS coil dimensions are contracted in the DOP binary solvent, resulting in a reduced number of intermolecular entanglements. By comparing the viscosities of solutions PS/TCP and T.TCP.1, one can also estimate the intrinsic viscosity of HMPS in the TCP-containing binary solvent. $[\eta]$ thus calculated ($\approx$3 dL/g) is about 3 times as large in the TCP binary solvent as in the DOP binary solvent but is nonetheless still below the Θ value. This supports the idea that the coil size in the mixed solvent is smaller than in either of the solvent components.

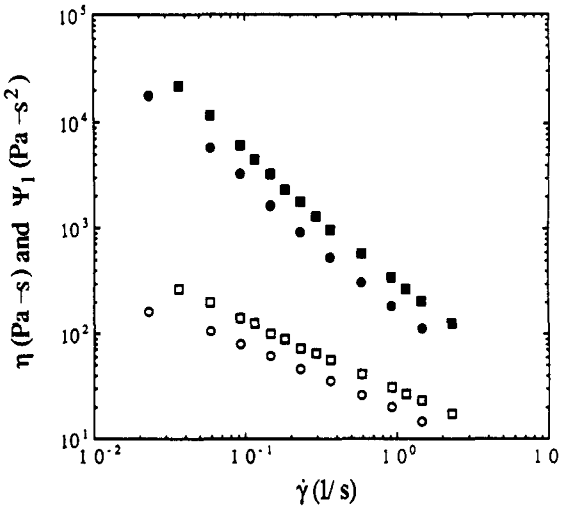

Figure 7. η and Ψ_1 vs shear rate for 2% binary solutions H2DOP (circles) and H2TCP (squares). The open and filled symbols denote η and Ψ_1, respectively. The test solution temperatures are 32.3 °C for solution H2DOP and 25.0 °C for solution H2TCP.

3. Semidilute Solutions. Despite the apparent contraction of HMPS in the binary solvent, the ternary solutions are definitely entangled when the solute concentration reaches 1% and higher, as evidenced by Figures 4 and 5. In these two figures, power-law dependences of η and Ψ_1 on shear rate are exhibited by the 1% and 2% ternary solutions. Also note that the binary solvent contribution to the total viscosity is negligible for these fluids. At this high level of solute concentration, rheological properties are measurable even in a low-viscosity pure solvent such as DOP or TCP, without the added low-molecular-weight polystyrene. Two such solutions were prepared: a 2% solution of HMPS in TCP, and a 2% solution of HMPS in DOP (H2DOP and H2TCP in Table IV). The latter solution may be used to investigate ternary mixing effects, since it is identical with the corresponding ternary solution, except for the absence of low molecular weight polymer. The shear-rate dependences of η and Ψ_1 are shown for these two entangled binary solutions in Figure 7. Because HMPS/DOP binary solutions show evidence of flow demixing at room temperature (section VI), results shown in Figure 7 for this system were measured at elevated temperatures.

By choosing a solute like HMPS with such an extraordinarily high molecular weight (20 × 10^6), it becomes possible to create a large number of entanglements N_e with the polymer volume fraction remaining relatively low. For example, using eq 1 and $M_e = M_c/2$, where M_e is the molecular weight between entanglements, we find $N_e \approx 23$ for a solution containing only 2% by weight of HMPS. By contrast, most rheological data in the literature for entangled solutions have been generated using polymer solutes of lower molecular weights and higher volume fractions. This is the difference between the so-called "semidilute entangled" and "concentrated entangled" concentration regimes.[27] To test the influence of polymer volume fraction in entangled solutions on rheological properties such as N_2, two additional binary solutions were prepared. The first is a 6% solution of MMPS1 (M_w = 1.8 × 10^6) in DOP; the second is a 6% solution of MMPS2 (M_w = 1.9 × 10^6) in TCP. The former solution was prepared in the laboratory of Professor G. G. Fuller of Stanford University. For both of these solutions, $N_e \approx 6$.

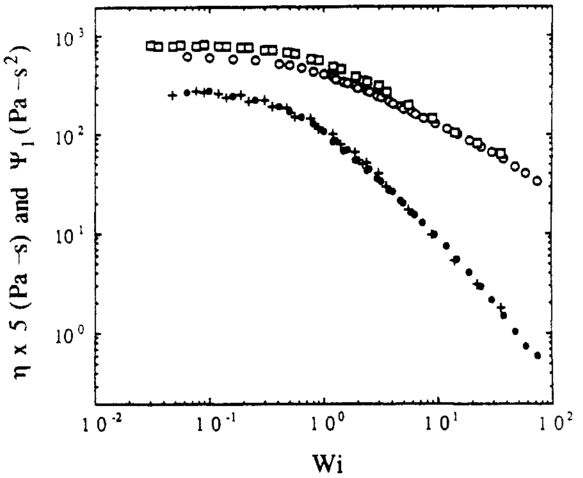

Figure 8. η and Ψ_1 vs Weissenberg number (Wi) for 6% binary solutions. The open circles and squares denote η for solutions M6DOP and M6TCP, respectively, and the filled circles and the crosses, Ψ_1 for solutions M6DOP and M6TCP, respectively. The tested solution temperatures are 22.2 °C for solution M6DOP and 25.8 °C for solution M6TCP. To clarify the comparison, measured η values have been multiplied by 5.

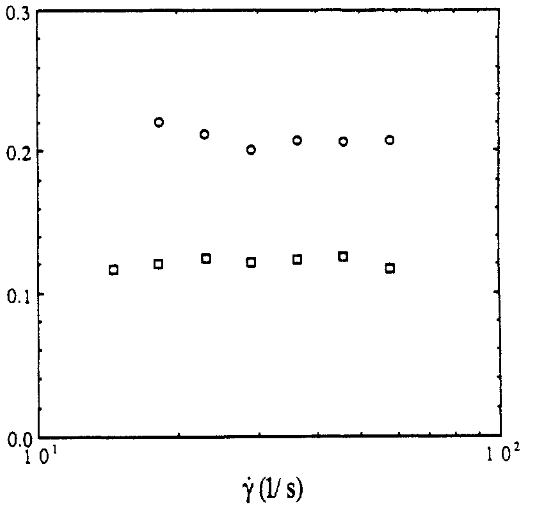

Figure 9. Normal stress ratio (Ψ) vs shear rate for Rouse-like binary solutions PS/DOP (○) and PS/TCP (□).

The shear-rate dependences of η and Ψ_1 for these two solutions are compared in Figure 8. Measurements were performed at slightly different temperatures. Fortunately, it was possible to measure the zero-shear-rate limits of η and Ψ_1 for these two fluids, which was not possible for the 2% solutions of HMPS. Therefore, the largest polymer relaxation times are accurately known for the two 6% solutions, and the dimensionless shear-rate Wi has been employed as the abscissa in Figure 8.

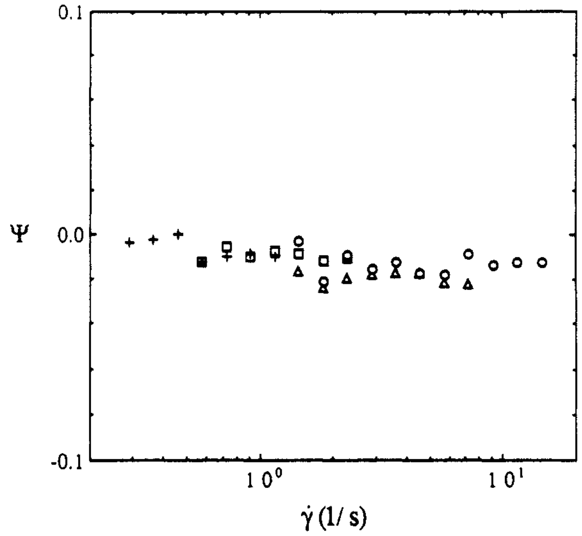

Figure 10. Ψ vs shear rate for dilute ternary Boger solutions. The symbols have the same meaning as in Figure 4.

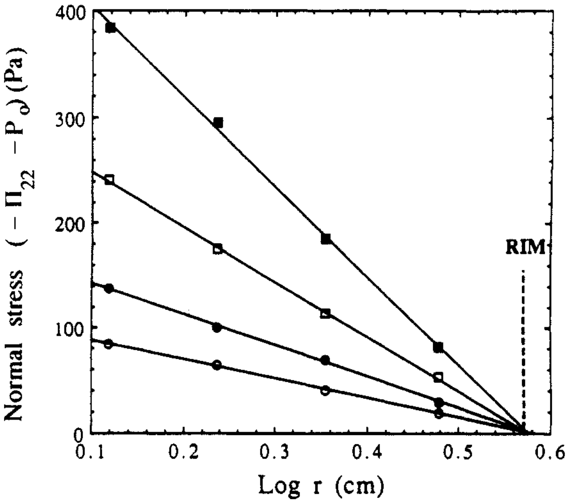

Figure 11. Measured stress profile against radial position for 2% ternary solution T2. The shear rates are 0.023, 0.037, 0.058, and 0.092 s^{-1}, increasing from bottom to top.

B. Second Normal Stress Difference. 1. Binary Solvents—Concentrated Unentangled Solutions. Binary solvents PS/DOP and PS/TCP in Table II should theoretically be described as concentrated yet unentangled "Rouse" solutions. The Rouse theory,[36] originally developed for dilute solutions, neglects excluded volume effects and hydrodynamic interactions between chain segments.[1] Application of the model to concentrated solutions is largely based on accumulated experimental experience,[2] experience which does *not* include measurements of Ψ_2. The applicability of the Rouse model to unentangled concentrated solutions is plausible, because excluded volume/hydrodynamic interactions should be negligible at high concentrations, due to "screening".[1] Figure 9 investigates the shear-rate dependence of $\Psi = -N_2/N_1$ for the two binary solvents. In the Rouse model, Ψ is predicted to be identically zero.[48] The measured value of Ψ, however, is fairly large and appears to be a function of solvent quality (TCP vs DOP). A molecular explanation for these observations is lacking.

2. Dilute Solutions. When a small amount of high-molecular-weight solute is added to the binary solvent to make a Boger fluid, Ψ_1 increases by 2 orders of magnitude. Ψ_2 is *not* increased proportionally, and thus the ratio $\Psi = -\Psi_2/\Psi_1$ becomes so small that it is indistinguishable from zero experimentally. Ψ is plotted as a function of shear rate for the four non-shear-thinning Boger fluids in Figure 10. The value of Ψ is close to zero at all shear rates, a result which confirms earlier measurements of Ψ for polydisperse Boger fluids.[44,49] These results are also consistent with molecular theory;[31,32,50] compare Figure 10 with Figure 2.

3. Semidilute Solutions. Upon addition of greater amounts of HMPS solute, enough to create significant shear thinning, one would expect an increase in the value of Ψ. As discussed in the Background, Ψ is predicted to be a strong function of entanglement density, rising from about zero for a dilute solution to about 0.3 for an entangled solution at low Wi. Figure 11 shows the stress profiles measured in the cone-and-plate rheometer for the 2% ternary solution of HMPS in LMPS/DOP. In Figures 4 and 5, this fluid has already been shown to be very shear thinning, with a large (≈0.4) power-law exponent for the viscosity. Nonetheless, in Figure 11 the value of the stress

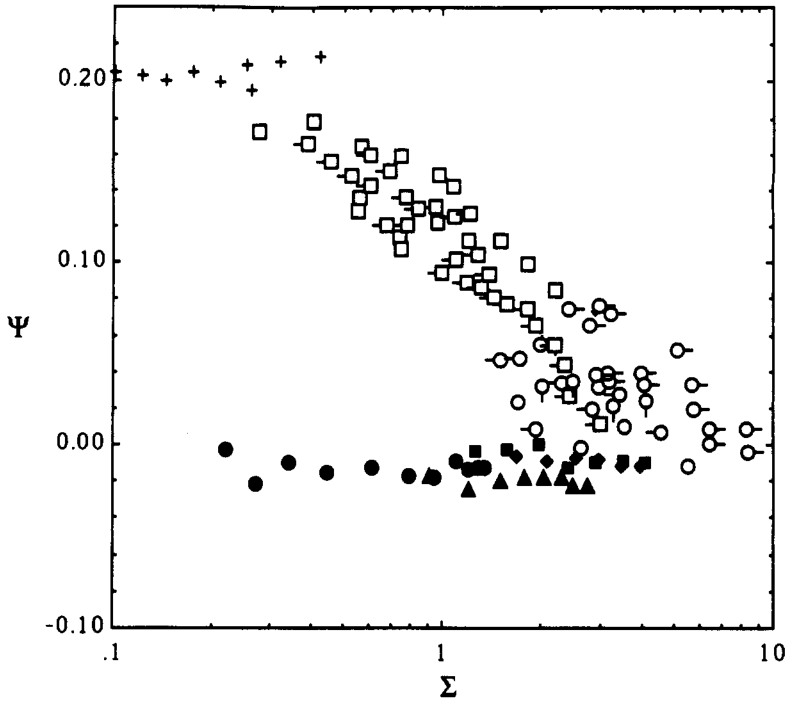

Figure 12. Ψ vs stress ratio ($\Sigma = N_1/2\tau_{12}$) for various solutions. The symbols indicate solutions M6DOP (-□), M6TCP (□), H2DOP (○), H2TCP (○-), T.1 (●), T.2 (▲), T.4 (◆), T.6 (■), T1 (-○), and T2 (♀). Data (+) for 0.13 g/mL polyisoprene (M_w = 9.42 × 10^5) in tetradecane are also included for comparison.[45] The filled symbols indicate dilute solutions, and the unfilled symbols indicate entangled solutions. All measurements were made at 25 °C except solution H2DOP, which was measured at 48 °C.

extrapolated to the rheometer rim is only slightly above zero, yielding a value for Ψ from eq 6 which is surprisingly small: Ψ = 0.03 ± 0.01. This same fluid exhibits an elastic instability in Taylor–Couette flow,[19] the same type of instability which has been well-studied for dilute polymer solutions.[8,18] Since calculations show that even a relatively small value of the normal stress ratio Ψ should suppress the instability,[18,19] the existence of the instability in both cone-and-plate and Taylor–Couette flow suggests that Ψ is surprisingly small for this highly entangled solution.

The small values of Ψ for this solution are perhaps not so surprising when one notes that the Weissenberg numbers for these shearing flows were all in excess of unity. Figure 2 shows that Ψ is predicted to drop considerably as *Wi* increases. The stresses at low *Wi* were too low to measure for solution T2, due to the combination of high solute molecular weight and low solute concentration. Figure 12, however, contains Ψ values measured for *ten* different polystyrene solutions. In Figure 12, filled symbols represent unentangled solutions, and unfilled symbols represent entangled solutions. Included in the data are binary solutions, ternary solutions, solutions containing DOP, and solutions containing TCP. The abscissa is a dimensionless shear rate Σ defined as

$$\Sigma = (\Psi_1\dot{\gamma})/(2\eta) \tag{8}$$

To compare with the theoretical prediction for entangled solutions in Figure 2, it would be preferable to use as the abscissa *Wi* instead of Σ, but unfortunately the largest polymer relaxation time needed to calculate *Wi* is not known for all ten solutions. For a dilute solution, Σ is proportional to *Wi*, independent of shear rate.[19] However, since shear thinning reduces the ratio Σ/*Wi* at high Σ, the true dimensionless shear rate has been *under*estimated for highly unentangled solutions in Figure 12. There is no obvious difference between binary and ternary solution results in Figure 12 nor between results for TCP- and DOP-containing solutions. However, a large qualitative difference is apparent between entangled and unentangled solutions: Ψ is nearly constant at around zero for unentangled solutions, whereas Ψ is shear thinning for all the entangled solutions. Thus qualitative agreement between experiment and theory in the shear-rate dependence of Ψ is obtained for both dilute and entangled solutions; compare Figures 2 and 12.

VI. Time-Dependent Behavior

While shear-flow material functions for these polystyrene solutions were measured, rheological evidence was obtained for three distinct time-dependent phenomena. The first phenomenon appears to be a viscoelastic flow instability related to the elastic Taylor–Couette instability discussed in the sequel to this paper.[19] The mechanical signature of this phenomenon is a sudden, quickly repeatable rise in stress levels (see discussion below). It was also possible to induce two other types of changes in the solution structure by cone-and-plate shearing, changes which were irreversible on a time scale of about 1 h. These changes were taken as evidence of "flow demixing". The following brief discussion highlights the salient experimental observations of time-dependent behavior. Systematic study of the phenomena has *not* been attempted. Possible mechanisms for flow demixing are discussed in more detail in ref 17.

A. Sudden Rise in Stress: Elastic Instability. Figure 13 examines the time dependence of N_1, as measured for the 4000 ppm Boger fluid at a relatively high shear rate. Results observed for a fresh sample are denoted by circles; the crosses indicate the results of the repeat experiment performed 5 min after the end of the first experiment. Both curves have the same plateau value, a plateau value which is consistent with Ψ_1 values measured for this solution at lower shear rates. However, at some later point in time, N_1 rises dramatically above the plateau value and exhibits chaotic behavior for all times thereafter. The repeatability of the experiment demonstrates that the apparent shear thickening is *not* associated with any long-lasting changes in the fluid structure. We believe that this behavior is caused by an elastic flow instability which is predicted to occur for Oldroyd-B fluids in cone-and-plate flows[23] and was directly observed in flow visualization experiments on polyisobutylene Boger flu-

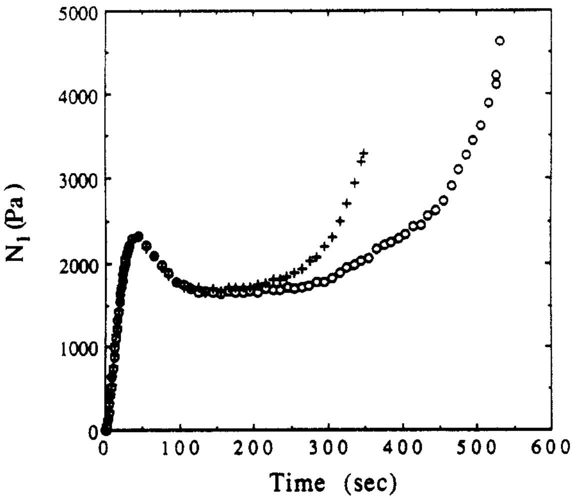

Figure 13. N_1 as a function of shearing time at shear rate 2.91 s^{-1} for the ternary solution T.4. The circles denote the transient response for the fresh solution. The crosses denote the transient response at the same shear rate, repeated after a 5-min rest, following the previous shearing.

ids.[7,8] For the dilute PS boger fluids ($c < 6000$ ppm), observation of this behavior came as no surprise, because the Oldroyd-B constitutive equation is expected to approximate these solutions,[1] and a flow stability analysis with this constitutive equation shows that an elastic instability should occur.[23] Somewhat more surprising was the observation of this behavior at much higher concentrations where the Oldroyd-B equation does not apply. Ten of the thirteen solutions listed in Tables II–IV exhibit evidence of an elastic instability, the sole exceptions being the two Rouse fluids (i.e., the binary solvents) and the 6% solution of MMPS2 in TCP (which shows "edge fracture"[51] instead). The generality of this phenomenon can be explained by analogy to theoretical calculations of ref 19 for shear-thinning liquids in circular Couette flow. There it was shown that an elastic instability should occur for both dilute and entangled shear-thinning fluids at high Σ, if Ψ is small. A similar conclusion probably applies to cone-and-plate flows. Since most of the solutions exhibit small Ψ values at high shear rates (Figure 12), the general occurrence of unstable behavior supports the theoretical prediction. The connection between the value of Ψ and the onset of unstable behavior is most compellingly demonstrated by two entangled binary solutions: 2% HMPS in TCP and 6% MMPS1 in DOP. For both of these solutions, a fairly large Ψ value was measured at lower shear rates. At higher shear rates, the onset of the instability occurs very near the shear rate at which Ψ appears to change sign ($\Sigma \approx 10$ and 5, respectively).[39]

B. Second Stress Overshoot: Shear-Induced Demixing. This phenomenon was only observed in the binary PS solutions containing DOP and is believed to be a manifestation of flow-induced phase separation. These are the same binary solutions for which flow-enhanced light scattering has already been shown to occur.[20,39] At low *Wi*, the theory of Helfand and Fredrickson[24] provides an excellent qualitative description of the light-scattering data. Figure 14 shows the time-dependent approach of N_1 to its steady-state value, for HMPS in DOP at a shear rate of 1.46 s^{-1} and a temperature of 32 °C. This shear rate corresponds to $\Sigma \approx 5$. When shear is imposed on a fresh sample, the transient value of N_1 exhibits *two* overshoots on its approach toward steady state. The first overshoot is not unusual and is associated with the transient stretching of polymer chains.[1] The second overshoot is anomalous and disappears during the repeat run, unless the fluid is given 12 h or more of recovery time.

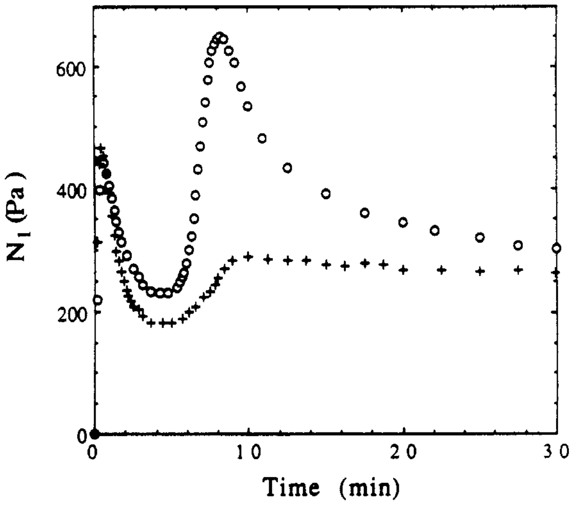

Figure 14. N_1 as a function of shearing time on the binary solution H2DOP at 32.3 °C and shear rate 1.46 s^{-1}. The circles denote the transient response for the fresh solution. The crosses denote the transient response at the same temperature and shear rate after a 25-min rest, following the previous shearing.

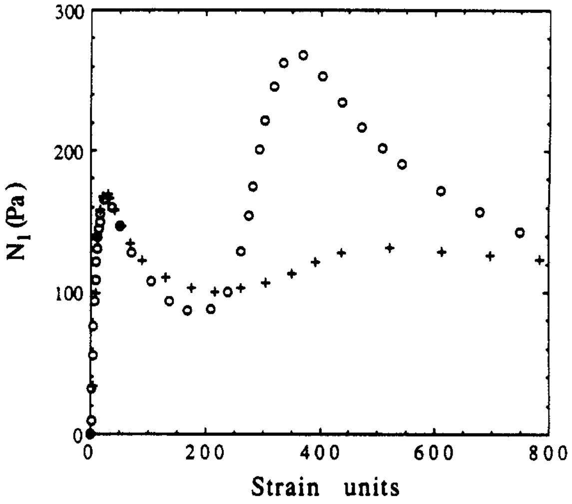

Figure 15. Effect of temperature for the transient N_1 response for the fresh binary solution H2DOP. The circles denote the response at 25.2 °C and shear rate 0.231 s^{-1}. The crosses denote the response at 32.3 °C and shear rate 0.580 s^{-1}.

The length of time required for the solution to recover the ability to generate a second overshoot shows that this phenomenon is not caused by individual molecular relaxations but by a change in the structure of the solution. Other reports of second overshoots can be found in the literature,[13,17,41] and in these systems, the anomalous behavior has been definitively linked to phase separation.

The magnitude of the second overshoot is quite sensitive to temperature, as might be expected for a phase-separating system. Figure 15 compares the start-up behavior of N_1, as measured for fresh samples at two different temperatures. The shear rates have been adjusted so that the magnitude of the first overshoot is the same in both experiments. The magnitude of the second overshoot is clearly much reduced at elevated temperatures.

Figure 16 investigates the start-up behavior of N_1 at a higher shear rate, high enough to induce an elastic flow instability. The shape of the curve suggests that both phase separation and flow instability can occur during the course of a single flow experiment. For the repeat experiment, only the flow instability can be observed.

There does *not* seem to be a critical *Wi* value necessary for the occurrence of the second overshoot. As one decreases the value of *Wi*, the second overshoot also

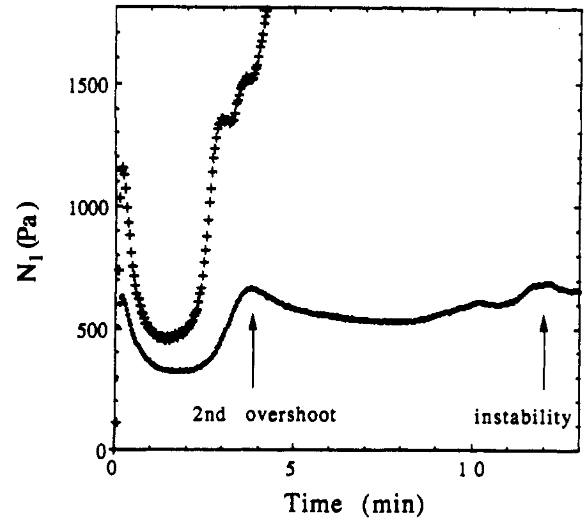

Figure 16. N_1 as a function of shearing time at 40.5 °C for the binary solution H2DOP. The small filled circles denote the transient response for a fresh sample at shear rate 4.60 s^{-1}. The crosses denote the transient response at shear rate 7.30 s^{-1} after a 7-min rest, following the previous shearing.

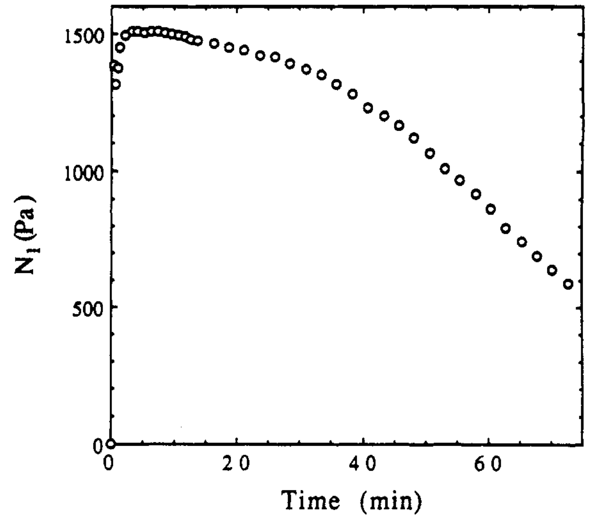

Figure 17. N_1 as a function of shearing time for fresh ternary solution T.1 at shear rate 14.6 s^{-1}.

decreases in magnitude until it becomes indistinguishable from experimental noise. The theory of Helfand and Fredrickson[24] also predicts a gradual change in rheological behavior.

A second overshoot is not observed in our ternary solutions, perhaps because the low-molecular-weight polymer makes the solution thermodynamically more stable. This may seem paradoxical, since we observed earlier that the HMPS molecules were more contracted in size in the binary solvent than in pure DOP. However, if the polymer molecules contract because they preferentially attract the better solvent (namely LMPS) to themselves,[47] then the coil contraction in these solutions does *not* in any way indicate that the solution is more prone to demix, only that the solution can become more stable by shrinking the coil dimensions.

C. Slow Stress Decrease: Unexplained Phenomenon. An interesting time-dependent phenomenon can be observed by shearing the ternary solutions for a very long time at a shear rate below the critical value for onset of the viscoelastic instability discussed above. The gradual downward drift of the apparent N_1 value during such an experiment is demonstrated in Figure 17. Thermocouple measurements confirmed that the sample temperature was constant over the course of the experiment, and for this particular fluid (1000 ppm Boger fluid), the shear viscosity was also fairly constant. Here it should be recalled that the viscosity of dilute Boger fluids is dominated by the solvent contribution. Therefore the mechanism responsible for the downward drift in Figure 17 undoubtedly involves the high-molecular-weight solute. Repeat experiments show that the solution eventually recovers from the changes induced by shearing, with recovery times of about 1 h. Initially, we believed that the downward drift of N_1 was a manifestation of the radial migration of polymer chains toward the tip of the cone, a phenomenon which has been predicted to occur by Dill and Zimm[22] and by Doi and Osaki.[21] However, the *shape* of the measured radial stress profile is unaffected by the changes induced by continuous shearing (Figure 18). This would seem to rule out radial migration, because a radial variation in the polymer concentration should cause a radial variation in the slope of the stress profile. Also the time required for significant radial migration can be estimated from molecular theory; for our very viscous solutions, significant migration is estimated to take months or years. An alternative explanation might be the migration of polymer chains in the direction *normal* to the rheometer plate, due to the variation in the velocity gradient tensor along this direction.[3] However, we can also exclude this explanation, because solution T.1 also exhibits a slow stress decrease when subjected to torsional shearing between parallel disks. For this flow geometry, there is no variation in the velocity gradient tensor normal to the rheometer plate.[3] Therefore the molecular origin of the slow stress decrease remains mysterious. Ternary mixing effects may play a role, because the phenomenon was not observed for any of the binary solutions. This last observation is consistent with the following speculative hypothesis. During continuous shearing, the solvent environment around a given high-molecular-weight solute gradually changes, becomes more rich in low-molecular-weight polystyrene. As a consequence, the large polymer chain becomes more glassy and less flexible, and the normal stress becomes smaller and smaller.

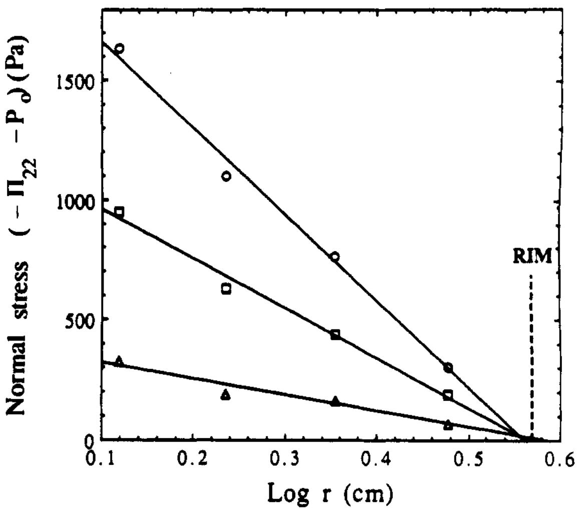

Figure 18. Variation of radial stress profile with shearing time for the same experiment as shown in Figure 17. Stress profiles were measured after shearing for the following amounts of time: 10 min (circles), 60 min (squares), and 100 min (triangles).

VII. Perspective and Directions for Future Work

By studying sluggish polymer solutions made from nearly monodisperse components at a variety of concentrations, molecular weights, and solvent components, we have found distinct patterns of rheological behavior that in most cases accord reasonably well with available theories. The dilute solution behavior of both Ψ_1 and Ψ_2

can be accounted for by beads-and-springs theories that incorporate shear-rate-dependent hydrodynamic interactions[31] and finite extensibility.[32] For semidilute entangled polymer solutions, $-\Psi_2/\Psi_1$ is around 0.20 at low Weissenberg numbers *Wi* and decreases toward zero as *Wi* becomes large, in good qualitative agreement with the Doi–Edwards theory.[34] By contrast, $-\Psi_2/\Psi_1$ has been reported to be 0.27 for concentrated entangled polystyrene solutions, with no indication of shear thinning.[52] This discrepancy is probably caused by a difference in *Wi* values studied; this conclusion is supported by our most recent experiments.[53] Large *Wi* values are difficult to measure for concentrated polymer solutions due to the occurrence of the edge fracture flow instability.[51]

The shear-thinning behavior of $-\Psi_2/\Psi_1$ implies, according to linear stability analyses,[19,37] that these solutions should be susceptible in circular Couette and cone-and-plate flows to an elastic instability at high *Wi*. This prediction is confirmed in our experimental studies.[19] The time-dependent rheological signature of this instability, namely an abrupt rise in η and Ψ_1, is distinct from other time-dependent rheological phenomena that are associated with polymer diffusion, both in the type of time dependence and in the time the solution must rest after shearing stops before the phenomenon can be reproduced. For the elastic instability, the phenomenon can be reproduced within a few polymer relaxation times, i.e., within minutes. Other time-dependent phenomena, namely a second overshoot in Ψ_1 and a slow downward drift in Ψ_1, take hundreds of strain units to be induced and require hours of rest to be reproduced. The second overshoot has been definitively identified elsewhere[13,41] with shear-induced demixing, and our observations are consistent with this. The downward drift in Ψ_1 appears not to be radial migration[21] both because the time required for significant migration is estimated to be too great and because our measured pressure profiles do not show the changes in slope one would expect if radial inhomogeneities in concentration were developing. A careful search for similar phenomena in other Boger fluids might yield clues to an explanation of this mysterious phenomenon.

With the new results presented here and in many other recent publications, it may soon be possible to understand the complex time-dependent phenomena in sluggish dilute and semidilute polymer solutions that hve been reported over the years. This has been made possible by advances in molecular theory,[24,31,32] optical and rheological measurement techniques,[20,39] and recent theories of flow instabilities[8,18,19] and flow-induced diffusion.[21]

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