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The state-of-the-art understanding of entangled linear polymers is based on the concept of physical network formation from entanglements. The physical network is characterized by a plateau modulus in linear viscoelastic (LVE) measurements. However, linking the two free ends of a linear polymer, thereafter called a ring polymer, has dramatic consequences. For example, non-concatenated rings have much lower zero-shear-rate viscosity compared to their linear entangled counterparts. A plateau modulus is not observed in LVE measurements for ring polymers [1].

Due to the difficulties in synthesis, which leads to very limited amount of samples, well-defined ring polymers have never been studied in extensional flow. In this work, we present the first results of extensional rheology of a ring polystyrene (PS) melt with the molecular weight 185k (Ring-185k). We show that the ring PS is surprisingly strain hardening in extensional flow, and reaches the same extensional steady state viscosity as its linear counterpart (Lin-185k) when the stretch rate is fast enough. We further present the extensional rheology of blends made of Ring-185k and Lin-185k, with weight fraction of 5%, 20%, and 30% of Ring-185k, respectively. We show that in the transient stress-strain responses, stress overshoot is observed for the samples containing 20% and 30% Ring-185k, while the stress overshoot is not observed for the pure Ring-185k and Lin-185k.

The present results shed light into the fascinating flow properties of polymers without free ends, while they also advance the state-of-the-art in polymer physics. At the same time, they open the route for understanding the response of folded proteins and chromosome territories under strong external fields.

[1] Pasquino et al., ACS Macro Lett. 2013, 2, 874−878