

Threading–Unthreading Transition of Linear-Ring Polymer Blends in Extensional Flow

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the blend compared to the pure linear melt. Thus, rings uniquely alter the mechanisms of transient elongation in linear polymers.

he dynamics of entangled ring polymers have recently L received renewed attention, not only because of their unique conformational and dynamic properties but also because of their implications in biological function.^{1,2} Blending entangled ring polymers with their linear counterparts has also revealed intriguing features which set these systems apart from other architectural blends.³⁻⁹ The linear viscoelastic (LVE) response of a nearly pure ring melt is extremely sensitive to the presence of linear molecules even in minute amounts.^{10–16} In the other limit, the LVE response of an entangled linear polymer matrix is substantially affected by the presence of a small fraction of rings, giving rise to a nonmonotonic dependence of blend viscosity on the ring fraction of the blend.^{3,17–19} This regime is of particular interest because the increase of linear polymer viscosity upon addition of small amounts of (less viscous) rings could be an effective means to tailor polymer rheology.^{2,17,18}

The next crucial step is to understand the nonlinear response of such blends. Fragmented information for shear flow behavior showed that a polystyrene linear-ring mixture with molar mass 185 kg/mol and ring fraction 15% has a shear thinning response very similar to that of the pristine linear melt but drastically different from the weaker thinning of pure rings.²⁰ In another study, DNA-based rings were examined in semidilute polymer solutions during planar extensional flow using a microfluidic cross-flow setup.²¹ The rings were found to undergo unusually large and time-persistent conformational fluctuations even at low fractions of linear chains, which was

attributed to transient threading of linear chains through stretched rings. In fact, threading of linear chains through rings has been demonstrated in the equilibrium state from both simulations and neutron scattering measurements.^{18,22–24} Besides linear-ring mixtures, such threading has also been reported in tadpole-shaped polymer melts.^{25–27} The findings motivate us to ask how these threading events emerge and affect the extensional rheology of a blended melt.

Recent measurements of entangled ring polystyrene melts in uniaxial extension revealed strong strain hardening and lowstrain-rate thickening of the viscosity.¹ Subsequent molecular dynamics (MD) simulations confirmed these observations and provided insights about their origin: a flow-driven formation of persistent links through mutual threadings that connect multiple rings into supramolecular chains as shown in Figure 1c.²⁸ The effect of mutual threadings on dynamics of pure entangled rings has also been discussed in several works including both simulations^{29–31} and experiments.^{32,33} By contrast, melts of linear chains do not form such links, instead creating conventional entanglements with each other (Figure 1a), and do not exhibit strain-rate thickening at low rates.

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Figure 1. Schematic illustrating snapshots of molecular interactions occurring in pure linear (left), linear/ring blend (center), and pure ring (right) melts during elongation. Linear melts (a) form transient entanglements, and pure ring melts (c) form persistent knots. Blends (b) develop a new transient coupling as rings become threaded into the linear entanglement network.

Thus, it is interesting to ask how a linear-ring blend with a relatively low ring fraction will respond to uniaxial extension.

While persistent links form in pure ring melts undergoing extension,²⁸ these rare events should be suppressed for ring fractions below the ring—ring entanglement threshold. Instead, we will show that the novel coupling in such a blend has a less permanent nature and is due to the transient threading of rings into the linear entanglement network as illustrated in Figure 1b. To do so, we will study a well-characterized linear-ring blend and compare its rate-dependent extensional rheology to that of pure melts of its constituents. Combining our extensional rheology with complementary MD simulations and ex-situ small-angle neutron scattering, we will directly relate rheological features to the changes in polymer dynamics and microstructure induced by these new couplings

The linear-ring blend under investigation is made of linear and ring polystyrenes with mass fractions of 70% and 30%, respectively. The weight-average molar mass of both components is 185 000 g/mol, and the dispersity is 1.01. This molar mass corresponds to 11–14 entanglements per chain for linear polystyrenes (see the Supporting Information, referred to as SI hereafter, for details). Details of synthesis can be found in refs 20 and 34–36, and blend preparation can be found in ref 18. The composition was chosen because it corresponds to the maximum zero-shear-rate viscosity of the blend.¹⁸ Importantly, this fraction of rings is above the estimated overlap concentration but below their entanglement concentration.¹⁸ The blend is named Lin/Ring-185k-70/30, while the linear and ring components are named Lin-185k and Ring-185k, respectively.

The linear viscoelasticity (LVE) of Lin/Ring-185k-70/30, Lin-185k, and Ring-185k has been characterized previously,^{1,18} and the results are summarized in the SI. The main message is that linear-ring threading slows down the stress relaxation of the blend relative to the slower linear component.¹⁸ The Rouse relaxation time $\tau_{R,Lin}$ of Lin-185k is used as a characteristic time to define the Weissenberg number below. The value of $\tau_{R,Lin}$ at 130 °C was reported to be 12 s¹⁸ or 64 s.³⁷ The difference is due to different methods of estimating the Rouse time: the former is based on the crossover frequency of the storage and loss moduli (see Figure S1), and the latter is based on model fitting to the LVE data. Details are explained in the SI. Here, $\tau_{R,Lin} = 64$ s is used to calculate the Weissenberg number for the purpose of comparing rheological measurements with MD simulations. However, we emphasize that the exact choice of $\tau_{R,Lin}$ does not affect the key observation and qualitative interpretation of the threading–unthreading transition that emerge by comparing experiments and simulations. As we will show, this transition occurs for a wide range of Rouse Wi.

The uniaxial extensional rheology of Lin/Ring-185k-70/30 was measured using a filament stretching rheometer (see SI for details) at 130 °C which is around 25 °C above the glass transition temperature of the blend.¹⁸ The stretch rate $\dot{\epsilon}$ was in the range of 0.0003 s⁻¹ to 0.03 s⁻¹, corresponding to a Rouse–Weissenberg number, Wi = $\dot{\epsilon}\tau_{R,Lin}$, from 0.02 to 2. The results are plotted in Figure 2 as the extensional stress growth



Figure 2. Time evolution of the extensional stress growth coefficient for the Lin/Ring-185k-70/30 blend (red stars) and its two pure constituents, linear (black squares) and ring (blue circles), at different extensional rates (indicated on the plot) and $T_{\rm ref} = 130$ °C. Inset: magnification of the overshoot region of the stress growth coefficient at 0.03 s⁻¹, which is unique for the blend (see text). The LVE envelopes are plotted by solid lines.

coefficient (η_E^+) versus time, where η_E^+ is defined as the measured stress divided by the stretch rate. The uniaxial extensional rheology of the pure constituents Lin-185k and Ring-185k has been measured previously,¹ and the data are also plotted in Figure 2 for comparison. The solid lines in the figure are the LVE envelopes calculated from the data in Figure S1 in the SI. As seen in Figure 2, while steady extensional flow is not achieved for the blend during the measurements (see also Figure S2 in the SI), an unexpected stress overshoot is observed at each stretch rate (with the exception of the lowest rate), in contrast to the two pure constituents which exhibit monotonic stress growth until steady flow. In addition, at each rate, the maximum η_E^+ value reached by the blend exceeds the η_E^+ of either constituent. These observations point to a transient coupling of linear and ring molecules.

Regarding the lowest rate (0.0003 s⁻¹) in Figure 2, a stress overshoot is not observed, and η_E^+ keeps increasing until the end of the experiment. Unlike fast extension where chain orientation/stretch-induced friction reduction³⁸ may facilitate unthreading, stress overshoot for slow stretching (Wi \ll 1) might occur at much larger strains. While there could be a critical onset Wi (which is associated with a threading relaxation time) for the overshoot to appear, experimental difficulties (e.g., too low force signals) limit the measurements at large strains for low stretch rates; hence, it is hard to determine if an overshoot exists. Therefore, such a critical Wi and the related threading relaxation time need further investigation (which is not performed in this work).

Figure 3a plots analogous startup η_E^+ data from MD simulations, including more results at larger Weissenberg



Figure 3. (a) η_E^+ versus reduced time for bead-spring simulations of pure Lin (black), Lin/Ring 70/30 blend (red), and pure Ring (blue) melts. Predicted LVE curves for pure melts are plotted with dotted and dash-dot lines. Wi for blend and pure Lin melts are the same as given in (a). Pure Ring data are from ref 28 and have different Wi that are given in (b). The transient stretch of entanglement segments relative to equilibrium are plotted for ring (b) and linear (c) polymers in the blend (solid lines) and pure melts (dashed lines).

numbers where experiments are not possible. A melt of M = 1288 polymers with N = 400 beads per chain ($Z \approx 14$) is elongated in uniaxial extension as in refs 28, 39, and 40. Prior results for melts of pure rings (blue) and new results for pure linear chains (black) are also shown to demonstrate correspondence with experiments for all three architectures. MD results are given in Lennard-Jones units, and MD– Weissenberg numbers (Wi) are normalized by the Rouse time of the N = 400 linear melt. More simulation details are provided in the SI. Both notable features observed in the experimental blend data, i.e., a stress overshoot and a higher maximum η_E^+ for the blend, are confirmed in the MD simulations.

Simulations can correlate these rheological features with changes in polymer microstructure. Figure 3b plots the stretch ratio λ_{Ring} of entanglement segments of length $n = N_{\text{e}}$ for rings in the blend and in the pure ring melt from ref 28 relative to equilibrium. Here, an overshoot is observed in the stretch of rings in the blend, which is absent for the pure rings. Similarly, Figure 3c plots the stretch λ_{Lin} of entanglement segments of linear chains in the blend and in the pure linear melts at matched Wi values. The linear chains in the blend also exhibit an overshoot in stretch (albeit weak compared to the rings in the blend) that is absent in pure linear chains. Both overshoots in stretch coincide with the maximum in η_{E}^+ of the blend. This suggests that the overshoot in viscosity is driven by the transient overstretching of both ring and linear macro-

molecules due to additional constraints of threaded rings (Figure 1b). Threaded rings are embedded in the linear entanglement network and are forced to orient and stretch affinely with it as it deforms. This produces excess tension in both linear and ring macromolecules until the threadings are released.

The threading–unthreading transition produces a distinct and measurable change in blend topology which we demonstrate with primitive path analysis (PPA). PPA is performed by fixing the ends of all linear chains while removing nonbonded interactions between both ring and linear polymers. This drives linear chains to contract to their primitive paths, constrained by entanglements, while rings will collapse to points, unless they are threaded and constrained by linear chains.

Figure 4 plots the probability distribution for ring primitive paths $P(L_{pp})$ at contour length L_{pp} for the Wi = 0.4 simulation



Figure 4. Distribution of contour length of the primitive path length L_{pp} of the rings after Hencky strain $\varepsilon_{\rm H}$ = 0, 1, 3, and 5 for Wi = 0.4.

at Hencky strains (defined as $\varepsilon_{\rm H} = \dot{\epsilon}$ t) of 0, 1, 3, and 5. The equilibrium state shows a narrow distribution centered around $L_{\rm pp} \sim 100\sigma$. This large $L_{\rm pp}$ is due to linear threadings holding rings open. At strains of 1 and 3, the distribution broadens and develops a long tail of large primitive paths, corresponding to rings that are highly stretched by the deforming entanglement network. Most notable is the change that occurs between $\varepsilon_{\rm H} = 3$ and 5, after the overshoot in $\eta_{\rm E}^+$. At $\varepsilon_{\rm H} = 5$, the high $L_{\rm pp}$ tail is diminished and is replaced by a peak at small $L_{\rm pp}$ that is not supported by the equilibrium topology. This is the PPA signature of the changing topology of the unthreading transition. The number of threaded linear chains decreases by about 20% in the steady state compared to the equilibrium state for Wi = 0.4.

The forced affine elongation of embedded rings is clearly shown in Figure 5 by plotting the nematic orientational order P_2 of simulated polymers relative to the extension axis versus Hencky strain $\varepsilon_{\rm H}$. Here, $P_2 = 1.5(\langle \cos^2\theta \rangle - 0.5)$, with θ being the angle between the end-end vector and the extension axis. Rings lack ends, so we define an effective end-end vector as the maximum distance spanned by any pair of monomers that are separated by N/2 bonds. Figure 5a shows P_2 data for rings in the blend and pure melts. Notably, while pure ring orientation is rate-sensitive and grows slowly with Wi, rings



Figure 5. Nematic orientational order P_2 of Ring (a) and Lin (b) polymers versus Hencky strain from MD simulations of the 70/30 Lin/Ring blend (solid lines) and pure melts (dashed lines). Curves correspond to the same Wi as indicated in Figures 3(a) and (b).

in the blend orient strongly and follow a rate-independent curve at all Wi. This transition to strain-controlled orientation of rings in the Lin/Ring blend is reminiscent of the orientation typically seen for linear chains and shown in Figure 5b. Here, P_2 for linear chains in both the Lin/Ring blend and pure melts exhibits weak rate dependence and rapidly approaches comparably high orientation values. This is the expected behavior for linear chains which orient affinely with their entanglement network at large scales. It is noteworthy that the fraction of embedded rings, which is below their entanglement concentration, does not appear to significantly affect the orientation dynamics of the linear chains in the blend.

The excess stretching of the linear entanglement network due to the presence of rings (Figure 3c) can be observed directly with small-angle neutron scattering (SANS) experiments. To provide contrast for SANS, a small amount of the linear chains in both Lin/Ring-185k-70/30 and Lin-185k were substituted by deuterated chains of a similar molar mass. To distinguish from the samples used in the rheological measurements, here the two samples containing deuterated chains are named Lin/Ring-d and Lin/Lin-d, respectively. The Lin/Ringd sample is a blend with weight fractions of 30% hydrogenous ring polystyrene, 60% hydrogenous linear polystyrene, and 10% deuterated linear polystyrene. The Lin/Lin-d sample is a blend of 90% hydrogenous linear polystyrene and 10% deuterated linear polystyrene. Here, the molar mass of the linear chains (for both hydrogenous and deuterated) is slightly higher than those in Lin/Ring-185k-70/30 and Lin-185k, with also a slightly higher dispersity (see the SI for details).

Due to the limited number of samples, we focus on the 0.003 s⁻¹ system which displays the largest overshoot in stress and viscosity relative to the pure linear melt (see Figure 2). The Lin/Ring-d blend was stretched at 0.003 s⁻¹ and 130 °C to a strain $\varepsilon_{\rm H,max}$ where the maximum in $\eta_{\rm E}^+$ is located. Our MD simulations predict that $\varepsilon_{\rm H,max}$ is also where the maximum overshoot in $\lambda_{\rm Lin}$ occurs in the blend. The sample was then quenched to room temperature for subsequent ex-situ SANS experiments. During quenching, the melt solidifies in a time less than 3 s,⁴¹ which is much shorter than the relaxation time of the melt. For comparison, Lin/Lin-d was stretched and quenched under the same conditions. SANS experiments were performed at the VSANS instrument of the NIST Center for Neutron Research (MD, USA). The SANS data were corrected for detector sensitivity, and blocked beam measurements were

subtracted according to standard procedures. To account for a different amount of materials in the neutron beam for the two samples, the data sets were scaled based on the level of incoherent scattering (which is a good measure of the amount of sample in the beam; see the SI for details). Figures 6a and



Figure 6. 2D SANS-pattern of Lin/Ring-d blend (a) and Lin/Lin-d (b). (c) Result of subtracting the data of Figure 6b from that of Figure 6a. (d) Prediction from MD simulations for the difference pattern in (c).

6b show the 2D SANS patterns of Lin/Ring-d and Lin/Lin-d, respectively. Both patterns are anisotropic and extend in the vertical direction, indicating that the linear chains are elongated along the (horizontal) extension axis.

The difference between the patterns of Lin/Ring-d and Lin/ Lin-d is subtle and difficult to discern by the eye. However, the subtle change in structure that we expect is revealed in Figure 6c, where data of Figure 6b are subtracted from Figure 6a. Figure 6d shows the same subtraction for MD systems at Wi = 0.4 (see the SI for details) and agrees well with the experimental pattern in Figure 6c. Both observe an excess transverse intensity in the Lin/Ring blend relative to the pure linear melt. This indicates that the linear molecules in the Lin/ Ring blend are on average slightly more contracted in the direction perpendicular to stretching, which correlates with increased elongation along the direction of stretching, and thus also contribute to the emergence of the overshoot in $\eta_{\rm E}^+$. Additional results for both Lin/Ring-d and Lin/Lin-d blends stretched and quenched at a Hencky strain smaller than $\varepsilon_{\rm H,max}$ together with the corresponding 1D plots, are included in the SI.

In summary, linear-ring polymer blends exhibit unique nonlinear rheological behavior in extensional flows. By adding 30% of ring polystyrenes into a linear matrix of the same molar mass, the stress growth coefficient is enhanced compared to the pure melt components and develops an overshoot not observed in either constituent. Selected ex-situ SANS data indicate that linear chains stretch a little more in the presence

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of rings compared to their pure melt. MD simulations confirm this finding and demonstrate that it is due to the coupling between linear and ring polymers. Rings thread into the linear entanglement network and stretch affinely with it until undergoing a threading—unthreading transition at the stress maximum. While further investigations on linear-ring blends of different weight fractions and different molar masses are still needed in order to fully understand these new and intriguing effects, this study reveals new mechanisms for tuning the rheological properties of polymeric composites.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmacrolett.0c00607.

Materials, details of experiments and simulations, and supporting figures (PDF)

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Notes

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