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Viscoelastic Flows in Abrupt Contraction-Expansions

I. Fluid Rheology

In this note (I of IV) we summarize the rheological properties of the test fluid in shear and extension.

The viscoelastic fluid consists of an 0.025 wt% solution of monodisperse polystyrene (PS) (Scientific Polymer Products, Inc.) with a polydispersity of 1.03. The polystyrene is dissolved in oligomeric styrene (Hercules Piccolastic A5) to yield a dilute solution with $c/c^* = 0.24$. A careful GPC characterization was performed after the solution had been thoroughly mixed. The average molecular weight was determined to be 2.03×10^6 g/mol, slightly smaller than the manufacturer's reported value of 2.25×10^6 g/mol. The resulting solution falls into the class of Boger fluids which are highly elastic with an almost constant viscosity [1]. Table 1 lists all the relevant viscometric properties of the PS solution.

	Notation	Description	Value of Parameter
Known:	c	Concentration of High Molecular Weight Polystyrene	0.025% (= 2.6×10^{-4} g/cm^3)
	M_w/M_n	Polydispersity	1.03
	M_w	Molecular Weight	2.03×10^6 g/mol
	$b = L^2$	Extensibility Parameter	7742
	T_0	Reference Temperature	298 K
Fitted:	η_0	Zero Shear Rate Viscosity	22.75 Pa·s
	η_s	Solvent Viscosity	20.9 Pa·s
	λ_{ps}	Solvent Relaxation Time	2.5×10^{-4} s
	h^*	Hydrodynamic Interaction Parameter	0.1
Calculated:	λ_z	Zimm (Longest) Relaxation Time	3.08 s
	λ_s	Characteristic Relaxation Time for Contraction Flows	0.148 s *
	Ψ_{10}	First Normal Stress Coefficient	6.72 Pa·s^2

Table 1: Parameters characterizing viscometric properties of the 0.025% PS/PS solution.

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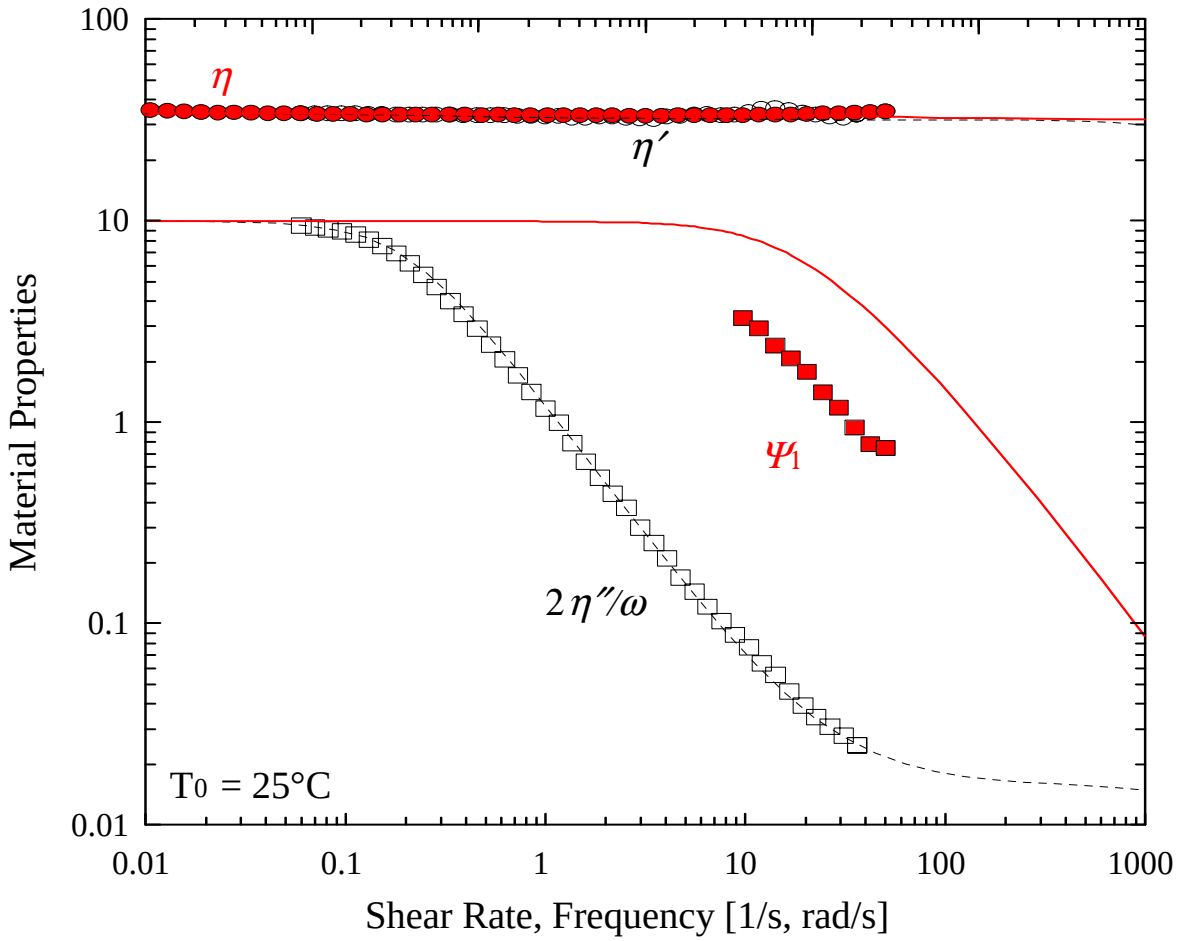

Figure 1: Rheological material functions of the 0.025wt% monodisperse polystyrene in oligomeric polystyrene solution. The data includes: '●', steady shear viscosity $\eta(\dot{\gamma})$ [Pa·s]; '○', dynamic viscosity $\eta'(\omega)$ [Pa·s]; '□', dynamic rigidity $2\eta''(\omega)/\omega$ [Pa·s^2]; '■', first normal stress coefficient $\Psi_1(\dot{\gamma})$ [Pa·s^2]; and the corresponding FENE-P and Zimm model fits plotted as solid lines '—' and dashed lines '– –' respectively.

*See Note II on relaxation times.

Figure 1 shows a master curve of the material functions for the 0.025% PS/PS solution at $T_0 = 25\,^{\circ}C$, measured with a controlled stress device (TA Instruments, Model AR1000N). The linear viscoelastic properties are well described by the Rouse-Zimm bead-spring model [2] which accurately predicts the frequency response of the measured dynamic rigidity $2\eta''(\omega)/\omega$. At medium frequencies, $1/\lambda_z << \omega << 1/\lambda_{ps}$ the slope of this data allows an approximate determination of the hydrodynamic interaction parameter h^* [3] which plays a large role in determining the spectrum of relaxation times

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$$\lambda_j = \frac{\lambda_z}{j^{(2+\sigma)}} \tag{1}$$

where $\sigma = -1.40\,(h^*)^{0.78}$ [4]. The linear viscoelastic modulii are then

$$G' = \frac{cN_A k_B T}{M_w} \sum_{j=1}^{N_m} \frac{(\lambda_z \omega)^2}{j^{2(2+\sigma)} + (\lambda_z \omega)^2} + \frac{\eta_s}{\lambda_{ps}} \frac{(\lambda_{ps}\omega)^2}{1 + (\lambda_{ps}\omega)^2} \tag{2}$$

$$G'' = \frac{cN_A k_B T}{M_w} \sum_{j=1}^{N_m} \frac{(\lambda_z \omega)^2 j^{2+\sigma}}{j^{2(2+\sigma)} + (\lambda_z \omega)^2} + \frac{\eta_s \omega}{1 + (\lambda_{ps}\omega)^2} \tag{3}$$

Ferry suggests that the molecular weight for a single 'spring' in PS is $M_s \sim 10^4$ g/mol giving $N_m = M_w/M_s \sim 200$.

In the limit $h^* = 0$, the free-draining Rouse model incorporates no hydrodynamic interaction and $2\eta'' / \omega \sim \omega^{-3/2}$, whereas in the Zimm (non-free-draining) limit $h^* \approx 0.25$ and $2\eta'' / \omega \sim \omega^{-4/3}$. For the 0.025wt%PS/PS solution $2\eta'' / \omega \sim \omega^{-1.44}$ suggesting from the approximate solution of Thurston that $h^* \approx 0.1$ [4]. At low frequencies ($\omega \leq 0.01$ rad/s) the fluid is essentially Newtonian and the phase angle $\delta \to 90°$ so that significant experimental error is expected in the measurements. However, at high frequencies ($\omega \geq 1000$ rad/s) the Zimm model predictions deviate from the experimental measurements due to the small but finite elasticity of the oligomeric solvent. This additional elasticity can be modeled by an extra Maxwell element for the solvent with a relaxation time $\lambda_{ps} \simeq 2.5 \times 10^{-4}$ s which is in good agreement with the range of values reported by Mackay and Boger [5] and Quinzani *et al.* [6].

The solid line in Figure 1 represents the predictions of a single-mode FENE-P model for the steady shear data. If the finite extensibility is computed from the molecular weight and radius of gyration of the chain we obtain

$$L_{mol} \equiv b_{mol}^{1/2} = \frac{R_{max}}{\langle R_g^2 \rangle^{1/2}} = \frac{n^{1/2} \sin(\theta/2)}{C_\infty^{1/2}} = 88 \tag{4}$$

where R_{max} is the full extension of the polymer chain, n is the number of bonds, θ is the bond angle

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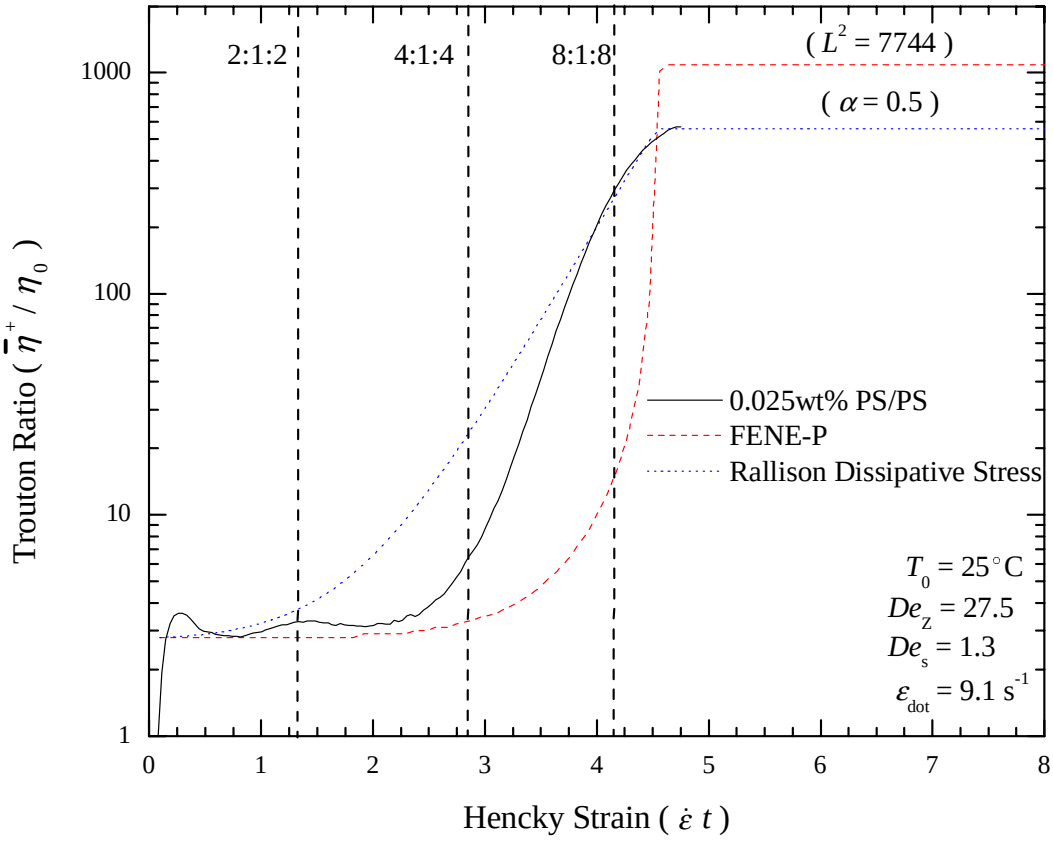

Figure 2: Transient Trouton ratio for the 0.025wt% monodisperse polystyrene in oligomeric polystyrene solution. The data includes experimental uniaxial elongation measurements represented by the solid line '—' and the corresponding FENE-P and Rallison Dissipative Stress model fits plotted as dashed lines '---' and dotted lines '· · ·' respectively.

of the polymer chain backbone and C_∞ is the characteristic ratio (C_∞ = 10 for PS). The FENE-P model contains no adjustable parameters, however, it is clear that a simple dumbbell model does not capture all of the physics observed at high deformation rates. The asymptotic slope of the expressionfor $\Psi_1(\dot{\gamma})$ at high shear rates cannot be changed. The much earlier onset of shear-thinning in $\Psi_1(\dot{\gamma})$ observed experimentally is most likely due to hydrodynamic interactions between the beads of the deformed chain which is not captured in the Zimm (pre-averaged) model [7] and motivates the choice of a lower value of b [8].

To completely characterize an elastic fluid it is necessary to investigate both the shear and the transient extensional rheology of the fluid. Figure 2 shows the transient Trouton ratio ($Tr = \bar{\eta}^+ / \eta_0$)

of the 0.025wt% PS/PS solution as it varies with Hencky Strain ($\varepsilon = \dot{\varepsilon} t$) in a filament stretching experiment. Also shown are the predictions of the single mode FENE-P (L = 88) [4] and Rallison Dissipative Stress (α = 0.5) [9] models. In addition we show the FENE-PM model at a Deborah number of De_z = 27.5. Here we use the Zimm longest relaxation time to compute the Deborah number because this is the relevant timescale for a polymer chain in an extensional flow. This value of Deborah number was chosen to correspond to a strain rate of $\dot{\varepsilon} = 9.1 s^{-1}$ which is representative of strain rates attained in the abrupt-constriction geometry. Using the time constant λ_s = 0.147s gives a Deborah number of De = 1.3 which corresponds to a region where the extra pressure drop has increased but the flow remains stable. Additional transient extensional rheology data at strain rates of $\dot{\varepsilon} = 6.5 s^{-1}$ and $11.25 s^{-1}$ are available. It should be noted that for values of $De_z > 1.0$ the transient extensional viscosity of the solution is largely independent of Deborah number. The stress growth at intermediate strains is much greater than predicted by the FENE-P model and is an indication of the stress-orientation hysterisis [10]. Finally note that we indicate by the vertical dashed lines the total Hencky strain experienced by a fluid element flowing along the centerline from far upstream into the center of the throat.

$$\varepsilon \equiv \int_0^{t_1} \dot{\varepsilon}\, dt = \int_{v_z(-\infty)}^{v_z(z = 1/2 L_c)} \frac{dv_z}{v_z} = \ln(\beta^2) = 2\ln(R_1/R_2) \qquad \textbf{(9)}$$

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