New experiments for improved theoretical description of nonlinear rheology of entangled polymers
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Abstract

The present work discusses four classes of new experiments that could provide clues about how to improve the current theoretical description of nonlinear rheology of entangled polymers. First, a slowly imposed step strain is found to result in non-monotonic evolution of the entanglement structure during quiescent relaxation, consistent with previous particle-tracking velocimetric studies that suggest chain disentanglement after step shear. Second, the stress relaxation upon a sizable step strain is found to be identical to that for small step strain, indicating that a strained entangled melt can resist any accelerated change of chain conformations such as chain retraction. Third, the ability of a step-strained polymer to undergo elastic recovery is found to be the same up to strain amplitude of unity. Moreover, a sample sheared for a period much longer than the Rouse time is shown to still undergo nearly full elastic recovery. Fourth, an entangled melt, stretched at a rate significantly lower than the Rouse relaxation rate, undergoes full elastic recovery until the point of tensile force maximum. We have discussed alternative pictures of how the entanglement network responds to large deformations without ruling out the possibility that the tube model could be remedied to provide a way to characterize rheometric measurements such as those presented in this work.

† In commemoration of the 40th anniversary of de Gennes’ celebrated publication of the reptation idea.
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I. Introduction

Viscoelastic properties of entangled solutions and melts are an important component of physical behavior of polymeric materials. The subject of polymer dynamics is universal and applies to all species with different chemical structures because it deals with polymers in their disordered liquid state. Research on rheology of entangled polymers intensified ever since 40 years ago when de Gennes opened a new era in polymer physics with his proposal of the idea of reptation, envisioning a probe chain to perform snake-like motions in a cross-linked polymeric gel.\(^1\) This notion was subsequently developed by Doi and Edwards into a tube model in a series of four publications.\(^2,3,4,5\) In the tube model, inter-chain excluded volume effects are treated by the insightful idea of Edwards\(^6\) who perceived an impenetrable tube to mimic the constraint due to chain uncrossability. Today, the reptation/tube theory is a common and familiar depiction of chain diffusion and relaxation as well as nonlinear rheology of entangled polymers. Its successes and merits have a great deal to do with how the theory simplifies the extraordinarily complex many-body problem into something tractable and comprehensible. For example, the elusive scaling of zero-shear viscosity \(\eta_0\) with linear chain's molecular weight \(M_w\) as \(\eta_0 \sim M_w^{3.4}\) can be approximately explained. It is proportional to a product of an elastic plateau modulus \(G_{pl}\) (dependent on the entanglement structure, independent of \(M_w\)) and reptation time \(\tau_0\) associated with a test chain that scales at least as \(M_w^3\) due to the tube-like confinement arising from the chain uncrossability. On the 40th anniversary of the reptation idea, it is appropriate to study its major beneficiary, the tube model, in light of an emerging experimental background. To appreciate the molecular-level understanding offered by the tube model from a historic perspective, it is helpful to mention the prior attempts.

Earlier efforts to describe rheological properties of entangled polymers and other viscoelastic materials was dominated by attempts to search for suitable constitutive equations based on continuum mechanics principles.\(^7,8,9,10,11\) Like the Navier-Stokes equation involving a constant Newtonian viscosity, the various available constitutive models including the K-BKZ model\(^12,13\) all have parameters that are constant in space and time. In other words, the starting point of a typical constitutive equation approach is to assume that the liquid structure, e.g., the state of chain entanglement in the case of entangled polymeric liquids, does not vary spatially and can be regarded as a continuum under external deformation. Today, various constitutive models are still popularly employed in finite-element numerical computations to depict fluid mechanics of entangled polymeric liquids.

A large fraction of the constitutive models grew out of modification of the successful rubber elasticity theory\(^14\) that is also known as the neo-Hookean network model in the rheology literature, where the zeroth order picture is to simply evaluate the measured stress in terms of the entropic changes associated with the deformation of all Gaussian strands between chemical crosslinks. By allowing the "crosslinks" to have finite lifetimes, transient network models\(^15,16,17\) (TNM) emerges in 1950s to offer a phenomenological
account of the role played by intermolecular interactions in polymeric liquids. In order to explain such nonlinear and non-Newtonian behavior as shear thinning, TNM allowed the junction lifetimes to depend on the applied rate in some phenomenological manner. Consequently, they are not a first-principles description of polymer rheology.

In the modern tube theory, imagining a chain restricted to tube-like confinement, one simplifies the treatment of many-body inter-chain excluded volume interactions and avoids the formidable challenge to characterize the active role of intermolecular interactions arising from the chain uncrossability. The proposal of the tube constraint for a test chain is actually phenomenological. Specifically, the construction of the tube model is based on the assumption that affine deformation first stretches the entanglement network and then the deformed chains would retract freely in their tubes after a startup deformation has been exerted for a period longer than the Rouse time $\tau_R$. As a consequence, the fraction of stress due to chain stretching involves a short time scale of $\tau_R$, whereas the stress due to orientation would take a reptation time $\tau_0$ to relax upon termination of external deformation. This ansatz of barrier-free chain retraction ensures that the widely observed stress overshoot could emerge in the tube model. Thus, the tube model seems to have provided a description of an essential nonlinear rheological phenomenon. Since its structure is similar to that of the K-BKZ model, the tube model has provided a molecular-level justification of the K-BKZ model. In short, the tube model has been hailed as a great triumph in polymer physics.

All integral-form constitutive models including the Lodge network theory model, the K-BKZ model and the Doi-Edwards tube model, have two common features. (A) The constitutive equation involves the spectrum of equilibrium relaxation times. (B) There is a memory function in the integral for the stress tensor, indicating that the stress would constantly arise from recoverable deformation over a period of time in the past prescribed by the equilibrium relaxation spectrum. In our view, it is not obvious a priori that the equilibrium dynamic characteristics could dictate the non-equilibrium responses.

The goal of the present work is three fold: (a) depict the structure of the tube model in terms of its construction, (b) reveal several key pieces of experimental information that must be accounted for in any theoretical description of large deformation behavior of entangled polymer solutions and melts, and (c) indicate an alternative set of theoretical considerations. Here and below "the tube model" refers to any version of the tube theories including the latest unless specified otherwise. On the other hand, by the Doi-Edwards tube model we refer to the version established by their first four papers.

The following text will first discuss the conditions, under which nonlinear rheology of entangled polymers is dealt with. Then we describe how the tube model treats the subject. After presenting several new experimental results, we conclude by raising the question of whether the experimental findings would require a different set of theoretical concepts and treatment.
II. What are large deformations and when nonlinear responses occur?

The Maxwell model identifies an essential property of viscoelastic materials: a dominant relaxation time $\tau_0$, also known as the terminal relaxation time or reptation time for entangled polymers. According to Maxwell, linear response of viscoelastic materials takes place when the external deformation is either small or taking place sufficiently slowly so that their underlying structures remain intact. Thus, to describe linear response behavior of entangled polymers, an explicit account of the intermolecular interactions may not be necessary in a zeroth order picture. In other words, when the cohesion due to chain entanglement is never overcome, it may be adequate for the tube model to approximate the physics of polymer dynamics by erecting an infinitely high confinement barrier for a test chain.

![Figure 1 Depiction of startup shear at a nominal shear rate of $\dot{\gamma} = V/H$, for which, the time required to produce the first 100% of shear deformation is given by $t_1 = H/V = 1/\dot{\gamma}$.](image)

Taking startup simple shear deformation with rate $\dot{\gamma} = V/H$ for example, Figure 1 shows that $t_1 = H/V = 1/\dot{\gamma}$ is the time required to produce one unit of shear strain. Weissenberg introduced a dimensionless number, $Wi = \tau_0/t_1 = \dot{\gamma} \tau_0$, to gauge whether the applied shear is fast or slow. The degree of the initial elastic deformation is upper bounded by $Wi$. This measure can be straightforwardly extended to other modes of deformation such as uniaxial extension at a Hencky strain rate $\dot{\varepsilon}$ so that $Wi = \dot{\varepsilon} \tau_0$. When $Wi \ll 1$, molecular level dynamic theories may be formulated without concern about how the transformation takes place from the initial elastic deformation to the eventual flow at long times. Because the degree of elastic deformation, bounded by $Wi \ll 1$, is negligible, the entanglement structure only gets renewed on the time scale of $\tau_0$ by the molecular diffusion. In other words, a theoretical description of linear responses can avoid the challenge of dealing with any stress-induced structural rearrangement. When $Wi \gg 1$, linear response is also possible only if the imposed strain does not exceed a critical level, which can be identified empirically. For the example of entangled polymer solutions and melts in simple shear, this critical strain is known to be on the order of unity.

Upon a startup deformation with $Wi \gg 1$, the key question is what happens when the external strain grows beyond a critical value. Do we expect the mechanical response to
be solid-like up to $t \sim \tau_0$, corresponding to a strain of $Wi >> 1$? When does the "solid" turn into a "liquid"? Before an entangled polymer suffers irrecoverable deformation, we can expect nearly full elastic recovery upon letting go stress free. Thus, the moment when the system loses its ability to have full elastic recovery seems to be a special point of interest.

Extensive research on the subject of nonlinear rheology of entangled polymers has convinced us that macroscopic yielding is a key concept to reckon with. Upon a startup deformation with $Wi >> 1$, we must wonder when the initial elastic deformation ceases and flow begins (i.e., irrecoverable deformation), and how this transformation, i.e., yielding, takes place.\textsuperscript{21} In other words, being solid-like initially as any Maxwell-type viscoelastic liquid is, some type of cohesion should be identified on time scales shorter than $\tau_0$. Therefore, the zeroth-order affair should be to delineate whether the entanglement network breaks down in response to large deformation, i.e., how chain disentanglement takes place, leading potentially to macroscopic strain localization.

Beyond the phenomenological meaning of macroscopic yielding,\textsuperscript{21} there is the deeper mechanistic question about what causes the transformation from solidity to fluidity at a molecular level. For entangled polymeric liquids, the solidity is due to the effect of inter-chain excluded volume. For chains of sufficient length, such an excluded volume effect amounts to chain uncrossability, confining chains in an entanglement network. Yielding must occur upon startup deformation with $Wi >> 1$ because the network (derived from the chain uncrossability) cannot sustain an arbitrarily large amount of strain. In particular, it is straightforward to recognize that the resisting intrachain elastic force due to chain deformation could not grow without bound during continuous deformation. In other words, chain disentanglement via chain mutual-sliding is expected to occur\textsuperscript{22,23} when intermolecular gripping forces (due to the chain uncrossability) are insufficient to allow further chain deformation and corresponding growth of the elastic retraction force. Here the effect of chain relaxation by reptation on the time scale of $\tau_0$ is negligible under the condition of $Wi >> 1$ because the disentanglement occurs at $t \ll \tau_0$.

Figure 2 A cartoon to depict an entangled polymer in terms of a network like picture. It intends to state that the strand between entanglements gets strained to $\gamma$. The elastic retraction force $f_{\text{retract}}$ originates from the molecular deformation that occurs because of the intermolecular gripping force $f_{\text{im}}$ whose origin is chain uncrossability due to excluded volume.

Specifically, it is straightforward\textsuperscript{22} to depict how the elastic retraction force $f_{\text{retract}}$ grows with the external strain $\gamma$ in the limit of affine deformation for the case of simple shear, as shown in Figure 2. We simply have $f_{\text{retract}} \sim \gamma f_{\text{ent}}$, where $f_{\text{ent}}$ was the entanglement force or confining force that would keep a test chain localized in a tube like environment on
time scales shorter than the reptation time $\tau_0$. As $\gamma$ increases, $f_{\text{retract}}$ will eventually exceed the intermolecular gripping force $f_{\text{im}}$ that was effective and adequate to produce the chain deformation up to the point when $f_{\text{retract}} \sim f_{\text{im}}$. We visualize that chain sliding must occur at this point, leading to chain disentanglement and a decline in the measured stress. In other words, in this network picture, the well-known shear stress overshoot upon startup shear is due to the breakdown of chain entanglements, and is thus termed the yield point whose microscopic origin may be chain disentanglement due to the force imbalance. At a crude single-chain level, the concept of disentanglement agrees with the phenomenological notion of "yield" because it implies that prior to this yield point an entanglement strand remains locked in at the two entanglement points on its two ends, and beyond this point, the chain mutual sliding produces irreversible changes in the entanglement structure. In other words, after the stress overshoot, macroscopic deformation should become irrecoverable.

### III. Two key elements of the tube theory

Lodge pointed out in 1989 that there are two fundamentally different kinds of theoretical treatment, either "strong, localized interactions of the network junction type", or "smoothed-out, uniform interactions representing a mean field". The former recognizes the explicit role of intermolecular coupling at the entanglement points. Lodge regarded the tube model to be the latter type, where a tube was introduced to account for the chain uncrossability in a smoothed-out, uniform way.

Although the tube theory has been widely accepted and extensively applied as the standard model in polymer rheology, scrutiny of its foundation and structure has only occasionally received some attention. Here we expose the construction of the tube model in terms of its assumptions and approximations so that we may see more clearly in face of the new experimental results how the tube model could be improved.

#### 1. Barrier-free chain retraction on the Rouse time scale: the ansatz

In the regime of nonlinear response where an entangled polymer is subjected to large external deformation at $Wi > 1$, significant chain deformation can take place. Specifically, the tube model imagines that upon startup of external straining affine deformation would occur until the test chain would inevitably retract within the tube on a characteristic time scale, i.e., the Rouse time $\tau_R$. This conjecture of chain retraction separates the molecular deformation into chain stretching and orientation respectively and leads to decoupling of the orientation dynamics from with the chain stretching dynamics.

By definition, when $\dot{\gamma} \tau_R$ or $\dot{\varepsilon} \tau_R = Wi_R << 1$, the amount of chain stretching is negligible. The extent of chain stretching is determined by the new dimensionless number $Wi_R$ that we shall call Rouse-Weissenberg number. To be able to produce significant chain stretching, the applied rate needs to exceed the reciprocal Rouse time, i.e., $Wi_R > 1$.

To reiterate, the construction of the tube model rests on the basic conjecture of barrier-free chain retraction on the Rouse time scale, where the perceived retraction inside the...
tube would only meet frictional resistance instead of any entropic barrier. Three specific consequences follow from this ansatz of barrier-free chain retraction:

A. **Spontaneous stress decline at** $\tau_R$ for $Wi_R > 1$

Significant chain retraction is expected to occur in a barrier-free fashion for any level of imposed strain produced with $Wi_R > 1$. In particular, this process is expected to produce an appreciable stress decline for a step strain even for amplitude $\gamma_0 < 1$ (simple shear) and $\lambda < 2$ (uniaxial extension). Here we use a simple version of the tube model to describe the effect of chain retraction on stress relaxation after a large step strain. Eq. (7.123) in the Doi-Edwards book gives

$$\sigma_{\alpha\beta} \sim Q_{\alpha\beta}(\mathbf{E})(1 + \alpha(\mathbf{E}) - 1)\exp(-t/\tau_R)^2 G_{eq}(t), \quad (1)$$

where the tensorial orientation function $Q$ and stretching factor $\alpha$ each respectively depend on the type of the deformation field $\mathbf{E}$, and $G_{eq}$ is the equilibrium relaxation modulus. The consequence of the barrier-free chain retraction is a decline in the stress as the time-dependent factor represented by $(1)$ decreases from $\alpha^2$ at $t = 0$ to 1 when $\exp(-t/\tau_R) \ll 1$. Here we only need to include the longest Rouse time in the curled brackets to capture the effect of chain retraction on the time-dependent stress.

Figure 3 shows how $\alpha^2$ varies with the step strain amplitude respectively for both step shear of amplitude $\gamma$ and uniaxial extension with stretching ratio $\lambda = L/L_0$ ($L_0$ being the original sample length). Specifically, for simple shear with $\gamma = 0.7$, $\alpha^2(\gamma=0.7) \cong 1.13$. In the case of uniaxial extension at $\lambda = 1.5$, $\alpha^2(\lambda=1.5) \cong 1.15$. We choose to consider such modest strain values of $\gamma = 0.7$ and $\lambda = 1.5$ because we suspect that in reality such strains may not produce sufficiently high elastic retraction forces to overcome the entanglement force arising from the uncrossability whose origin is inter-chain excluded volume and chain connectivity (cf. Figure 2).
In both cases, at modest deformations, e.g., below $\gamma = 1$ and $\lambda = 2$, $\alpha^2$ is discernibly above unity so that a stress drop in magnitude of $(\alpha^2 - 1)$ is experimentally measurable. For the case of shear the same feature describes the steady-state relationship between $\sigma$ and $Wi$. Note that the peak occurs at time $t_{\text{max}}$ is much longer than $\tau_R$ as long as $Wi_R << 1$.

**B. Little chain stretching and lack of elastic recovery for $Wi_R << 1$**

The Doi-Edwards tube model states that "the stress is mainly due to the intramolecular entropic force; the intermolecular force acts primarily to keep the volume of the system constant and is not important for the anisotropic part of the stress." Following the classical rubber elasticity theory, the tube model assumes affine deformation upon startup deformation up to the Rouse time $\tau_R$. The omission of the essential role of intermolecular interactions to balance the intrachain elastic retraction forces the tube model to hypothesize barrier-free chain retraction on the time scale of $\tau_R$.

Thus, under the condition of $Wi_R << 1$ and $Wi > 1$, a test chain undergoes little stretching, implying lack of affine deformation beyond $\tau_R$. A test chain would only orient while keeping its contour length constant. In this picture, upon shearing to one and two strain units the neighboring chains would have disjoined as shown in Figure 5a. In contrast, if the chain deforms affinely or partially affinely under the imposed shear, the chain would continue to be connected to other chains and extended as represented by the two red dots in Figure 5b.

Moreover, the relaxation after cessation of a stepwise deformation of any magnitude (imposed with $Wi_R << 1$) would follow the reptation dynamics toward the isotropic state, according to the tube model. In other words, the oriented entanglement network would only heal toward its isotropic equilibrium state during the relaxation. Currently, there is no evidence of any kind that either contradicts or supports this key depiction of polymer dynamics.

**C. Non-monotonicity arising from excessive chain orientation for $Wi_R << 1$**

Under the condition of $Wi_R << 1$ and $Wi > 1$, the Doi-Edwards tube model suggests that the shear stress arises entirely from the chain orientation during startup shear according to

$$\sigma_{xy}(\dot{\gamma}, t) = G_{pl} \int_{-L/2}^{L/2} d(s/L) \langle u_x(s, t) u_y(s, t) \rangle = G_{pl} \int_0^1 dt' \mu(t') Q_{xy}(\dot{\gamma} t')$$

(2)

where the first equality is Eq. (7.178) of Ref. 30 or Eq. (1.2) of Paper 4 of Doi-Edwards, and the second equality arises from the averaging $\langle \cdot \rangle$ under the condition that the primitive chain segmental vector $\mathbf{u}$ could orient affinely upon a startup shear at rate $\dot{\gamma}$. Here $G_{pl}$ is the elastic plateau modulus, $\mu$ is a memory function involving the full equilibrium relaxation spectrum $\{\tau_p\}$, with $\tau_p = \tau_0/\rho^2$, and $Q_{xy}(x)$ is the orientation function that can be approximated by $Q_{xy}(x) \equiv x/(1+x^2/5)$. This non-monotonic function $Q_{xy}$
describes the shear stress overshoot upon startup shear as well as the steady-state stress that exhibits a maximum with respect to the imposed shear rate $\dot{\gamma}$. In other words, $\sigma_{xy}$ would reach a maximum with growing shear strain $\gamma = \dot{\gamma} t$ given by the maximum in $Q_{xy}(\gamma)$, i.e., around $\gamma_{\text{max}} = \sqrt{5} = 2.24$ and $\sigma_{\text{max}} = 1.1 \cdot G_{pl}$, that takes place at time $t_{\text{max}} \sim \tau_R (\gamma_{\text{max}} / W_i R) \gg \tau_R$ under the condition of $W_i R \ll 1$ as detailed in Figure 4. The stress maximum was found to originate from excessive chain orientation. In other words, the stress maximum would not be a result of any structural breakdown of the entanglement network according to the tube model.

Additionally, in steady state, the $\sigma_{xy}$ versus $\dot{\gamma}$ curve would be depicted by $\sigma_{xy} \parallel G_{pl} Q_{xy}(W_i)$ and would show a maximum at $W_i = \dot{\gamma} \tau \sim 2.24$ as shown in Figure 4. Such a non-monotonic character of the curve has been exploited as a mechanism for shear banding. We will return in a subsequent section to comment on whether or not such non-monotonicity is relevant to the experimental observation of shear banding.$^{31,32}$

Figure 5 (a) Cartoons showing the "shapes" of and relationship among three initially mutually entangled chains in an entangled polymer undergoing startup shear in the original state of $\gamma = 0$, after one shear strain at $\gamma = 1$, and two strain units $\gamma = 2$ respectively. (b) The end-to-end vector is depicted by the blue bar at $\gamma = 0$. At the various strains, in contrast to the green bars anticipated by the tube model, the chain ends would be at where the red dots are if the chain did not slip away to escape the imposed shear.

Figure 6 (a) As stretching continues (i.e., stretching ratio $\lambda$ increases), the number of chains in the specimen decreases in proportion to the area reduction: $A/A_0 = 1/\lambda$. Such a picture would be consistent with Doi-Edwards tube model depiction of startup extensional deformation with $W_i R \ll 1$. An alternative view shows how the number of load-bearing strands in the entire cross-section of the system remains nearly constant during initial elastic deformation in (b) and only show significant decrease upon yielding as depicted in (c).
Similarly, under the condition of $Wi \ll 1$, the Doi-Edwards tube model also evaluated the mechanical response of an entanglement network to startup uniaxial extension. Because the calculations were made for a constant tube diameter, it actually implicitly assumed that the number of load-bearing strands (LBS) per unit cross-sectional area would stay constant during the startup extension as depicted in Figure 6a. In other words, the elastic network deformation (leading to a geometric condensation of LBS) as depicted in Figure 6b would not occur in the framework of the tube model. Instead, the system would skip the transitional phase (i.e., yielding) depicted in Figure 6b to flow as shown in Figure 6a. When chain stretching is negligible for $Wi \ll 1$, the Cauchy (true) stress $\sigma$ would arise from chain orientation alone and would actually level off, i.e., $\sigma \sim \sigma_\infty = \text{constant}$ after sufficient straining so that the engineering stress $\sigma_{\text{engr}} = \sigma / \lambda$ would decline with $\lambda$ as shown in Figure 4. This tensile force decline beyond $\lambda_{\text{max}} = 2.36$, anticipated by the Doi-Edwards tube model, arises from the shrinkage of the cross-sectional area, but does not reflect any structural breakdown of the entanglement network. Lack of affine deformation, reflected in Figure 6a, would start at $\tau_R$, according to the tube model. On the other hand, the maximum of $\sigma_{\text{engr}}$ occurs at $t_{\text{max}} = \ln (\lambda_{\text{max}} / \dot{\varepsilon}) = (0.86/Wi_R)\tau_R > > \tau_R$ for $Wi \ll 1$. Therefore, the Doi-Edwards tube model actually would not regard the decline in the tensile force to arise from its assumed barrier-free chain retraction. In other words, the peak engineering stress $\sigma_{\text{engr(max)}}$ does not signify any alternation of the entanglement network. Some critical experiments are desired to verify this conclusion of the tube model.

2. Incorporation of convective constraint release (CCR): a revision of tube model

The most well-known symptom (often regarded as the flaw) of the Doi-Edwards tube model is its prediction of the so-called stress maximum, i.e., the steady-state shear stress $\sigma_{xy}$ declining with increasing applied shear rate $\dot{\gamma}$ just beyond $Wi = \sqrt{5} = 2.24$, as shown in Figure 4. To remove this undesirable feature, it was proposed that the effect of convective constraint release (CCR) be introduced to modify the relaxation dynamics. The incorporation of the CCR is a confirmation that the Doi-Edwards tube model cannot describe the transformation from elastic deformation to flow.

Historically, the CCR was first introduced in an ad hoc manner in hope to remove the non-monotonicity in the predicted flow curve of $\sigma_{xy} \sim Q_{xy}(Wi)$ in Figure 4. Specifically, under the condition of $Wi_R < < 1$ and $Wi > 1$ in steady shear, an effective relaxation time $\tau_{\text{eff}}$ was proposed to be of the form: $1/\tau_{\text{eff}} = 1/\tau_0 + A \dot{\gamma}$, perceiving that the chains would be displaced past one another at a rate proportional to $\dot{\gamma}$ in steady shear. Through the CCR, the stress maximum can be made to disappear. However, such a modified tube model cannot prescribe a priori whether the non-monotonicity should be absent or not.

For $Wi_R > 1$, the tube model envisions the shear stress decline after the overshoot during a startup shear to arise from a combination of chain retraction at the Rouse time $\tau_R$ and the CCR that accelerates chain relaxation. Since the CCR is coupled to the barrier-free chain retraction, the stress overshoot can be expected to occur on the time scale of $\tau_{\text{eff}}$.
\( \tau_R \), i.e., \( t_{\text{max}} \sim \tau_R \). The experimental data\(^{37} \) appear to indicate (a) the stress overshoot could occur much earlier than \( \tau_R \) and (b) \( \gamma_{\text{max}} \) appears to scale like \( \gamma_{\text{max}} \sim \dot{\gamma}^{1/3} \) instead of \( \gamma_{\text{max}} \sim \dot{\gamma} \) that is anticipated by the tube model.\(^{38} \)

In summary, the tube model is clearly an effective theory that can successfully account for the effect of inter-chain excluded volume in the limit of linear response. Since it builds its foundation on the idea that chain retraction would occur in a barrier-free manner within the tube on the Rouse time scale\(^{39} \), the tube model has the following features: (i) Upon startup shear with \( W_{iR} \ll 1 \), a chain would not suffer any stretching and its excessive orientation would produce stress overshoot. (ii) Non-affine deformation begins after an initial strain of \( W_{iR} \ll 1 \). Because of the perceived chain retraction, the entanglement structure would undergo, after a period of \( \tau_R \), irreversible change from its initial state. (iii) Upon a sudden strain produced with \( W_{iR} > 1 \) (starting \( t = 0 \)), chain retraction is expected to occur around \( t = \tau_R \) regardless of the strain amplitude, leading to a measurable acceleration in the relaxing stress. Even when chain retraction occurs, the tube constraint would still be present. In other words, the lateral chain motions are still prohibited. This preservation of chain localization is in contrast to the alternative picture of the breakdown of the entanglement network.

**IV. Key experimental revelations**

1. **Summary of existing experimental findings**

   **A. Shear banding is only metastable**

   Ever since the first report of shear inhomogeneity in startup shear of entangled polymer solutions,\(^{40,41} \) it has been suggested to us that the Doi-Edwards tube model\(^{42} \) contained a prediction for the experimental observations because it prescribed a non-monotonic relationship between the shear stress and rate in steady state as discussed in subsection III.1.C. However, a recent investigation shows\(^{43} \) that shear banding may be only metastable and is not a steady state property. Specifically, occurrence of shear banding requires startup shear at high rates that can produce large elastic deformation within the reptation time \( \tau_0 \), i.e., \( Wi > 1 \). When the condition of \( Wi > 1 \) was imposed over a long period of time, e.g., through slow ramp-up of the applied rate, shear banding no longer occurred in the same system that exhibited shear banding during sudden startup shear. In other words, whether shear banding emerges or not depends on how an entangled polymer is brought under deformation. This observation forces us to give up the suggestion that the Doi-Edwards model could describe the strain localization. In absence of the non-monotonicity property and any spatial variation of the shear stress along the velocity gradient direction, it is challenging for any existing constitutive model to depict the observed metastable shear banding.\(^{43} \)

   **B. Non-quiescent relaxation after step strain**

   One of the most remarkable particle-tracking velocimetric (PTV) observations\(^{44,45} \) is the discovery of macroscopic motions after step strain when it exceeds a critical strain about
unity for simple shear\textsuperscript{46} and a Hencky strain around 0.7\textendash0.8 for uniaxial extension.\textsuperscript{47} The finding invalidates a large number\textsuperscript{48} of favorable\textsuperscript{49} and unfavorable\textsuperscript{50,51} comparisons between the stress relaxation experiment and the damping function of the tube model. There is even the worst form of macroscopic motions when wall slip takes place.\textsuperscript{52} Such macroscopic motions can produce strong strain softening. An earlier study\textsuperscript{53} based on the free energy function of the tube model has offered an explanation for the ultra-strain-softening reported of step shear of 1,4-polybutadiene\textsuperscript{54} that is capable of massive wall slip.\textsuperscript{55} In our analysis, both wall slip and internal breakup motions are a result of inhomogeneous breakdown of the entanglement network.\textsuperscript{56}

There is evidence that the concept of chain retraction from the tube model may be irrelevant to the phenomenon of non-quiescent relaxation. A recent PTV study\textsuperscript{45} showed that crack-like failure occurred after a step shear of an entangled melt that was produced at rate satisfying $Wi_R << 1$. According to the tube model, there would be negligible chain stretching to cause any structural damage to the step strained sample. In other words, without the chain retraction, there would be no other process imaginable by the tube model to produce the observed macroscopic motions. Moreover, it was found\textsuperscript{45} that when the imposed step strain was of a moderate magnitude, the strained melt would remain motionless for a period much longer than the Rouse time, whereas the current tube model could only perceive chain retraction to take place on the Rouse time scale.

2. Further experiments

In the remaining of this article, we focus on several new experiments to provide additional ingredients for the plausible theoretical picture that was briefly outlined at the end of Section II. These new experiments depart from the previous studies\textsuperscript{40,41,45} in one crucial way: While the past studies concentrated on the delineation of strain localization in both shear and extension, these new experiments involve no macroscopic deformational inhomogeneity because both startup deformation and step strain produces a uniform deformation field at all times. In absence of any constitutive instabilities, the results provide valuable and relevant information for comparison with the current tube model.

Specifically, the following four different rheometric measurements have been carried out to

1. Probe the state of chain entanglement during relaxation from an imposed strain produced at $Wi_R << 1$. According to the tube model the strained sample would only heal toward its equilibrium state during relaxation.

2. Examine stress relaxation after moderate degrees of step strain involving $Wi_R >> 1$, for which the tube model anticipates measurable stress decline due to the barrier-free chain retraction.

3. Use elastic recovery measurements to determine the state of chain entanglement during startup shear and after step strain. It is difficult within the tube model to imagine that a strained system could undergo full elastic recovery if the duration of deformation well exceeds the Rouse time.
4. Elucidate the nature of the maximum in engineering stress $\sigma_{\text{engr}}$ under the condition of $W_{\text{R}} \ll 1$ in startup uniaxial extension. In the tube model, this maximum has no structural significance.\textsuperscript{57}

Below we summarize the key results from these new experimental studies, which in combination with the results reviewed in the preceding subsection, should stimulate future theoretical work in this area of nonlinear rheology of entangled polymers.

1. State of entanglement after a finite amount of strain produced with $W_{\text{R}} \ll 1$

Under the condition of $W_{\text{R}} \ll 1$, the entanglement network would suffer little chain stretching according to the tube model. Thus, after an imposed strain produced with $W_{\text{R}} \ll 1$, there would be no chain retraction, and the oriented network would simply relax toward its equilibrium state by molecular diffusion. In other words, the oriented state of chain entanglement should evolve monotonically toward equilibrium. One effective method to probe any structural evolution of the relaxing sample is to subject it to a fast startup shear at various stages of relaxation since the stress overshoot in response to startup shear can be used to delineate the state of chain entanglement.

Consider a protocol of a three-stage shear as depicted in Figure 7a. We apply this procedure to a model system based on a 5% 1,4-polybutadiene solution, made of monodisperse long chain with $M_w = 1.05 \times 10^3$ and $M_n = 1.01 \times 10^3$ kg/mol dissolved in a 1,4-polybutadiene matrix with $M_w = 10.5$ kg/mol and $M_n = 8.9$ kg/mol. This 1M5%-10K sample has 18 entanglements per chain, a terminal relaxation time of $\tau_0 = 19$ s and a Rouse time $\tau_{\text{R}}$ equal to 0.35 s. This solution is designed\textsuperscript{52, 58} to undergo only homogeneous shear upon startup shear and quiescent relaxation after a finite amount of imposed strain so that the rheometric measurements can provide a meaningful comparison with the tube model description. We first verified that the stress peak $\sigma_{\text{2max}}$ associated with $\dot{\gamma}_2 = 15$ s$^{-1}$ indeed remains constant during relaxation upon a small strain...
of $\gamma = 0.3$. After a strain of $\gamma = 1.5$, produced with a rate corresponding to $W_{R} = 0.1$, the state of chain entanglement during relaxation is probed with $\dot{\gamma}_2 = 15$ s$^{-1}$ in a series of discrete tests using the protocol of Figure 7a. In Figure 7b we see a non-monotonic relation between $\sigma_{2\text{max}}$ and the duration $t_w$ of the stress relaxation period. First, the stepwise shear has produced a weaker entanglement state because the very first red circle is appreciably lower than the circles at long times (when the system has recovered the equilibrium state). The emergence of a minimum in $\sigma_{2\text{max}}$ vs. $t_w$ would be consistent with the possibility that the entanglement network has suffered further damage after cessation. We have termed this phenomenon "elastic yielding". Currently, we are unsure whether any current tube models contain the necessary ingredients to depict this behavior of elastic yielding. Since there would be no chain retraction within the tube model framework, there would be no molecular mechanism to produce the observed weakening of the entanglement structure after shear cessation from a slowly imposed shear of only 1.5 strain units. On the other hand, since the observed effect is small we cannot rule out that a comparably small amount of chain stretching on the order of $W_{R} = 0.1$ could not be the origin. More detailed experiment along this line is desired.

2. Barrier to chain retraction upon modest deformation made with $W_{R}>1$

Linear response occurs in entangled polymers when external deformation is too low to affect the equilibrium microscopic structure. In other words, at a step strain of sufficiently low amplitude $\gamma$, stress relaxation dynamics should be independent of the value of $\gamma$. Under such a condition, the entanglement structure should remain intact until the reptative process renew the network. What keeps a strained network from accelerated stress relaxation? At what value of $\gamma$ would the entanglement network start to undergo faster stress relaxation? The tube model has definitive answers to these questions. In particular, it hypothesizes that chain retraction would occur about a Rouse time $\tau_R$ after shear cessation from a step strain of any amplitude. Linear response would cease to be observed whenever the perceived barrier-free chain retraction would produce a measurable acceleration of the stress relaxation as depicted in eq 1.

![Experimental data](image1)

![Theoretical expectation](image2)

Figure 8 (a) Stress relaxation behavior from two discrete step strains of respective amplitudes $\gamma = 0.1$ and 0.7, where the latter was produced at a rate of 35 s$^{-1}$ corresponding to $W_{R} = 455$. The indiscernible difference is truly remarkable, thanks to the latest rheometric precision offered by the ARES-G2 from TA Instruments. Since the
resulting shear stress after the step strain of $\gamma = 0.7$ deviates 4% downward from a perfectly linear relationship of $\sigma = G\gamma$, we have shifted the data for $\gamma = 0.7$ upward by 4% to compare with $G(t, \gamma)$ measured from the step strain of $\gamma = 0.1$. (b) Taking $G(t, \gamma=0.1)$ as $G_{eq}(t)$ in eq 1, the relaxation modulus $G(t, \gamma=0.7)$ can be estimated from the tube model that assumes the barrier-free chain retraction as described in eq 1.

We carried out the following series of step shear experiments on a monodisperse entangled polymer melt, i.e., styrene-butadiene copolymer rubber (SBR) that has $Z = 33$ entanglements per chain, corresponding to $M_w = 161$ kg/mol and $M_e = 4.8$ kg/mol (25.6% styrene, 74.4% butadiene that has 70% vinyl). At $T = 30^\circ C$, the reptation time $\tau_0$ of this melt is 1340 s and the Rouse time $\tau_R$, estimated according to three methods, is around 13.4 s. Figure 8a shows the normalized shear stress relaxation as a function of time for both $\gamma = 0.1$ and $\gamma = 0.7$. The identical time dependence of the stress relaxation suggests that the entanglement structure was intact after the step strain of $\gamma = 0.7$. In other words, up to a step strain of $\gamma = 0.7$, there exists a sufficiently high barrier against any fast equilibration of the strained network toward the equilibrium state. If we take the experimental data of $G(t, \gamma=0.1)$ from the step strain of $\gamma = 0.1$ as the equilibrium relaxation modulus $G_{eq}(t)$, we can estimate the relaxation modulus $G(t, \gamma)$ from the tube model using eq 1 and $\alpha$ values in Figure 3. We would expect a 13% difference as shown in Figure 8b that indicates how the barrier-free chain retraction would have caused $G(t, \gamma=0.7)$ to drop below $G_{eq}(t)$. The comparison between Fig. 8a and 8b indicates that the tube-model-anticipated faster relaxation did not occur in experiment.

We may suggest that the tube model could still be mended by introducing a barrier against chain retraction so as to reproduce the experimental data in Fig. 8a. Erection of such a barrier may only be possible in some ad hoc manner within the tube model framework. At large step strains, the ad hoc barrier would be overcome and the chain retraction could occur within the deformed tube. In other words, such retraction could only take place along the tube. This process may be different from chain disentanglement produced by the elastic yielding. Namely, in our picture of elastic yielding the chain disentanglement may lead to chain delocalization whereas the chain retraction leaves the tube constraint intact within the tube model framework and the chains would still be laterally restricted.

3. Elastic recovery after startup deformation

There is another way to demonstrate the existence of a finite barrier that resists rapid structural rearrangement. If a barrier-free chain retraction would take place even for a step strain with $\gamma < 1.0$, the strained entanglement network may show signs of memory loss, i.e., could reduce its ability to undergo elastic recovery. We performed a series of interrupted shear experiments at $W_R > 1$ with different amplitudes and set the strained sample stress-free after a given amount of time $t_w$ for relaxation. Based on the same sample as studied in Figure 7b, we show in Figure 9 the normalized strain recovery as a function of the strain amplitude $\gamma$, for six different waiting times $t_w$ all longer than the Rouse time $\tau_R$. The data in Figure 9 indicate that up to $\gamma \sim 1.0$ the entangled polymer...
solution did not lose its ability to undergo elastic recovery relative to that for $\gamma = 0.1$. Thus, the results of these elastic recovery tests are fully consistent with the preceding demonstration by stress relaxation measurements in Figure 8a that first revealed the existence of a finite barrier against any accelerated return of the strained state to the equilibrium state.

Finally, according to the conceptual picture of the tube model depicted in Figure 5, the entanglement network may not undergo any significant elastic recovery after a shear strain $\gamma = 2$ produced with $W_i R << 1$. Using the same sample as studied in Figure 7b and 9, we conducted a combination of startup shear and elastic recovery experiments at different stages for various shear rates including $\dot{\gamma} = 0.3$ s$^{-1}$. Figure 10a shows the stress vs. time data for four rates ranging from 0.3 to 10 s$^{-1}$. To better understand the origin of the stress overshoot, we evaluate the degree of elastic recovery both before and after the shear stress maximum at the shear strain of $\gamma_{\text{max}}$. Figure 10b summarizes how the ability to undergo elastic recovery varies as a function of the imposed strain $\gamma$, normalized by $\gamma_{\text{max}}$.

![Figure 9](image_url)  
**Figure 9** Discrete elastic recovery tests for six waiting times $t_w$, measured relative to the Rouse time $\tau_R$, after shear cessation from shear strain of amplitude $\gamma$ produced with a rate corresponding to $W_i R = 5.5$. Note that at $T = 5 ^\circ C$, $\tau_R = 1.1$ s. The ability to undergo elastic recovery is unchanged below $\gamma = 1$.

![Figure 10](image_url)  
**Figure 10** (a) Shear stress vs. the imposed strain $\gamma = \dot{\gamma} t$, showing stress overshoot in each of the four applied rates. For the first rate of 0.3 s$^{-1}$, the stress declined 40% from its peak at a strain that is about 4.7 times $\gamma_{\text{max}} = \dot{\gamma} t_{\text{max}}$. (b) The recoverable strain $\gamma_r$ as a function of imposed strain $\gamma$, either before or beyond the stress maximum that occurs at $\gamma_{\text{max}}$, involving four values of $\dot{\gamma}$. The black filled circle designates one of the many data points associated with the test.
made at $W_R = 0.1$, where the shear was exerted until a strain of $\gamma = 4.7 \times 2.1 = 9.9$
when the recoverable strain $\gamma_r$ is only 14% of the imposed strain.

Figure 10b reveals some crucial information. (a) The entanglement network makes complete elastic recovery for $W_R$ as low as 0.1, suggesting that the network is still very much connected up to a strain of 2, in contrast to the picture of the tube model shown in Figure 5. (b) Nearly complete elastic recovery takes place up to $\gamma_{\text{max}}$ even though $t_{\text{max}} \gg \tau_R$. (c) The point of the stress maximum is significant, separating recoverable deformation from irrecoverable deformation. Thus, Figure 10b represents systematic evidence supporting the phenomenological notion of “yielding” at the stress overshoot.\(^{21}\)

4. Yielding after maximum in $\sigma_{\text{engr}}$ in startup extension

The Doi-Edward tube model predicts the tensile force or engineering stress $\sigma_{\text{engr}}$ would show a maximum around $\lambda_{\text{max}} = 2.36$ because the Cauchy stress $\sigma = \sigma_{\text{engr}}/\lambda$ would level off upon saturation of the chain orientation in absence of chain stretching (i.e., for $W_R << 1$). According to the tube model, $\sigma_{\text{engr}}$ declines when the chain orientation cannot further increase and the number of oriented chains in the system decreases, as illustrated in Fig. 6a. Based on another SBR melt with $M_w = 241 \text{ kg/mol}$ and $M_e = 2.4 \text{ kg/mol}$ (21% styrene, 79% butadiene that has 40% vinyl) that has $Z = 98$ entanglements per chain, reptation time $\tau_0 = 34 \text{ s}$ and $\tau_R = 0.12 \text{ s}$, we performed a combination of startup uniaxial extension and elastic recovery experiments to explore the nature of a maximum in $\sigma_{\text{engr}}$.

At a Hencky rate $\dot{\varepsilon} = 1.0 \text{ s}^{-1}$, $W_R = 0.12 << 1$, we show in Figure 11 that the elastic recovery, as measured by the degree of return to the original length $L_0$, is nearly complete when the stretched specimen is let go before the peak of $\sigma_{\text{engr}}$. The inset of Figure 11 indicates the corresponding rheometric information before and after the yield point at $\lambda_{\text{max}} \mu 3.0$. On the other hand, the Cauchy stress $\sigma$ monotonically grows in the explored range of the stretching ratio $\lambda$. It is clear that the maximum of $\sigma_{\text{engr}}$ is a special moment of structural importance during the startup extension. Beyond $\lambda_{\text{max}}$, the returned sample length $L_r$ is appreciably lower than $L_0$, indicating that the entanglement network suffered irrecoverable changes. The DE tube model does not assign any structural significance to the peak of $\sigma_{\text{engr}}$. It remains to be seen how remedies can be made within the framework of the tube model to provide a realistic physical picture for the observed yielding of entangled melts during startup uniaxial extension.
V. Contrasting viewpoints

Two pieces of experimental information from step strain cause us to wonder whether an alternative viewpoint is closer to the reality. First, Figure 7b appears to show that the state of chain entanglement in a strained polymer may be weaker during relaxation from a step strain produced with $W_i R << 1$. According to the tube model, there would be no chain retraction during relaxation, and the oriented tube as well as the primitive chain is only expected to evolve monotonically toward a state of disorientation. Thus, it is unreasonable to expect any tube model to be able to account for the non-monotonic response during relaxation to a second startup shear of high rate as observed in Figure 7b. Second, there appears to be a finite cohesion barrier against any type of accelerated molecular relaxation such as chain retraction. Moreover, both Figure 8a and Figure 9 are inconsistent with the basic conjecture of the tube model that chain retraction would occur in a barrier-free manner after any magnitude of external deformation.

When yielding does occur, as shown in Figures 10b and 11 beyond the stress maximum during startup continuous deformation of either shear or extension at $W_i R << 1$, what is the microscopic picture for the observed stress decline? The tube model perceives the non-monotonicity to arise from excessive tube/chain orientation. But the lack of elastic recovery beyond the stress maximum seems to indicate something structurally significant. Thus, an alternative viewpoint would be that for both $W_i R << 1$ and $W_i R > 1$ the cause of the stress decline beyond the overshoot is yielding of the entanglement network, i.e., loss of chain entanglement in the sense that chains are sliding past one another at the entanglement points.

Finally, it is worthwhile to remind ourselves of the case of non-quiescent relaxation after step strain.44-45,47,61 In our assessment, the phenomena indicate breakup of the strained entanglement network after cessation of external deformation. This behavior forced us to consider the existence of finite cohesion associated with chain entanglement that amounts to the existence of an entropic barrier, confining chains to the entanglement
network. At this length scale of chain entanglement, we proposed,\textsuperscript{22} based on a dimensional analysis, that an entanglement force $f_{\text{ent}}$, confining a chain in the network on time scales shorter than $\tau_0$, is on the order of $k_B T/l_{\text{ent}}$, where $l_{\text{ent}}$ is the entanglement spacing. A large interrupted strain could produce significant molecular deformation, resulting in a residual intrachain elastic retraction force $f_{\text{retract}}$ that is roughly of the form $f_{\text{retract}} = \gamma f_{\text{ent}}$ for simple shear and $(\lambda-1/\lambda^2)f_{\text{ent}}$ for uniaxial extension. We have proposed that an elastic breakdown of the entanglement network can occur when there is force imbalance,\textsuperscript{22} i.e., $f_{\text{retract}} > f_{\text{ent}}$. Sufficiently large step strains in either shear\textsuperscript{45} or uniaxial extension\textsuperscript{47,61} can produce such a condition. This elastic yielding, i.e., disentanglement via chain mutual sliding driven by the residual elastic retraction, could occur uniformly throughout a macroscopic sample in simple shear when the system is moderately entangled as is the case studied in the present work. If the system is strongly entangled,\textsuperscript{62} the elastic yielding (EY) ends up in localized breakup of the entanglement network (i.e., strain localization), producing macroscopic motions, which is evidently inhomogeneous decohesion on macroscopic scales.

In closing this section, we mention that by explicitly accounting for chain uncrossibility, Sussma and Schweizer have recently developed a first principles microscopic theory for the transverse tube confinement potential of topologically entangled solutions of rod-like polymers.\textsuperscript{63} They predict that the maximum confining force keeping a rod in the tube is of the form of $k_B T/l_{\text{ent}}$ in agreement with our estimate based on the scaling argument at the coarse-grained level of entanglement spacing. They also show that the presence of sufficient stress can result in microscopic yielding, i.e., chain delocalization out of the confining tube.\textsuperscript{64}

\section*{VI. Summary}

Forty years ago, de Gennes’ idea of reptation\textsuperscript{1} revolutionized the study of the dynamics of entangled polymeric liquids, and subsequently the Doi-Edwards tube model\textsuperscript{2} illuminated a new direction of research in polymer rheology. Due to these theoretical advances, we have achieved an unprecedented level of understanding\textsuperscript{19} concerning linear viscoelastic properties of linear and long-chain branched polymers. It has been widely known that the tube model also attempted to describe many of the nonlinear rheological characteristics. However, the recent particle-tracking velocimetric observations of various constitutive instabilities such as shear banding\textsuperscript{40,41} and nonquiescent relaxation\textsuperscript{44,45} have caused us to search for an alternative theoretical depiction.

In this paper, after briefly discussing what we may expect from large deformation of entangled polymers, we first described the construction and structure of the tube model. We then reviewed two major classes of previously reported strain localization phenomena in the experimental Section IV before delineating four new experiments carried out in absence of any inhomogeneity and edge fracture. It is apparent that these experimental results are at odds with the available theoretical description. The source of the discrepancy between experiment and theory seems to originate from the oversimplified treatment of the dynamic intermolecular (excluded volume) interactions in
terms of a static tube. It remains to be seen whether some new mending within the tube-model framework can actually (a) describe non-monotonic changes in the entanglement structure during relaxation after a slowly imposed step strain as shown in Figure 7b; (b) account for the observed barrier to any form of accelerated rearrangement of chain conformations as revealed in Figure 8a. One major challenge is that the tube model would always perceive presence of tube like constraint, making it conceptually difficult to describe any decohesion of the entanglement network. On the other hand, plenty of experimental information suggests that decohesion does take place both during and after fast deformation.

It appears that the new theoretical description will have to prescribe a finite cohesion due to the entropic barrier associated with the chain entanglement and to allow decohesion to take place under two different conditions: (a) after a large strain, there is a sufficient amount of elastic retraction force associated with the chain deformation; this force could overcome the confining (entanglement) force and cause decohesion in the form of chains sliding past one another at the entanglement points during relaxation. (b) Upon startup of continuous deformation, the growing intrachain elastic retraction force (due to chain deformation) at some moment $t_{\text{max}}$ reaches a magnitude equal to the intermolecular gripping forces. Beyond this point, the force imbalance occurs: Further chain deformation is no longer possible, and mutual chain sliding ensues, leading to breakdown of the entanglement network in presence of external deformation. We have called this moment at $t_{\text{max}}$ the "yield point", which corresponds to the peak in either shear stress or tensile force (i.e., engineering stress $\sigma_{\text{engr}}$) in the case of uniaxial extension.

Since no revision to the tube model has been made to include the new ingredients revealed in this work, it is too early to conclude that the tube model cannot be further improved to provide a way to describe the rheometric measurements such as those presented here. It is also remains to be seen whether a new analytical theory will emerge to deal with the nearly intractable challenge to account for the inter-chain excluded volume interactions that produces chain entanglement because of the chain connectivity. For rigid rods, some promising steps have already been taken.

Molecular dynamics computer simulations are expected to play an important role to elucidate the molecular pictures behind the various macroscopic observations and indicate necessary ingredients to include in a more realistic theoretical description of nonlinear responses of entangled polymers to large fast deformation. In particular, they could elucidate whether lateral constraints are still present during the accelerated stress decline involving either startup deformation or interrupted deformation. Such simulations will be different from those that have been performed so far based on a static characterization of chain entanglement via primitive path analyses.

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For Table of Contents only:

New experiments for improved theoretical description of nonlinear rheology of entangled polymers

Shi-Qing Wang, Yangyang Wang, Shiwang Cheng, Xin Li, Xiangyang Zhu and Hao Sun

\[ Ll_{ent} = R^2 \]

force balance and imbalance

\[ f_{im} \quad f_{retract} \sim \gamma f_{ent} \]
References and Notes

6 Edwards, S. F.,
21 The concept of "yielding" is new in the literature on melt rheology of entangled polymers. Here and through the text, we use this terminology in a crude phenomenological sense to convey the notion that irreversible deformation must replace the initial elastic recoverable deformation during continuous external deformation. It is in a phenomenological sense that Matsuoka used the phrase "yielding" to anticipate the response of polymer melts upon startup of continuous deformation in his monograph: Matsuoka, S. Relaxation Phenomena in Polymers. Hanser Publishers: 1992. See p. 180 and 194 for some relevant statements. The word yielding is frequently used in solid mechanics of metallic, colloidal and polymeric glasses, gels, dense suspensions, semi-crystalline polymers, granular materials etc. In the solid mechanics of these materials, the concept of yield is frequently associated with the material failure that occurs by strain localization. For glasses, yielding is a common term to describe loss of solid-like response: Stress builds upon continuous external deformation that produces a state where the rate of structural relaxation increases many orders of magnitude to approach the rate of external deformation. This event of plasticity is clearly a flow state because structural changes have to occur on the time scale of the reciprocal rate of deformation instead of the quiescent relaxation time that are many orders of magnitude longer. There is also the concept of yield-stress for materials that are solid-like at rest, possessing relaxation times too long relative to the...
experimental time scale, but can be made to flow beyond a certain stress level. Such materials can also display stress overshoot, see, e.g., Divoux, T.; Barentin, C.; Manneville, S. *Soft Matter* 2011, 7, 9335.

In our discussion of nonlinear rheology for entangled polymers, the concept of yielding simply marks the occurrence of irreversible deformation on a macroscopic length scale. Unlike other solid-like materials where the concept of yielding has been routinely invoked, e.g., Lindstrom, S. B.; Kodger, T E; Weitz, D A. *Phys. Rev. Lett.* 2011, 106, 248303, the experimental systems of the present study, i.e., entangled polymer solutions and melts, have a terminal flow regime accessible by a rate of deformation that is lower than $1/\tau_0$. Because of the existence of this flow zone, workers in the community have been reluctant to think about nonlinear responses of entangled polymers in terms of the concept of yielding. In our view, the presence of a flow regime characterized by $Wi << 1$ is irrelevant to an experiment involving $Wi >> 1$. In other words, with $Wi >> 1$, entangled polymers are forced to undergo structural change (e.g., disentanglement) on time scales much shorter than $\tau_0$ when yielding occurs. Thus, for $Wi >> 1$, the deformation of entangled polymers is not so conceptually different from deformation of solids that are either glassy or possess yield-stress. Thus, the concept of yielding also captures the essence of nonlinear responses of entangled polymer solutions and melts. Moreover, yielding does not have to result in strain localization. For many viscoelastic materials (e.g., modestly entangled polymers) where the elastic state is not greatly different from the yielded state in terms of their mechanical characteristics, yielding, i.e., the transition from elastic deformation to flow, can take place homogeneously.


25 For the linear response regime, recent computer simulation works have been carried out to examine the foundation of the tube model. See Everaers, R.; Sukumaran, S. K.; Grest, G. S.; Svaneborg, C.; Sivasubramanian, A.; Kremer, K. *Science* 2004, 303, 823; Tzoumanekas, C.; Theodorou, D. N. *Macromolecules* 2006, 39, 4592.


28 The potential difficulty facing the tube model has been mentioned in Graessley, W. W., *Polymer Liquids & Networks: Dynamics and Rheology*, Garland Science: 2008 on p. 548: "It seems in fact possible that rapid and sustained deformations, those responsible for nonlinear response, alter the liquid structure in ways that are not intrinsic to the (tube) theory, thus requiring new mechanisms to be added."

29 Doi, M. *Journal of Polymer Science: Polymer Physics Edition* 1980, 18,1005. Theoretically, "step strain" is understood to involve imposition of a finite external strain in an instant. In experiment, any magnitude of step strain would take a finite time to realize. If the time required by a rheometer to produce the desired strain amplitude is negligibly short relative to the material relaxation times, then the test can be regarded as a step strain.


Private communication with R. Graham. In order to understand when the effect of the CCR emerges, we have to know what it depicts and where it comes from. Since the CCR represents irreversible changes of the entanglement network it should not occur until the onset of chain mutual sliding that leads to yielding of the entanglement network. In other words, it cannot occur from the beginning upon a startup deformation. In the tube model, the CCR is assumed to be coupled to chain retraction that occurs on the Rouse time scale. Thus, for \( \text{Wi}_R << 1 \), the tube model expects the CCR to be turned on well before the stress overshoot, i.e., effectively from the beginning.


For a step strain with amplitude \( \gamma > 1 \), some previous experiments reported that the “time-strain separability”, beyond which the time-dependence of the relaxing shear stress becomes identical to that observed for \( \gamma << 1 \), occurs at times significantly longer than \( \tau_R \): Inoue, T.; Yamashita, Y.; Osaki. K *Macromolecules* **2002**, *35*, 1770 and Archer, L. A.; Sanchez-Reyes, J.; Juliani *Macromolecules* **2002**, *35*, 10216. A variation of the tube theory (Mhetar, V.; Archer, L. A. J. Non-Newtonian Fluid Mech. **1999**, *81*, 71) indicates this separability should occur at \( \tau_D \), not \( \tau_R \). It also suggests that the barrier-free chain retraction may not completely restore the contour length. Since such a formulation shares the same foundation as the tube model including chain retraction for \( \text{Wi}_R > 1 \) and lack of chain stretching for \( \text{Wi}_R << 1 \), it is not fundamentally different from the other tube models.


Boukany, P. E.; Wang, S. Q. *Macromolecules* **2010**, *43*, 6950, which was based on entangled DNA solutions. Cheng, S. W.; Wang, S. Q., to be submitted, which was based on entangled polybutadiene solutions.

Adams, J. M.; Fielding, S. M.; Olmsted, P. D. *J. Rheol.* **2011**, *55*, 1007. This work attempted to depict transient shear banding using a simplified version of the most comprehensive tube model (Ref. 20). In absence of a constitutive non-monotonicity, shear inhomogeneity could arise only if the system experiences a shear stress gradient along the velocity gradient direction. However, in our opinion, the strain localization may reflect a genuine structural breakdown of the entanglement network. Whether it is visible or not, i.e., produces observable strain localization or not, depends intimately on whether or not the disentangled state is sufficiently different from the entanglement state, and on how the external shearing is imposed (cf. Ref. 42).


Often more information can be obtained if the rheometer applies a given shear rate and
interrupts the startup shear within a certain amount of time to attain a prescribed value of strain.
Throughout this paper, we adopt a generalization of the concept "step strain" and use the phrase
to refer to any interrupted startup deformation involving a prescribed rate of deformation.


Larson, R. G.; Khan, S. A.; Raju, V. R. J. Rheol. 1988, 32, 145; Sanchez-Reyes, J.; Archer, L.


219802. In our Comment  Phys. Rev. Lett. 2009, 103, 219801, we emphasized that monotonic
models cannot produce non-quiescent relaxation behavior in absence of any artificial stress
gradient. As confirmation to our assertion, the Reply (p. 219802) had to invoke a visible artificial
stress gradient to produce non-quiescent relaxation after step strain, as observed in our PTV
experiments.

The DE tube model had to invoke a non-structural argument, frequently related in the literature
to the Considère criterion, to suggest occurrence of non-uniform extension. But emergence of a
maximum in \( \sigma_{\text{eng}} \) does not have to result in necking when the tensile force decline originates from
yielding, i.e., the transition from elasticity to plasticity.

Whether wall slip, shear banding and non-quiescent relaxation would occur depend on a
specific material parameter known as the extrapolation length \( b \) that can be reduced sufficiently
by employing entangled polymeric solvents to insure homogeneous shear and quiescent
relaxation. See Ref. 31 and Ref. 32 for more detailed discussion of this crucial point.

The Rouse time can be estimated in two ways. We found similar values: According to the
Osaki formula of \( \tau_{\text{R}} = \frac{\rho M}{\pi^2 \eta^2 RT \ell^2} \) where \( M_c \) is chosen to be \( 2M_w \), we have 13.5 s.
When evaluating from the high frequency data according to \( \tau_{\text{R}} = \frac{\rho M}{\pi^2 \eta^2 RT \ell^2} \left( \frac{M_w}{M_c} \right)^{3/2} \) where \( \ell \) is the
prefactor for the scaling behavior of the storage modulus \( G' = \alpha \ell^{3/2} \), we get 13.2 s. See a

Private communication with M. Cates.


In this zero order picture, we regard the structure of an entangled polymer to be statistically
uniform at all levels down to the scale of entanglement spacing. For the sake of conceptual
simplicity we have discussed the force imbalance as a single molecular event that occurs at the
yield point corresponding to the force maximum. In reality, dynamic yielding, i.e., the transition
from solid-like to liquid-like due to reduced molecular confinement can be expected to occur well
before the whole system exhibits the global yield point at the force maximum. We have also
recognized recently that there may be a spectrum of entanglement strength distribution, implying
occurrence of sequential disentanglement: Wang, Y. Y.; Wang, S. Q. Macromolecules 2011, 44,
5427.

There have been suggestions in the literature that the polymer entanglement dynamics may be
spatially inhomogeneous. There is even speculation that the chain entanglement is more of