



# Watching shear thinning in creep: Entanglement-disentanglement transition



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## ABSTRACT

We have carried out various rheometric experiments to probe the nonlinear rheological behavior of two well-entangled 1,4-polybutadiene solutions using both stress-controlled and rate-controlled startup shear. At a polymer concentration of 2% neither wall slip nor shear banding occurs, and there is no visible edge failure. At a moderate level of shear stress, the shear rate can take an induction time  $t_{\text{ind}}$  longer than the reptation time to rise toward an eventual steady-state value. The time  $t_{\text{ind}}$  for the entanglement-distanglement transition (EDT) shortens exponentially with increasing stress. The state of entanglement also changes in response to a sinusoidal stress  $\sigma_0 \sin \omega t$  when its amplitude  $\sigma_0$  is beyond a threshold to produce a sufficiently high strain amplitude  $\gamma_0 (>1)$ . Moreover, the evolution of the state of chain entanglement during and after constant-stress creep has been studied using two different protocols. The first switches from creep to rate-controlled startup shear to determine the stress overshoot characteristic. In the second protocol, after creep to different stages, the sample is evaluated for its ability to undergo elastic recovery. We found that the overshoot response to the rate switching weakens and the ability to undergo elastic recoil deteriorates as the EDT progresses. These changes are clearly inherent because edge instability could not produce such effects. Thus, it is confirmed that an entanglement-disentanglement transition is a leading characteristic rheological response of these solutions.

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## 1. Introduction

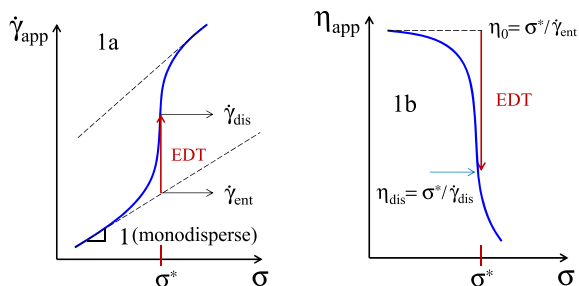
As an integral part of polymer science, nonlinear rheological behavior of entangled polymer systems has been investigated over the past several decades [1] both experimentally [2–9] and theoretically [10–14]. Most previous experimental studies involved application of the rate-controlled shear. This tradition of rate-controlled measurement perhaps arose from the desire to compare with the available molecular theories that are usually formulated for a given deformation field. On the other hand, rheological responses of entangled polymers to startup creep can reveal more insightful information about how polymer entanglement evolves under applied stress [15].

Strongly entangled polymers display significant shear thinning as depicted in a steady-state flow curve in Fig. 1a that is characterized by a stress plateau, i.e., saturation of the shear stress around  $\sigma^*$  over a wide range of rate. This well-known phenomenon suggests that the state of chain entanglement must have undergone

considerable changes from the initial fully entangled state possessing the zero-shear viscosity  $\eta_0$  to a new steady flow state with greatly reduced viscosity  $\eta_{\text{dis}}$ , as illustrated in Fig. 1b. In other words, the essence of shear thinning may be more vividly witnessed in the creep mode involving a stress level around  $\sigma^*$ . Measurements based on stress-controlled shear have revealed this to be an entanglement-disentanglement transition (EDT) [15,16], signified by the rising shear rate over time at a fixed applied shear stress. In this work, we will continue to adopt this phrase to achieve continuity with the past work. However, the meaning of EDT is phenomenological: Since the high zero-shear viscosity is due to strong chain entanglement, any strong decrease of the viscosity at a given stress is an indication of reduced entanglement, or disentanglement. Here disentanglement does not mean complete disentanglement. The EDT phenomenon initialized our curiosity about the origin of shear thinning and the possibility of shear banding in entangled polymers. In particular, the phenomenon motivated the application [17] of particle-tracking velocimetry (PTV) to supplement conventional rheometric measurements. The report of EDT also attracted attention [18–20] concerning the origin of the EDT. These studies have attributed the observed rise in the

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**Fig. 1.** a) Depiction of resulting shear rate versus imposed shear stress in steady state for entangled monodisperse polymers, where a transition like feature emerges around a critical stress level, corresponding to the stress plateau. The “transition” is continuous from the lower branch of full entanglement to the various partially disentangled states. b) This entanglement-disentanglement transition (EDT) shows up in the form of a remarkably sharp drop in the shear viscosity around the stress level of  $\sigma^*$ .

speed of the shearing surface to a progressive loss of sample within the cone-plate device. Indeed, the amount of the sample loss could be exaggerated by running repeatedly within the same sample loading, well after the EDT, as Inn et al. found out.<sup>19</sup> These contrary studies prompted a further study [16] that adopted a cone-partitioned plate device to circumvent the difficulty associated with the edge instability.

The ability to characterize the shear field during startup via PTV has offered us significant insight into the nature of the rheological responses of entangled polymer solutions. Specifically, the PTV observations [17,21] vividly revealed a structural breakdown during the stress decline after the overshoot. Consequently, the stress overshoot should be viewed as a sign of yielding, i.e., a transition from predominantly elastic deformation to irrecoverable deformation (i.e., flow). Presumably the macroscopic yielding is due to a breakdown of the chain entanglement network, where chains mutually slide past one another due to the force imbalance between the intrachain elastic retraction force and intermolecular grip forces [22,23]. Such a picture is alternative to the prevailing viewpoint from the tube model [11]. In the tube model it is not straightforward to relate the stress behavior with any structural change of the entanglement network. By construction, it does not self-consistently account for interchain network-like many-body interactions [24]. On the other hand, it is not difficult for the latest version [25] of the tube model to provide quantitative accounts of the stress overshoot phenomenon as well as other rheological properties [26].

The present work applies both controlled-stress and controlled-rate modes to examine the nonlinear responses of entangled polymers to startup shear and to quantify the state of chain entanglement before, during and after the EDT by either switching from creep to high controlled-rate shear or to conduct elastic recovery tests after creep to various stages. By designing our model system to avoid any shear banding and wall slip, we show that the EDT is inevitable in entangled polymer solutions and can occur during homogeneous shear in absence of any edge instability.

## 2. Experimental

### 2.1. Materials

This study is based on two entangled 1,4-polybutadiene (PB) solutions that are blends of high and low molecular weight PB. The two high  $M_w$  PB was synthesized at the University of Akron in Dr. Quirk’s lab. The low  $M_w$  PB was made at Bridgestone-America via courtesy of Dr. Xiaorong Wang. Their basic characteristics are listed in Table 1. The 1M(5%)-10 K solution contains 5 wt.% of 1M-PB and

**Table 1**  
Molecular characteristics of polybutadienes.

Sample	$M_w$ (kg/mol)	$M_w/M_n$	$\eta_s$ (Pa·s)	Source
4M-PB	$4.03 \times 10^3$	1.04	N/A	Univ. of Akron
1M-PB	$1.05 \times 10^3$		N/A	Univ. of Akron
PB10K	10.5	1.18	14	Bridgestone

is made by dissolving both the parent high molecular weight PB and low molecular weight PB “solvent” in toluene. The 4M(2%)-10 K solution was prepared similarly involving THF as the dissolving solvent. In each case, the solvent-containing PB mixture was placed in the hood for several days to slowly evaporate most of the solvent from the uniform solution. The remaining few-percent solvent was removed in a vacuum oven at room temperature. Using a cone-plate rheometer (Physica MCR-301 from Anton Paar), linear viscoelastic characteristics of the two solutions were determined based on frequency sweep measurements of small amplitude oscillatory shear (SAOS). Fig. 2a–b shows the storage and loss moduli  $G'$  and  $G''$  as a function of the oscillation frequency  $\omega$ , where the reference temperature was 25 °C. The full curves involve SAOS measurements at both 25 °C and 5 °C.

Table 2 lists the basic information obtained from SAOS. The number in the parentheses indicates the weight fraction of the high molecular weight PB. The number after the dash line is the molecular weight of low molecular weight “solvent”. The terminal relaxation time  $\tau$ , also known as the reptation time, is taken as the reciprocal frequency where storage modulus  $G'$  and loss modulus  $G''$  are equal.

The elastic plateau modulus  $G_{pl}$  of the solution is taken as the value of the storage modulus  $G'(\omega)$  at the inflection point of the frequency sweep curve [27]. The number of entanglement per chain  $Z$  is estimated by  $Z = (M_w/M_e)\phi^{1.2}$ , where  $M_e$  is the entangled molecular weight for the pure PB, and  $\phi$  is the volume fraction (i.e., the weight fraction) of the parent polymer. The extrapolation (slip) length  $b = l_{ent}(\eta/\eta_s)$  of these solutions is estimated to be much lower than 1 mm where  $l_{ent} = 26$  and 39 nm for the 1M(5%) and 4M(2%) solutions respectively. Because  $b$  is negligibly small compared to the experimental gap  $H$  around 1 mm, homogeneous shear and quiescent relaxation prevail [28]. All the creep and rate-controlled experiments were carried out at room temperature around 23–25 °C.

### 2.2. Protocol

The stress overshoot during a startup shear is an important character of nonlinear responses in entangled polymer solutions [3,7,29–32] and melts [33–38]. The magnitude of the stress overshoot can be regarded as a measure of the strength of the entanglement network [7,34,39]. As a reference, the entanglement network in the equilibrium state produces the highest stress overshoot for a given rate above the terminal relaxation rate. Elastic recovery after a certain amount of shear also offers information about the state of chain entanglement. The degree of elastic recovery is an indication of how much irrecoverable deformation may have occurred [1]. Thus, both startup shear and elastic recoil can be used as a protocol to monitor the change of chain entanglement during or after shear. Specifically, we can consider a combination of different modes of shear as shown in Fig. 3.

In the first scenario, the sample is sheared at the constant shear stress  $\sigma_1$  for a period of time  $t_1$ , and then immediately probed by a rate-controlled shear with rate  $\dot{\gamma}_2$ . In the second scenario, we can learn about the effect of creep on the state of chain entanglement by allowing the system to undergo elastic recovery, i.e. setting  $\sigma_2 = 0$ ,  $t_2 = \infty$  to evaluate the level of elastic recovery. Both

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