

Entanglement-disentanglement transition free of edge effects

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Since the publication¹ of Tapadia and Wang in 2004, there has been confusion about whether the reported entanglement-disentanglement transition (EDT), observed at a constant applied torque in rotational rheometry, is a constitutive property of well entangled polymers or can be fully accounted for² by occurrence of edge fracture. As stated before, "upon this transition, the sample exhibits a steady-shear viscosity as low as 20 Pa s at $\sigma = 3.0$ kPa in comparison to its value of 25 000 Pa s before the transition. Since the high zero-shear viscosity is universally regarded as due to chain entanglement, the reduction of 3 decades in the shear viscosity could be due to a massive loss of chain entanglement. Thus, we term this yieldlike constitutive transition an entanglement-disentanglement transition (EDT)."¹ This communication shows that EDT must take place, resulting from the very existence of the nonlinear regime known as stress plateau as sketched in Figure 1(a) in spite of any complication arising from edge fracture, which would indeed cause the magnitude of EDT to be artificially enlarged as rightfully pointed out.^{2,3}

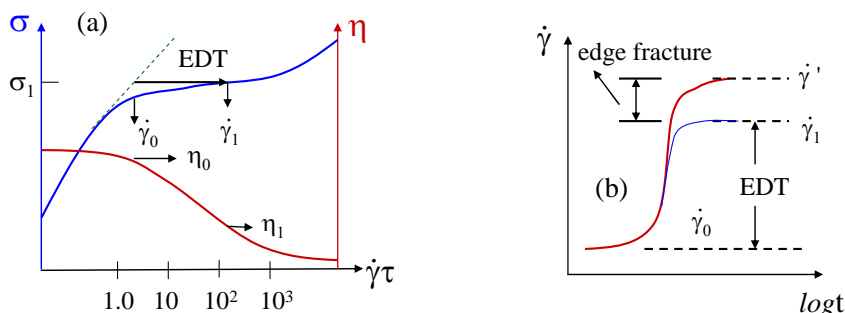


Figure 1 (a) Schematic flow curve and shear viscosity dependence on the Weissenberg number where the path under at a fixed stress σ_1 is clearly indicated, from η_0 to η_1 , where (b) the corresponding true values of the initial and final shear rates are indicated, as well as additional rise due to edge instability.

Priori to the work of Tapadia and Wang, rate-controlled measurements had already revealed the plateau character as illustrated in Figure 1(a) that nobody including the authors of Ref. 2 questioned. According to Figure 1(a), an applied shear stress σ_1 in the stress plateau regime would result in shear thinning of any well entangled polymer solution with an apparent viscosity $\eta_1 = \sigma_1/\dot{\gamma}_1$ that can be far lower than its initial value of $\eta_0 \sim \sigma_1/\dot{\gamma}_0$. How does it transform from its initial fully entangled state with η_0 to the

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final state of $(\sigma_1, \dot{\gamma}_1)$ during creep at stress σ_1 ? Before the entanglement network falls apart to yield the final viscosity of η_1 , the system has to undergo shear initially at a rate of $\dot{\gamma}_0$ before rising to a final rate of $\dot{\gamma}_1$ as depicted in Figure 1(b). In other words, we are bound to observe the initial state at $\dot{\gamma}_0$ because chain disentanglement cannot occur instantly and witness the rise in the apparent rate to its final value of $\dot{\gamma}_1$. As for the final state, indeed, any sample loss would produce a final rate $\dot{\gamma}'$ higher than the true rate $\dot{\gamma}_1$ as indicated in Figure 1(b). We have termed this feature illustrated in Figure 1(b) a dynamic entanglement-disentanglement transition (EDT) because the phenomenological significance of chain entanglement is associated with a high magnitude of shear viscosity whose reduction by definition implies chain disentanglement.

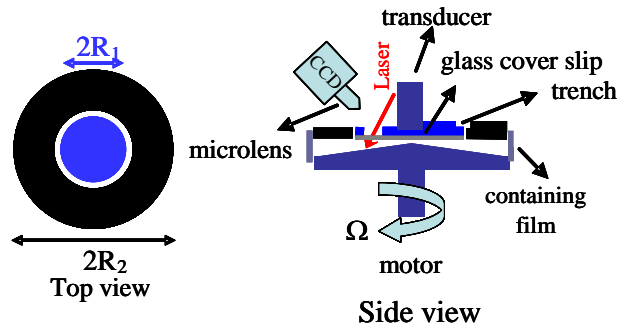


Figure 2 A cone-partitioned plate shear cell that avoids any edge effects on the rheological measurements, where the fixed upper surface is made of a circular disk of radius R_1 that is connected to a torque transducer and a ring of outer diameter $2R_2$ that is held fixed with small spacing between the disk and the ring. Also indicated is a particle tracking velocimetric setup that allows the velocity profiles to be determined at all times during shear in either mode.

Clearly, Tapadia and Wang might not have obtained a true flow curve of σ vs. $\dot{\gamma}$ even though their original polymer solution appeared to be different⁴ from any subsequently prepared solutions and was judged to show little edge fracture. Actually, we were recently able to show⁵ that edge fracture not only makes it implausible to obtain a truly reliable flow curve in the creep mode (i.e., constant torque mode) but also forces premature termination of startup rate-controlled shear in a conventional cone/plate setup. The reported lack¹ of overlapping between the two flow curves obtained in speed-controlled and torque controlled modes arose from errors associated with these difficulties. Nevertheless, adopting a design of cone-partitioned plate (C/PP) as shown in Figure 2, we can demonstrate that EDT is real and does occur in absence of any edge effects. Using this C/PP setup, we are specifically able to examine the rheological responses under various true stresses as shown Figure 3 where a true constant shear stress is achieved through an electronic feedback loop on Advanced Expansion Rheometric System (ARES). Here the 10 % polybutadiene solution, made with high MW equal to 10^6 g/mol (synthesized in R. Quirk's lab at Akron) dissolved in oligomeric PBD from Sigma-Aldrich (Cat. No. 20,0484), is in every way similar to that studied by Tapadia and Wang. Indeed, the apparent shear rate can increase by a factor of nearly 400 over a small stress range from 1400 to 2200 Pa. It is also clear that EDT does not occur at 1400 Pa.

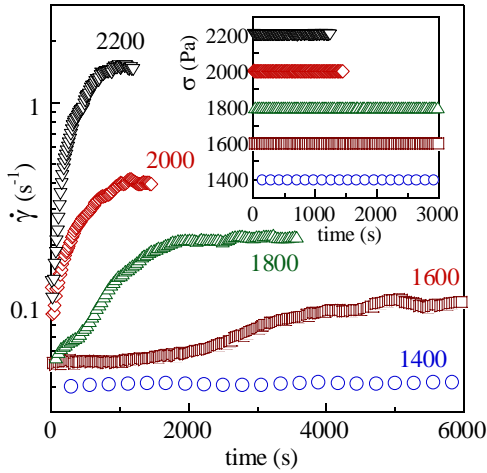


Figure 3 EDT observed at four different shear stresses, where the inset shows the actual shear stresses measured by the torque transducer that is linked to the inner disk as shown in the depiction of C/PP in Figure 2.

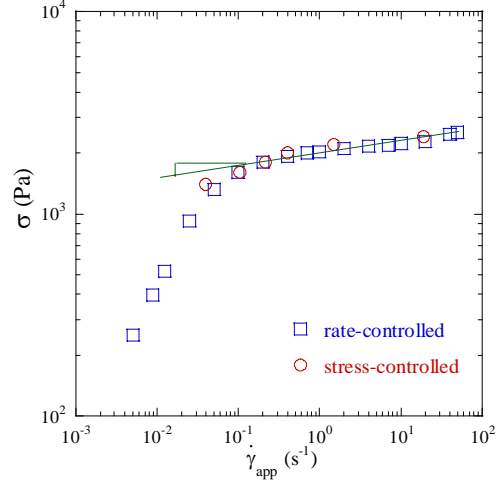


Figure 4 Flow curves obtained from both controlled-rate and controlled-stress modes. The evidence of approximating overlapping of the two curves is strong, so is evident that the curves are monotonic with a finite slope.

We were also able to show that the two flow curves overlap well and are smooth and monotonic, independent of which mode is used to perform steady state measurements, as shown in Figure 4, in sharp contrast to the self-conflicting conclusion that the EDT led to a discontinuous flow curve of Figure 8 in Ref. 1. This incorrect description of the flow behavior of entangled polymer solutions is clearly associated with the inability to apply true shear stress in a conventional cone/plate setup. The improved apparatus of Figure 2 allows fine variation in each discrete application of true stress and shows for the first time without ambiguity that the flow curve is monotonically continuous. However, the monotonicity does not assure that homogeneous shear would prevail upon startup flow. *In situ* particle tracking velocimetric (PTV) observations shown in Figure 5 confirm earlier findings^{6,7,8} that the sample was unable to undergo uniform shear even in steady state as speculated by Tapadia and Wang.

Finally, we emphasize that although the flow curve is not discontinuous contrary to the initial report,¹ shear thinning and EDT would only occur beyond a critical level of shear stress σ_c even though the magnitude of EDT can indeed be rather small and may vanish at σ_c if wall slip is insignificant. In the present case, σ_c is clearly between 1400 Pa and 1600 Pa according to Figure 3. The origin of EDT can be understood within a new theoretical framework recently put forward.⁹ According to our latest understanding, chain entanglement provides transient cohesion on time scales shorter than the terminal relaxation time τ , which is ca. 16 s for the current sample. When an externally applied true shear stress exceeds the cohesive strength of the entanglement network, the system is forced to undergo disentanglement instead of flowing via Brownian renewal of chain entanglement. It is the cohesive breakup of the entanglement network that produced EDT under a sufficiently high applied shear stress. Surprisingly, this process can take place inhomogeneously.⁵

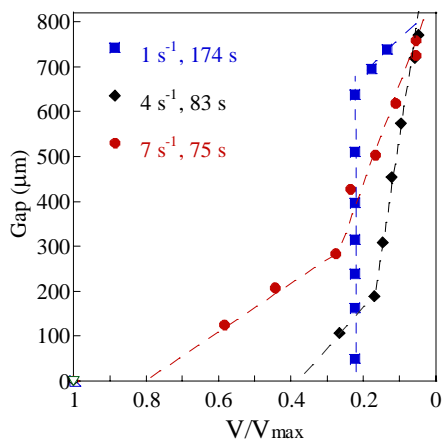


Figure 5 *In situ* PTV measurements of the steady state velocity profile that has been normalized for three discrete rates of 1, 4 and 7 s⁻¹.

In summary, with development of a C/PP apparatus as shown in Figure 2 we are finally able to support our assertion stated in Figure 1(a)-(b) that EDT is bound to take place in entangled polymers as long as they show shear thinning behavior. Specifically, our new experiment confirmed the occurrence of EDT, free of any edge effects as shown in Figure 3.

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References

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- ³ Sui, C.; McKenna, G. B. *Rheol. Acta* **2007**, *46*, 877.
- ⁴ It is relevant to formally indicate here that both of the present authors witnessed the sample studied in Tapadia and Wang (2004) and judged its appearance by visual inspection with hands and during shear to be different from any other samples subsequently prepared including the present one. In other words, the sample of Tapadia indeed underwent creep without exhibiting appreciable edge fracture. We have been unable to reproduce such an edge-fracture-free sample. This motivated us to design a C/PP device shown in Figure 2.
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