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Letter

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Do Repeated Shear Startup Runs of Polymeric Liquids Reveal Structural Changes?

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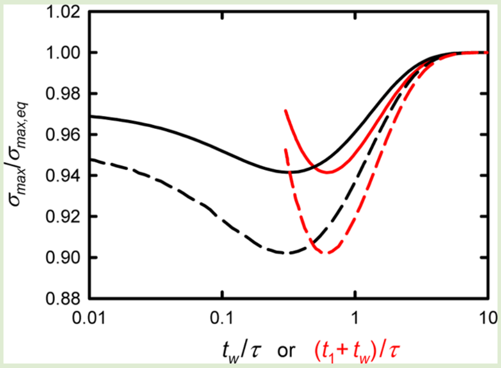
Supporting Information

ABSTRACT: Using the integral equation of the Doi−Edwards theory that only accounts for tube orientation of entangled linear polymers, we explore the behavior of the stress maximum typically observed in shear startup as a function of the waiting time t_w between repeated startup runs. Depending on whether the first run is interrupted before the maximum, or sufficiently beyond it, the magnitude of the peak in the second run comes out nonmonotonic with t_w or else monotonically increasing, respectively. A similar behavior has been observed in several experiments and commonly attributed to structural changes of the entangled network. By emphasizing the role played by the mere orientation of the network strands in faithfully reproducing all the observed behavior, at least qualitatively, our results help to put things in better perspective.



Entangled polymers in the liquid state exhibit a complex nonlinear viscoelastic behavior, even when the polymer chain is linear (no branches), and some of that complexity is often attributed to the entanglement dynamics, that is, to the fact that fast flows induce some disentanglement. It is also expected that, upon letting the polymer rest for a sufficiently long time, the polymer regains the equilibrium entangled structure. Over the years, many authors have reported experiments of repeated shear startup runs for linear polymers at shear rates for which a typical overshoot occurs in the stress versus time response.[1−9] They found that the magnitude of the overshoot peak decreases significantly upon repeating the startup run (at the same shear rate) after a short time of stress relaxation following steady state, whereas by waiting progressively longer times, the peak height correspondingly increases, to finally attain the original value of the first run. Most authors discuss these results in terms of a disentanglement process brought about by the first run and of re-entanglement kinetics during the period of rest.

More recently, Wang et al.[10,11] report more complex experiments of shear startup. In particular, in a sequence of experiments on a polybutadiene solution, a first run at a low rate (0.25 s^{-1}) is stopped before reaching the peak and then started again after some waiting time t_w, but at a higher rate (15 s^{-1}). The magnitude of the peak attained in the second run shows a nonmonotonic behavior. Specifically, it first decreases with increasing t_w from 0 to a few seconds, then slowly grows up with increasing the waiting time to finally reach the value associated with a single startup (starting from equilibrium) at the higher rate of 15 s^{-1}. Wang et al. interpret these (and other) data in terms of disentanglement, occurring when the elastic (entropic) force in the stretched subchains of the entangled network overcomes the intermolecular gripping force concentrated at the entanglements. In a subsequent comment to the paper of Wang et al.,[11] Graham et al.[12] use the Rolie-Poly model (based on standard tube model concepts) to show that a similar nonmonotonic behavior can in fact be predicted by that model. They say that a careful analysis of the model predictions reveals that "The nonmonotonic response in $\sigma_{xy,\max}(t_w)$ is due to the delayed relaxation of the normal stress σ_{yy}", and that "The postflow reduction of σ_{yy} is due to retraction of the small amount of stretching that accumulates during the flow."

In this letter, we want to show that, differently from the opinions of Wang et al.[11] and of Graham et al.,[12] the classical, purely orientational, integral equation of Doi and Edwards[13,14] already predicts a nonmonotonic behavior, in all, similar to that shown by the above-mentioned data. This will not imply that chain stretch and disentanglement do not occur (see later), but it may constitute a warning against drawing premature conclusions from data of repeated startup runs.

It is recalled that the original theory of Doi and Edwards predicts a stress that is based entirely on the orientational anisotropy of tube segments, the polymer chain within the confining tube remaining unstretched. Hence, in a shear flow, the shear stress at the generic time t is given by

$$\sigma_{xy} = \frac{15}{4} G_N^0 S_{xy}, \quad S_{xy} = \int_{-\infty}^{t} \frac{dt'}{\tau} \exp\left(-\frac{t-t'}{\tau}\right) Q_{xy}(t, t') \tag{1}$$

where G_N^0 is the plateau modulus, $S_{xy} = \langle u_x u_y \rangle$ is the average tube orientation ($\boldsymbol{u}$ being the unit vector tangent to the tube axis or "primitive chain"), and $\boldsymbol{Q}$ is a tensor that depends on the

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relative deformation between current time t and previous time t', that is, on $\gamma(t) - \gamma(t')$. For the sake of simplicity, we have limited the memory function to a single exponential, τ being the disengagement relaxation time of the chain from the tube. The numerical factor 15/4 is linked to tensor $\mathbf{Q}$ that, here and in the following, is taken to be the so-called rigorous one.[14,15] Should one take the tensor of the independent alignment approximation (IAA),[14,16] then the numerical factor becomes 5. The function $Q_{xy}(\gamma)$ goes through a maximum at $\gamma_{max} \approx 1.91$, and the peak magnitude is $Q_{max} \approx 0.254$.[17]

In a single startup, with the shear rate $\dot{\gamma}$, the integral in eq 1 is conveniently broken up in the sum of the integral between $-\infty$ and 0 ($t' = 0$ being the time when flow begins), integral that becomes $\exp(-t/\tau)Q_{xy}[\gamma(t)]$, plus the integral between 0 and current time t, to be calculated numerically. The result generates the function $S_{xy}(\gamma, Wi)$, where $\gamma = \gamma(t) = \dot{\gamma}t$ is the current deformation, and $Wi = \dot{\gamma}\tau$ is the Weissenberg number. Similar to $Q_{xy}(\gamma)$, also $S_{xy}(\gamma, Wi)$ goes through a maximum at the deformation $\gamma_{max} \approx 1.91$ independently of Wi, but the magnitude of the peak, $S_{max}(Wi)$, depends on Wi in the way shown in Figure 1. In the linear limit ($Wi \to 0$), the peak vanishes, while in fast flows, the peak magnitude approaches Q_{max} with increasing Wi.

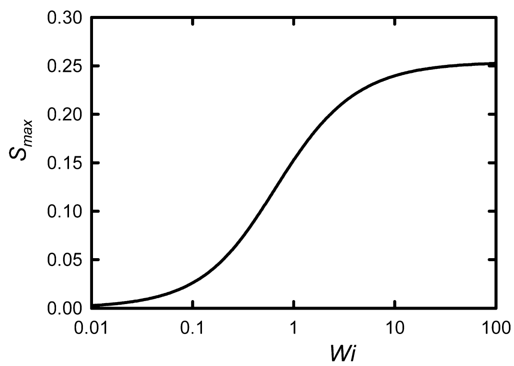

Figure 1. Magnitude of the S_{xy} peak in shear startup vs the Weissenberg number, as obtained from eq 1 with the rigorous tensor $\mathbf{Q}$ of Doi–Edwards theory.

In repeated startup runs like those mentioned before, the integral in eq 1 is best broken up in four parts, the integration time t' running from $-\infty$ to 0, from 0 to t_1, from t_1 to $t_1 + t_w$, and from $t_1 + t_w$ to current time t, respectively. Here t_1 is the time at which the first run is halted, and t_w is the waiting time before restarting. The shear rates in the two runs are generally different, but we shall first take them to be equal. For such a case, eq 1 generates the function $S_{xy}(\gamma, \gamma_1, Wi, t_w/\tau)$, where $\gamma_1 = \dot{\gamma}t_1$ is the deformation at which the first run is terminated.

We now need to distinguish the case where γ_1 falls before, or else beyond, the maximum. If $\gamma_1 < \gamma_{max}$, then in the second run a maximum of magnitude $S_{max}(\gamma_1, Wi, t_w/\tau)$ is predicted for all values of the three parameters. In Figure 2a, for the fixed value $\gamma_1 = 1.5$, we plot the shear stress ratio $\sigma_{max}/\sigma_{max,eq} = S_{max}(\gamma_1, Wi, t_w/\tau)/S_{max,eq}(Wi)$ as a function of t_w/τ, where $S_{max,eq}(Wi)$ is the peak magnitude for a single run starting from equilibrium, reported in Figure 1. As one would expect, such a ratio goes to unity both for $t_w = 0$, that is, when the first run goes on unperturbed, and for long waiting times, that is, when the second run starts again from equilibrium. However, for intermediate values of t_w, the magnitude of the maximum decreases, the more so the higher is the shear rate. Figure 2b shows similar results when γ_1 is changed, while the shear rate is held fixed ($Wi = 10$). The dip of the maximum becomes deeper as γ_1 approaches γ_{max}. (For an interpretation of the physics behind the results in Figure 2, see Supporting Information.)

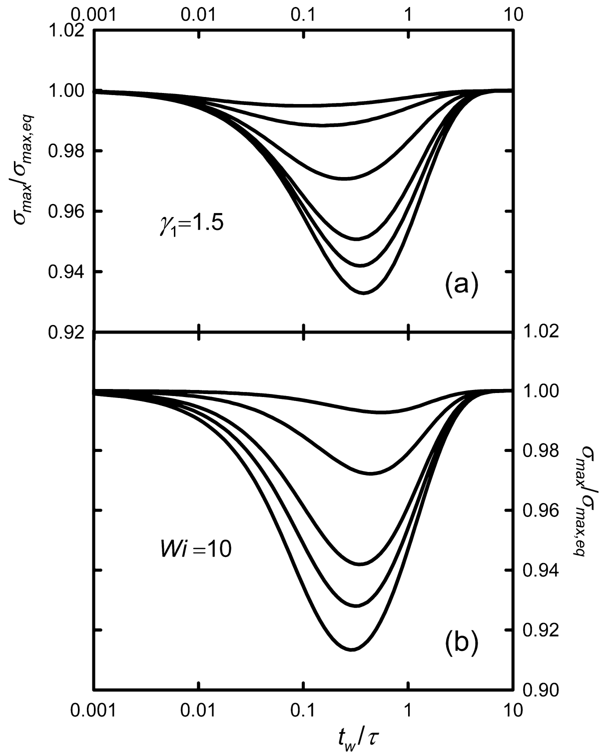

Figure 2. Peak magnitude ratio $\sigma_{max}/\sigma_{max,eq}$ as a function of the waiting time, the shear rate in the second run being the same as in the first, and γ_1 less than γ_{max}. (a) Curves for $\gamma_1 = 1.5$ at several values of the shear rate (Wi = 0.7, 1, 2, 5, 10, and 100, from top to bottom) and (b) for a fixed shear rate ($Wi = 10$) at several values of γ_1 (0.5, 1, 1.5, 1.7, and 1.9, from top to bottom).

Figure 3 instead shows what happens when $\gamma_1 > \gamma_{max}$ (at $Wi = 10$). Except when γ_1 is very large, no maximum is found for small values of the waiting time. Indeed, since the first run has been interrupted beyond the maximum, that is, when the orientation (hence, the stress) was already decreasing toward its steady-state value, for short resting times, no significant change

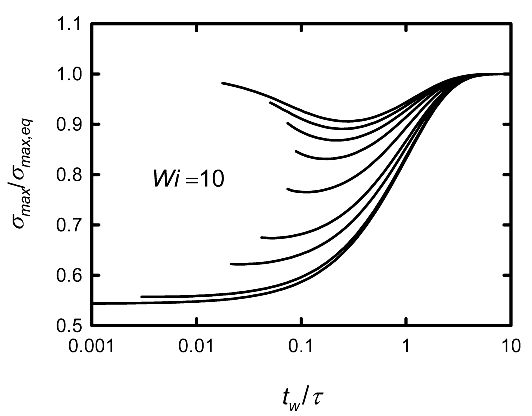

Figure 3. Effect of waiting time on $\sigma_{max}/\sigma_{max,eq}$ as in Figure 2b, but for γ_1 larger than γ_{max} (γ_1 = 2, 2.2, 2.5, 3, 4, 6, 8, 16, 32, from top to bottom). Each curve starts from the value of t_w/τ, where the maximum reappears in the second run.

occurs, and upon restarting the flow, the stress keeps decreasing toward the steady state. For longer waiting times, however, the maximum again appears. Depending on how much γ_1 is larger than γ_{max}, the behavior is nonmonotonic ($\gamma_1 < \sim 8$) or else monotonically increasing with increasing waiting time. The lowest curve in Figure 3 represents the recovery of the maximum when the starting condition is the steady state at the given value of the shear rate (Wi = 10). This last curve qualitatively represents the results reported by several authors.[1−9]

We finally move on to the case when the second startup is run at a higher rate than the first one, as in the data of Wang et al.[10,11] Because of the large number of parameters, we only consider a single case, roughly corresponding to the conditions of the Wang et al. experiment. We take for the first run $\gamma_1 = 1.5$ and $Wi_1 = 5$, and for the second run $Wi_2 = 50$. The two upper curves in Figure 4 represent the ratio $S_{max}(1.5, 5, 50, t_w/\tau)/S_{max,eq}(50)$ plotted both as a function of t_w/τ and of $(t_1 + t_w)/\tau$, to the left and to the right, respectively. The rightmost of the two curves should be compared to the data reported in the TOC figure of Wang et al.,[10] as well as in Figure 6 of Wang et al.[11] The qualitative resemblance of our red curve with the data in those figures is apparent, and it should be emphasized that our red (solid) curve comes out directly from eq 1 of Doi and Edwards, only accounting for tube orientation.

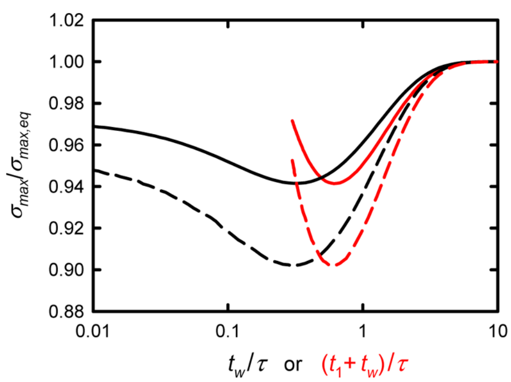

Figure 4. Results obtained when the shear rate in the second run is larger than in the first, as for the data of Wang et al.[10,11] Here $\sigma_{max,eq}$ refers to the high shear rate. Upper (solid) curves are from eq 1. Lower (dashed) curves are from eqs 2−4. Black and red curves are $\sigma_{max}/\sigma_{max,eq}$ vs t_w/τ and vs $(t_1 + t_w)/\tau$, respectively, t_1/τ being equal to $\gamma_1/Wi_1 = 1.5/5 = 0.3$. See text for values of other parameters.

What we have shown so far does not imply that chain stretch and chain disentanglement do not play any role. On the contrary, since the early work of Pearson et al.,[18] we know that in a shear startup chain stretch increases both the γ-location and the height of the shear stress maximum. Hence, if one wants to deal with the problem more quantitatively, chain stretch (based on Rouse time) cannot be ignored, not to speak of the oversimplification adopted here of taking a single orientational time. However, it can be shown (not reported here) that accounting for both chain stretch and for a spectrum of orientational times does not alter the above results qualitatively.

The possible role played by disentanglement, also referred to as "structural" change, is more controversial, as no widely accepted theory has been developed so far. On the other hand, it is undeniable that fast flows induce disentanglement. The molecular dynamics simulations run by Baig et al.[19] clearly show a reduction of topological constraints in the steady state of fast shear flows. Recently, we have proposed a simple model for the kinetics of disentanglement and re-entanglement processes.[20] For a shear flow, and in the absence of chain stretch, the model describes the rate of change of the entanglement density through the simple equation

$$\frac{d\nu}{dt} = -\beta\dot{\gamma}S_{xy} + \frac{1-\nu}{\tau} \tag{2}$$

where ν is the fractional density of entanglements at time t (ν = 1 implying equilibrium), and β is a convective constraint release (CCR) parameter of order unity. The negative term in eq 2 describes the loss rate of entanglements due to flow, while the positive term accounts for the diffusive reconstruction rate. A value of ν less than unity has two effects. On the one hand, it directly reduces the stress in proportion with ν itself because of the corresponding increase in the entangled network mesh size (see eq 4 below). A second effect is on the orientational relaxation time τ that also gets shortened because of the larger mesh size or tube diameter, a. By assuming reptation, and ignoring fluctuations, it is

$$\tau(t) = \tau_{eq}\nu(t) \tag{3}$$

where τ_{eq} is the disengagement time at equilibrium. A time-dependent τ also modifies the integral in eq 1 that becomes

$$\sigma_{xy} = \frac{15}{4}G_N^0 S_{xy},\ S_{xy} = \int_{-\infty}^{t}\frac{dt'}{\tau(t')}\exp\left(-\int_{t'}^{t}\frac{dt''}{\tau(t'')}\right)Q_{xy}(t, t') \tag{4}$$

The set of eqs 2−4 can be solved to produce, for β = 0.5, the two lower (dashed) curves in Figure 4, where it is understood that the parameters t_w/τ and $Wi = \dot{\gamma}\tau$ are now replaced by t_w/τ_{eq} and $Wi = \dot{\gamma}\tau_{eq}$. These curves show that also the structural changes, if quantitatively significant, do not alter qualitatively the results predicted by the merely orientational theory of Doi and Edwards.

A last remark concerns the characteristic time for structural reconstruction, which eq 2 assumes to be equal to the orientational relaxation time, as no other mechanism is known for the chains to interpenetrate one another's spatial domain different from diffusion (reptation). Is this assumption consistent with the experiments? Many authors find that the recovery of the shear stress maximum in repeated startup experiments occurs over a time longer, or even much longer, than the orientational relaxation time.[1,2,4,5,7−9] On the contrary, the results of Menezes and Graessley,[3] Sanchez-Reyes and Archer,[6] and Wang et al.[10,11] appear compatible with a recovery of the startup maximum in a time of the same order of magnitude of the orientational relaxation time, and it is noteworthy that the polymers used by them are more monodisperse. In this regard, one should remember that, for entangled linear polymers, (i) the orientational time is highly sensitive to the molar mass, growing with the 3.4 power of the latter, and (ii) in fast flows of polydisperse polymers, the shear stress maximum is dominated by the longer polymers that stretch more. Hence, the longer recovery times found by many authors could be due to polydispersity, although the problem certainly requires further analysis.

In conclusion, in this letter we have shown that (for linear polymers) the information obtained from repeated startup runs, specifically both the nonmonotonic and the monotonic recovery of the peak magnitude, cannot readily be interpreted, if at all, in terms of structural changes,[1,2,4−11] or of subtle effects of chain stretch.[12] Indeed, the purely orientational theory of Doi and Edwards already predicts, qualitatively, the observed behavior. Of course, chain stretch and disentanglement may, and often do, contribute to the quantitative aspects, and therefore, a quantitative theory accounting for all the known mechanisms (orientation, stretch, entanglement density change) might discriminate the specific contribution of the structural change. Unfortunately, no such all-encompassing quantitative theory is available to this day. The significance of this letter, however, is to be found in the fact that many people, especially those dealing with polymer processing, are convinced that the drop in peak magnitude is a distinctive mark of disentanglement, a concept that is here shown to be mostly a misconception.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Interpretation of the physics behind the results reported in Figure 2 and location of the maximum in repeated startup runs. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(17) These numerical values are **Q**-tensor dependent. With the IAA, they become $\gamma_{max} \approx 2.11$, $Q_{max} \approx 0.207$.[16] If $Q_{xy}(\gamma)$ is further approximated by the simple expression $Q_{xy} = \gamma/(5 + \gamma^2)$,[18] γ_{max} becomes the square root of 5, that is, $\gamma_{max} \approx 2.24$ and, hence, $Q_{max} \approx 0.224$. Also, all results reported in this letter are only marginally modified if approximate **Q** tensors are used instead of the rigorous one.
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