

Yieldlike Constitutive Transition in Shear Flow of Entangled Polymeric Fluids

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We describe an unexpected constitutive transition in entangled polymer solutions. At and beyond a critical stress, the initial spatially homogeneous and well-entangled sample transforms from its entangled (coiled) state into a fully disentangled (stretched) state over a period during which the resulting shear rate increases in a spatially inhomogeneous fashion. In the mode of controlled shear rate, the sample exhibits a stress plateau over three decades. Flow birefringence and normal stress observations unravel additional features of these flow phenomena.

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A central task in the physics of fluids is to determine the constitutive equation that relates the stress response of liquid to a well-characterized history of deformation and vice versa. Such a constitutive relation between stress σ and shear rate $\dot{\gamma}$, symbolized by $\sigma = g(\dot{\gamma}, t)$, is then used to depict and predict flow fields in complicated geometries. Ordinarily in steady state both the constitutive equation $\sigma = g(\dot{\gamma}, t = \infty)$ and its inversion $\dot{\gamma} = g^{-1}(\sigma)$ are continuous and analytical. The analyticity of the constitutive equation leads to the equivalence between controlled rate and controlled-stress experiments.

Two classes of flow systems are known to defy an analytical constitutive description. First, there are fluids that flow easily only when subjected to a level of stress, which is higher than a critical value σ_y , known as yield stress. This flow behavior does not reveal itself when examined in controlled rate measurements. Typically, the materials with yield behavior are multicomponent filled systems such as fluid suspensions. Granular materials as well as foams and gels also show yield behavior. Second, there are materials such as micellar solutions, which at low concentrations exhibit a shear-induced structural transition because the linear surfactant aggregates are able to respond to flow by adjusting their own length. Beyond a critical shear rate, the measured stress jumps, which corresponds to a buildup of a new phase called shear-induced-structures (SIS). This phenomenon is known as shear thickening [1]. Such fluids may exhibit different behavior when examined under controlled stress: the apparent shear rate displays a plateau, and upon increasing applied stress a larger fraction of SIS develops in the shear cell. At sufficiently high concentrations micellar solutions show the opposite rheological features: under controlled shear rate, the measured stress shows a plateau [2–4]. In the stress plateau, the fluid may be inhomogeneous with the shear band structure varying systematically with the applied shear rates [2].

Entangled polymer solutions and melts have been understood to exhibit shear thinning characteristics without becoming inhomogeneous in simple shear. In other words, the polymer viscosity is thought to be spatially

uniform and to decrease with an increasing rate of the imposed shear beyond the Newtonian regime. More importantly, the constitutive equation for polymeric fluids is generally assumed to be analytical so that the flow behavior could be probed equivalently by either controlled rate or controlled-stress measurements. At a sufficiently high stress (typically ca. 0.3 MPa), well-entangled melts may display an interfacial stick-slip transition (SST) where the apparent flow rate jumps discontinuously, from $\dot{\gamma}_{\text{no-slip}}$ to $\dot{\gamma}_{\text{slip}}$ due to a massive wall slip [5]. This behavior also shows up in highly entangled polymer solutions [6]. The molecular origin of SST has been proposed to arise from the disentanglement of the adsorbed chains on the wall with the free flowing chains beyond a critical stress.

In this Letter, we report the salient features of a *bulk* flow phenomenon involving entangled polymers. The observed behavior is expected to be generic for all entangled polymeric fluids including melts. To elucidate the essential physics, we study a model polymer solution made of polybutadiene (PBD) of very high molecular weight $M_w = 1.2 \times 10^6$ g/mol and $M_w/M_n = 1.2$ from Polymer Source, Inc. in a solvent of oligomeric polybutadiene with $M_n = 1000$ g/mol (Cat. No. 20 041-7 from Aldrich). Such a nearly monodisperse polymer solution has a terminal elastic plateau modulus around 6900 Pa at 10 wt % of the PBD and a rather long terminal relaxation time greater than 10 s at room temperature, where all the experiments were performed. To examine the constitutive flow behavior of such entangled polymeric fluids, we subjected the sample to a simple shear in either a cone and plate, a parallel plate or a Couette (made of concentric cylinders) flow geometry in a controlled-stress Bohlin CVOR rheometer. Although all features are the same regardless of the flow geometry, we will report only the rheological measurements obtained with the cone and plate whose diameter is 25 mm, and flow birefringence with both cone and plate and Couette geometries.

When examined in the mode of controlled rate, the polymer solution revealed a stress plateau just below the elastic plateau observed with oscillatory shear, as shown by the squares and diamonds in Fig. 1. This appears to

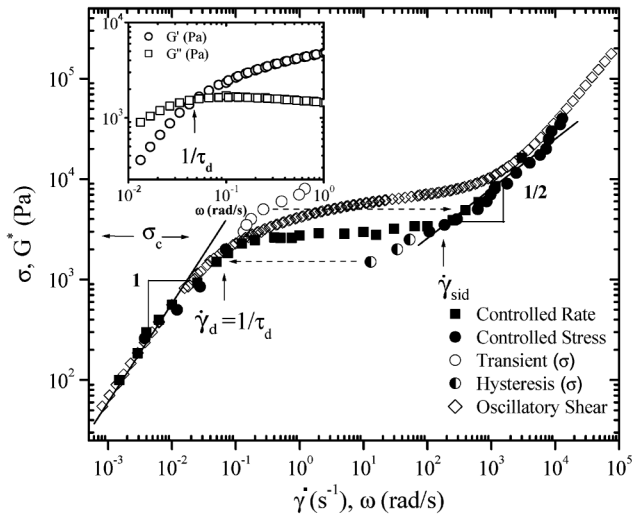


FIG. 1. Flow curves (10 wt % PBD solution) obtained in both controlled rate (in squares) and stress (in circles) modes, where the diamonds display the master curve from the oscillatory shear measurements at several temperatures, the open circles denote the initial shear rates before the constitutive transition brings the sample to the *stable* fast flow branch with a 1/2 slope, and the half-filled circles depict the hysteresis behavior observed upon reducing the applied stress. The inset is the storage and loss moduli G' and G'' vs the oscillation frequency, where the terminal chain disentanglement time τ_d is taken as the reciprocal of the crossover frequency.

indicate an extremely high level of continuous shear thinning, which is commonly known for monodisperse melts and solutions [7].

According to the conventional wisdom, such shear thinning would be associated with increased chain deformation and alignment in shear flow and with a continuously decreasing level of effective chain entanglement, such that the fluid can be sheared faster without generating much more shear stress [7]. A recent observation [8] of this stress leveling off has been used to support some theoretical ideas [9] that instead of a stress maximum with respect to the applied shear rate [10] only a quasi-stress plateau should be expected. However, the nature of such a stress plateau has not been experimentally interrogated. Is it a signature for formation of shear bands as theoretically speculated [9] and as observed in the deformation of many forms of solids, or does it merely indicate a continuously growing degree of chain deformation and stretching with the applied shear rate? In other words, is there a constitutive transition or is the constitutive equation analytical? Driven by the desire to search for *analytical* constitutive equations that can be used in numerical simulations, most theoretical efforts in the past decade have been made [11–14] to rescue the original de Gennes-Doi-Edwards reptation theory [10] from its prediction of a constitutive instability and to derive fully monotonic flow curves relating σ and $\dot{\gamma}$. A review of these theoretical activities has recently been published

[15]. The latest paper [16] gives the most comprehensive theoretical treatment of the subject.

What does the leveling off of the flow curve (in squares) in Fig. 1 reveal? Unfortunately, we cannot identify the origin of the observed stress plateau without making other observations to discern whether the entangled polymer solution is still homogenous or *stratified*. If shear bands would occur, it could imply that there would not be a one-to-one correspondence between the stress and shear rate. Therefore, before embarking on rheo-optical observations, we first sheared the sample in the controlled stress mode. At each applied stress, the resulting shear rate was monitored as a function of time. Below a critical stress level of σ_c the shear rate was found to attain its steady-state value immediately after the initial solidlike transient response. Beyond σ_c , we found the system to evolve in time in terms of the resulting shear rate and normal stress N_1 as shown in Fig. 2.

Denoting the transient initial values of shear rate in open circles and the steady-state values in filled circles, we add the controlled-stress data in Fig. 1 to indicate the transitional behavior as well as the associated hysteresis. Along the horizontal dashed line, the apparent shear rate increased from its initial value to its steady-state value, suggesting a transformation of the sample from the entangled to a disentangled state, where the subscript “*d*” is derived from the conventional notation [10] for the overall chain disentanglement time τ_d in quiescence and “*sid*” stands for stress-induced disentanglement.

The observed increase of the normal stress N_1 with time as shown in Fig. 2 indicates that the chain

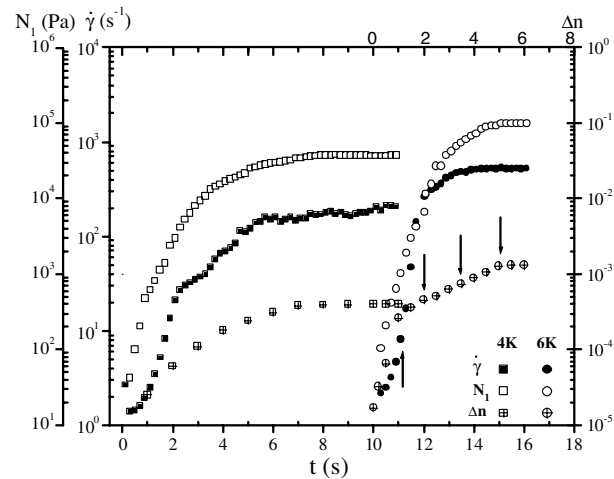


FIG. 2. Transformation from coil (entangled) to stretched (disentangled) state as depicted by three different properties at two applied stresses: the apparent shear rate, normal stress $N_1(t)$, and averaged flow birefringence $\Delta n(t)$ as a function of time, where the four vertical arrows denote the specific times for which video pictures of the retardation from the cone and plate flow cell were taken and presented in Figs. 3. The data at 4 KPa refer to the lower X axis, and those at 6 KPa refer to the upper X axis.

deformation in the bulk sample was still increasing during the transition period even after a hundred strain units. The subsequent rheo-optical observations to be described also indicate that strong molecular deformation and alignment took place in the bulk sample during the transition. Any interfacial wall slip or stick-slip transition (SST) would only involve disentanglement of the adsorbed chains with the bulk chains or chain desorption, and chain deformation in *the bulk* would remain unchanged during the SST. Moreover, a wall slip or SST would produce only a small change [17] in the measured shear rate and cannot explain the observed ratio on the order of 1000. Last, wall slip would be sensitive to the surface condition, which we did not find. Inconsistent with any wall slip, the behavior illustrated in Figs. 1 and 2 must have a different physical origin.

Returning to the characteristics of the constitutive transition shown in Fig. 2 under two applied stresses, we emphasize the different flow behavior in controlled rate and controlled-stress modes: Beyond a critical stress σ_c in the controlled-stress mode, no other values of $\dot{\gamma}$ were accessible in the steady state between its initial value $\dot{\gamma}_d$ and the steady state value of $\dot{\gamma}_{std}$. In the controlled rate mode, all values of the apparent shear rate were accessible, and the observed stress plateau coincided with the minimum level of the applied stress that produced the transitional behavior seen in Fig. 1.

To further probe the nature of the transitional behavior under controlled stress, we carried out flow birefringence measurements across the cone/plate flow cell, where two crossed linear polarizers were placed on either side of the cell, with two illuminating white lamps on one side to provide relatively uniform intensity and a CCD camera on the other along with a VCR. At an applied shear stress of 6 KPa, corresponding to the growing $\dot{\gamma}(t)$ and $N_1(t)$ as shown in Fig. 2, an increasing amount of retardation was observed as a function of time as shown in Fig. 3, where the radial color gradient in each frame arose from the varying thickness of the sample: $H(r) = r \tan \theta$ with θ being the cone angle of 5.4° .

Referring to the Michel-Levy chart [19] and Fig. 3, we can roughly quantify the changing retardation $R(r, t)$, from which an averaged flow birefringence Δn can be estimated from $R(r, t) = \Delta n(t)H(r)$. In this manner, we have obtained the corresponding dynamics depicting the mean flow birefringence Δn (crossed symbols in Fig. 2). The drastic growth of the flow birefringence Δn indicates that the PBD chains were considerably stretched during the transition from their coiled state.

We have further studied the dynamics of the constitutive transition by performing an additional rheo-optical experiment to interrogate the spatial and temporal development of chain stretching in the flow direction during the transition. To this end, we loaded a Couette (concentric cylinders) flow cell with a 7.5 wt % PBD solution and recorded, using the CCD camera attached to the VCR, the continuous evolution of the optical retardation in the gap

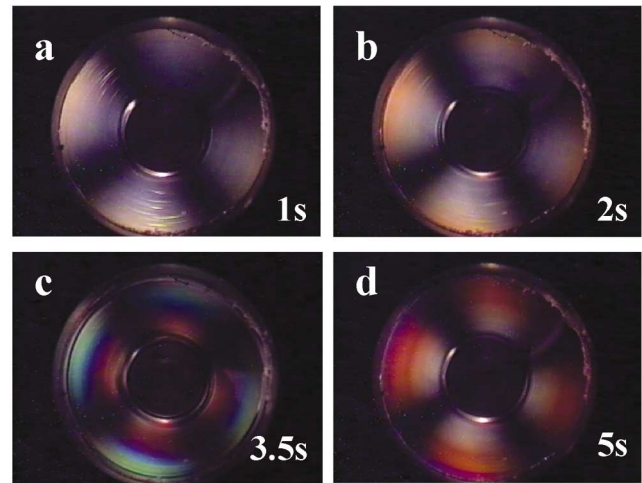


FIG. 3 (color). Top view of optical retardation $\sigma = 6$ KPa from the cone and plate geometry at $\sigma = 6$ KPa at different stages of the constitutive transition from the coiled to the stretched state.

between the two cylinders at different stages during the transition. Figure 4 shows the increasing shear rate at an applied shear stress of 2500 Pa and four corresponding snapshots of the retardation at different times. These pictures reveal that the buildup of the chain stretching (responsible for the observed birefringence) was spatially nonuniform and required a finite time to reach the steady state.

We note that the critical stress σ_c to produce the yield-like transition is not far from the value of the plateau modulus G_{pl} for the monodisperse entangled solution:

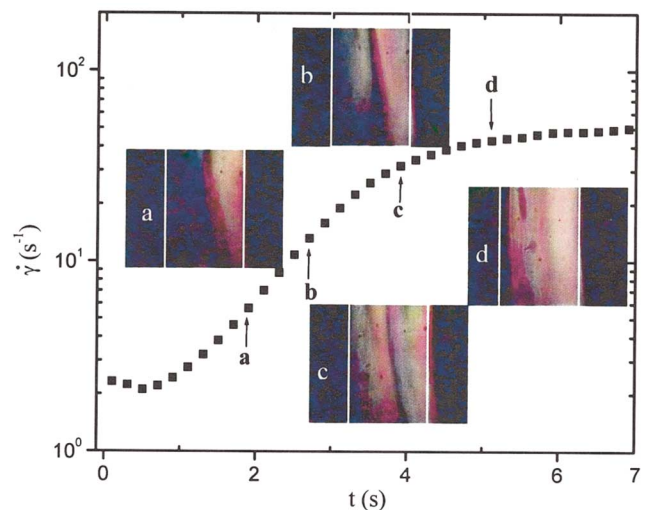


FIG. 4 (color). Measured shear rate (7.5 wt % PBD solution) as a function of time at an applied stress of 2500 Pa, along with four video pictures of the retardation through the gap in a Couette flow cell made of two concentric cylinders with diameters equal to 15 and 14 mm, respectively, where the sample height is about 20 mm.

$$G_{\text{pl}}(\phi) = G_N^0 \phi \left(\frac{a}{a_L} \right)^2 = \frac{\phi}{a_L^2} (k_B T / b), \quad (1)$$

where G_N^0 is the plateau modulus of an entangled PBD melt equal to 1.1 MPa, ϕ is the volume fraction of the PBD, b is the Kuhn segmental length, and a_L is the dilated tube diameter in a tube based reptation model, related to [17] the bare tube diameter a according to $a_L/a = \phi^{-0.6}$. Figure 1 indicates $G_{\text{pl}} = 6900$ Pa in agreement with Eq. (1). Thus, at the transition around $\sigma = 3000$ Pa, each entangled strand is subjected to a force on the order of $k_B T / b$, enough to produce substantial chain stretch. In the stretched (disentangled) state, all polymer chains in the sample behave Rouse-like with a relaxation time [18] $\tau_e = \tau_{e0} (a_L/a)^4$ corresponding to the confinement time of the dilated tube, where τ_{e0} is the bare tube confinement time given in Eq. (6.106) of Ref. [10]. In this regime, we expect the characteristic Rouse dynamics to exhibit shear thinning depicted by $\sigma = G_{\text{pl}} (\dot{\gamma} \tau_e)^{1/2}$, which is in agreement with the observed fast flow branch (in filled circles) in Fig. 1.

In summary, all the rheological and rheo-optical experiments performed in both controlled stress and rate modes have self-consistently depicted yieldlike flow behavior unknown previously to entangled polymers. Beyond a certain applied stress, the entangled solution “yielded” in the sense that the apparent shear rate jumped as the sample transformed to a stretched (disentangled) state from the initial coiled (entangled) state. In the controlled rate mode the measured stress exhibited a plateau over a wide range of shear rates. The potential significance of this finding lies in the likelihood that the yieldlike transitional flow behavior may be shared by most entangled polymeric fluids in some form. Therefore, a more thorough study may lead to new understanding of polymer flow behavior including the well-known shear thinning phenomenon. Experiments are underway in our lab on entangled solutions of different molecular weights at various concentrations and with different molecular weight distributions, on different polymer melts of various molecular weights and molecular weight distribution, and on filled polymeric fluids to explore the universality of the yieldlike constitutive behavior elucidated in the present study.

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