Nonlinear rheology of entangled polymers at turning point

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Abstract

Thanks to extensive observations of strain localization upon startup or after stepwise shear, a conceptual framework for nonlinear rheology of entangled polymers appears to emerge that has led to discovery of many new phenomena, which were not previously predicted by the standard tube model. On the other hand, the published theoretical and experimental attempts to test the limits of the tube model have largely demonstrated that the most experimental data appear consistent with the tube-model based theoretical calculations. Therefore, the field of nonlinear rheology of entangled polymers is at a turning point and is thus a rather crucial area to carry out further examinations. In particular, more molecular dynamics simulations are needed to delineate the detailed molecular mechanisms for the various nonlinear rheological phenomena.

I. Introduction

Nonlinear polymer rheology aims to establish guiding principles that can be applied to achieve more efficient and effective processing. The central questions facing nonlinear rheology of entangled polymers are (a) where chain deformation comes from and (b) when molecular deformation ceases to be affine like. To answer them, we must figure out what chain entanglement is and is not, and how it transforms in response to fast large external deformation. These are long-standing mysteries that have attracted extensive attention for decades.[1,2,3,4] Constitutive continuum-mechanical modeling cannot depict molecular origins of various rheological characteristics. Stochastic simulations such as the network model with sliplinks[5,6] and primitive chain network (PCN) model[7,8] do not describe polymer entanglement self-consistently. The single-chain tube theory[4,9] offers a smoothed-out depiction of interchain interactions that is not self-consistent, as noted by Lodge[10] and many others. The simplified description of the collective (many-body) nature of chain entanglement has made it difficult for the tube theory to depict how chain disentanglement takes place.[11]

To depict the rheological state, the experimentalist needs to determine both the deformation field and the corresponding stress field. Most rheometric measurements of entangled solutions and melts prior to 2006 were predicated on the premise that the deformation field can be prescribed *a priori*, e.g., homogeneous straining prevails. The particle-tracking velocimetric (PTV) observations of shear banding upon startup shear[12,13,14,15] and non-quiescent relaxation after stepwise shear[16,17] contradict this textbook assumption of homogeneous deformation.[18] They raise the question of how to depict chain disentanglement and breakdown of the entanglement network,[19] calling for new efforts to carry out molecular-dynamics simulations and to work out alternative microscopic theories.

The subject of nonlinear polymer rheology has been undergoing a deep transformation. Have we reached a point of no return? The purpose of this Opinion Article is to bring the outstanding challenges into focus and to demonstrate that the field is a cross road. We see surely where it is heading because we have already developed significant conceptual understanding toward a theory that "is confirmed by observing things which it predicts that are otherwise unexpected".[20]

II. A molecular networking paradigm that makes predictions

When long chains mutually intertwine in a polymer melt of high molecular weight, they are constrained due to interchain uncrossability, giving rise to an entanglement network whose building-block is an entanglement strand (EntS) of coil size l_{ent} between two neighboring entanglement points/junctions. An EntS would meet an entropic barrier if it would try to free itself from entanglement without waiting for chain diffusion to renew its topological relationship with surrounding chains: For an EntS to disengage requires a conformational entropy change on the order of k_BT. Unlike the perception provided by the tube model that a test chain is constrained laterally by an unbreakable tube but meets no longitudinal resistance along the primitive path, we envision a finite strength associated with the entanglement network.[19] Disentanglement can take place after large stepwise deformation that has caused the EntS to acquire an elastic retraction force f_{retract} (associated with its conformational change) beyond a threshold on the order of $f_{\mathrm{ent}} \sim k_BT/l_{\mathrm{ent}}$: The network is elastically driven to yield via chain disentanglement (i.e., sliding of EntS at entanglement points). If this yielding is sufficiently localized, as is the case for highly entangled melts,[17] non-quiescent relaxation ensues.[16,17]

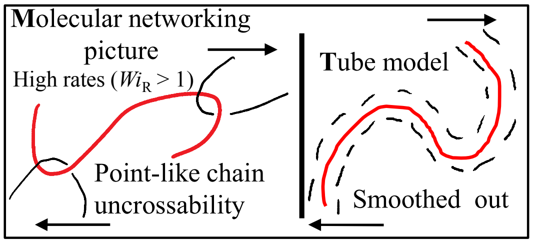

Fig. 1

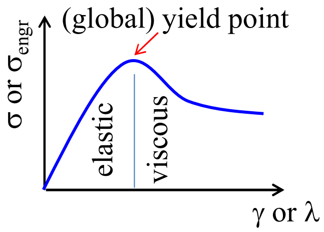

Fig. 2

Fig. 1 Molecular networking picture recognizes the formation of a chain network due to explicit interchain uncrossability that provides point-like coupling during fast external deformation (where the product of strain rate and Rouse time, i.e., $Wi_R > 1$). In contrast, the smoothed-out treatment of interchain interactions in the tube theory is elegant and can successfully depict linear response behavior, however, it lacks self-consistency in dealing with how entanglement responds to fast large deformation. For example, the tube theory is unable to treat the situation where interchain interactions become point-like at high rates.

Fig. 2 Shear stress σ (or engineering stress σ_{engr}) overshoot upon startup simple shear (or uniaxial extension), where shear strain is γ, and λ is the stretching ratio. The stress maximum is a macroscopic yield point, which must be caused by molecular yielding, e.g., plausibly due to chain disentanglement leading to failure of the entanglement network as the number of EntS diminishes.

It is this entropic cohesion that allows molecular elastic deformation to take place at low rates. But such elastic straining of the entanglement network does not continue forever upon startup deformation because f_{retract} cannot grow beyond f_{ent}. As an indication of the arrival of this point, shear stress (or engineering stress) upon startup shear (or extension) shows a maximum. The elapsed time can be significantly shorter than the reptation time τ_d. There emerges the concept of molecular yielding during ongoing deformation when EntS dissolves by sliding at the network junctions, relieving stress through chain retraction, which eventually leads to a structural breakup of the entanglement network.

At rates comparable to and higher than the reciprocal Rouse time, entanglement points (i.e., network junctions) emerge explicitly upon startup shear or extension. Fig. 1 depicts two such points arising from the intermolecular uncrossability and rapid chain displacement in opposite directions during external deformation. The strength of such junctions can be represented in terms of an average intermolecular gripping force (IGF) whose magnitude depends on the local chain relaxation dynamics.[21,22] Macroscopic yielding at the stress overshoot,[23] as depicted in Fig. 2, is due to the growing f_{retract} reaching IGF, leading to the event of force imbalance at the molecular level. At even higher rates, chains form "permanent knots" so that f_{retract} grows monotonically until the point of rupture as if the melt was crosslinked.[24,25,26]

In comparison, in the tube theory[27] the tube is always present. Because of smoothed-out single-chain treatment of interchain interactions, the tube theory envisions barrier-free chain retraction upon large deformation. But if any stretched chain is to return to a non-stretched state, shouldn't it have to drag the surrounding chains during the chain retraction? In absence of self-consistency, the chain retraction in the tube model was not perceived to destroy or modify the tube. Consequently, the tube model has limited ability to envision and depict chain disentanglement. It turns into a theory that can fit but cannot predict.[28] The power of the alternative paradigm[11,19] resides in its ability to anticipate phenomena that are otherwise unexpected. For example, below we list nine important rheological phenomena that were previously unexplored. In other words, most of these phenomena were first envisioned according to the emergent theoretical picture[19] before being discovered in the lab, some of which were indeed rather counterintuitive.

1. Arrested wall slip: If wall slip occurs at strain γ_s during startup shear, it can take place when the same startup shear is terminated at a lower strain $\gamma < \gamma_s$.[29]

2. Yielding in startup extension: Force imbalance and yielding also occur in startup extension when the engineering stress peaks,[30] leading to strain localization for Weissenberg number $Wi > 1$. No homogeneous steady flow state can be reached.[24,30,31] In contrast, others have carried out experimental and theoretical studies[32,33,34] to report "steady" extensional flow properties of entangled solutions and melts.

3. Faster elastic yielding and stress relaxation at lower stress: Earlier macroscopic breakup and faster stress relaxation take place after stepwise shear, which is produced at a lower rate and correspondingly lower stress.[35]

4. Elastic breakup upon stepwise extension: Stepwise extension also results in non-quiescent relaxation due to localized yielding.[30]

5. Long chain branching postpones elastic failure: Melts containing sufficient long chain branching remain intact[36] after large stepwise extension (e.g., at $\varepsilon = 2.0$)

6. Shear banding is metastable having little to do with constitutive non-monotonicity: When startup is replaced by a gradual rate rampup,[37,38] homogeneous shear can prevail.

7. Shear strain localization at die entry during extrusion: Deformation discontinuity occurs at the die entry during continuous extrusion of entangled melts.[39]

8. Different specimen failure modes upon startup extension: Three different modes of specimen failure show up during extension at various Hencky rates.[40]

9. Shear banding during squeezing creep: Shear banding is observed after a constant normal load (Z axis) to cause planar extension along Y axis at constant width (in X axis).[41]

III. Latest theoretical activities

The intriguing experimental findings outlined above prompted further theoretical activities. It was asserted[42] that the tube-model calculations captured all experiments but one although it cannot and does not describe how chain disentanglement takes place. On the other hand, recent molecular dynamics simulations[43,44,45] on the conformational and corresponding rheological responses to startup shear questioned the basic premise of the tube theory.

Separately, taking the coupling between stress and polymer concentration into account, a monotonic constitutive theory was constructed[46,47] to depict shear banding as due to a concentration stratification whose characteristic scale is that of the coil size instead of a macroscopic distance as observed in the PTV studies.

Along a different line, numerical studies have tried to show, based on either monotonic[48,49] and non-monotonic[50] versions of the tube theory, that continuum mechanical calculations can depict various forms of macroscopic phenomena such as non-quiescent relaxation after large stepwise shear and shear banding during startup. A similar attempt[51] was made to depict filament break up in melt extension. However, these studies cannot address questions such as whether any structural breakup takes place and what molecular events are involved.

There were also oppositions to the extensive reports of shear banding[12,13,14,15,52,53] and non-quiescent relaxation.[16, 54] The issues included a) whether shear banding was only transient,[1413,38,55,56] b) whether shear banding (observed in conventional rheometric setups) can take place when slip is dominant, which can be the case for shear apparatus with a much reduced gap distance of 40 ~ 50 μm,[57,58] c) whether previously reported shear banding[59] could be due to artifacts including edge fracture,[60] which was a speculation based on insufficiently entangled solutions that were only weakly sheared.[61,62] To remove any concerns including c), it is necessary to use samples and shear conditions identical to those involved in the past studies[14,15,59] and make sure that artifacts such as edge effects are removed as done in Ref. 15.

IV. Hopeful prospects

It is necessary to explore a self-consistent account of the many-body effects in nonlinear rheology of entangled polymers. Pioneering studies have been carried out by Sussman and Schweizer to depict entanglement involving large deformation of rigid polymers.[63,64,65,66] Their theory was able to identify limited cohesion and reveal finite tube strength not only for rodlike chains but also for flexible chains.[67,68] Under large deformation, tube confinement can diminish, leading to disentanglement,[64,65,66] similar to our initial ideas[19] of molecular yielding and breakdown of entanglement network. Consistent with the theoretical depiction, the single-molecule fluorescence imaging experiment revealed,[69] for large enough transverse displacement, a confining force independent of displacement, implying that the cohesion force f_{ent} (introduced at the beginning of Section II) is indeed finite and tube confinement potential is strongly anharmonic.

Computer simulations[70] are desired to help us elucidate molecular origins of various nonlinear rheological behaviors. Not all simulations are equal or equivalent. For example, if one chooses to simulate polymer entanglement in an *ad hoc* way, e.g., using a slip-link construct[7] to account for chain networking, he can produce an agreement[71] between the PCN simulations[7,8] and the tube theory. Such an agreement stems from the fact both PCN simulations and the GLaMM model[9] fail to depict the chain stretching[45] that contributes significantly to the stress even at shear rates lower than the Rouse rate. Molecular dynamics simulations are based on first-principles and should be a more appropriate method if we wish to learn about how entanglements respond to large deformation. The emergent Brownian dynamics simulations[43,44,45] show that the shear stress overshoot originates from retraction of stretched chain on a time scales far beyond the Rouse time whereas the chain orientation contribution to stress actually changes monotonically with increasing strain. In other words, the preliminary computer simulations failed to offer support for the basic premise of the tube model that the primitive chain would execute Rouse dynamics in an imaginary tube and would undergo barrier-free chain retraction inside the tube.

V. Closing comments

The field of nonlinear polymer rheology is undergoing unprecedented changes. The emergent experimental observations have forced us to search for an alternative conceptual framework.[11] We regard the developments as a healthy trend: there are two competing and mutually incompatible frameworks, each demonstrating its own strengths and merits. Macroscopic experiments by definition cannot prove which picture is more realistic. Thus, the challenge remains as to how to further our understanding of the response of chain entanglement to fast large deformation. New molecular level experiments would be highly desirable. More molecular dynamics simulations are necessary to determine which direction the field is turning. Further theoretical efforts are needed to place such concepts as molecular yielding, finite cohesion (and force), entropic barrier, IGF, molecular force imbalance on firmer grounds. In closing, we emphasize that a sufficiently high level of entanglement and sufficiently fast shearing are necessary to observe shear strain localization.[61,62] Indeed, only well entangled polymers at sufficiently high extrusion speeds show instabilities such as wall slip and melt fracture.

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