

Unraveling entanglement

Crazing Reveals an Entanglement Network in Glassy Ring Polymers

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Polymer entanglement determines rheological properties of polymer melts, important in a range of technological applications. Changing the polymer *topology* is a promising way to modify the entanglements without the need of changing the chemistry. A prototypical example, the melt of *ring* polymers, where each ring is unknotted and unlinked to others, exhibits striking viscoelastic differences in comparison to a melt of linear chains [1]. While the entanglements of linear polymers are relatively well understood, how the chains without ends entangle remains a big mystery.

Entanglements in *linear* polymers are described in terms of reptation theory, by which each chain diffuses within an effective tube imposed by the uncrossability constraints due to the presence of other chains [2]. The tube geometry determines the melt rheology and is governed by the entanglement length N_e that can be computed from experiments or simulations [3] and theoretical models on its microscopic origins are emerging [4, 5, 6].

In contrast, the entanglements of the *rings* are more involved. First, there is no obvious “tube”; the constraints, imposed by other chains, are not only excluding mutual chain overlap (as in linear case), but also have to respect the fixed trivial topology of the system i.e. rings cannot knot or link. As a result, the rings adopt self-similar crumpled conformations, as revealed by simulations [7]. Second, rings cannot “reptate” as they have no ends that would break the symmetry. Consequently their viscoelastic response exhibits a power-law [1], in contrast to the case of linears with an elastic response on intermediate time-scales. Third, ring topology supports a special kind of entanglement, by which chains form supramolecular structures and cause strong viscosity thickening observed in extensional flows [8]. Fourth, in contrast to third, both rings and linears exhibit viscosity thinning in shear flows [9]. All these effects (and some more) are impacted by the entanglements, but their description in the melt of ring polymers, as illuminating as the effective tube and entanglement length, is missing so far.

Wang and Ge explored the entanglement effects in the ring melt with an original approach using the fact that polymer melts are liquid precursors to solid polymer glasses that arise from quenching of the melt. The mechanical properties, such as response to tensile strain, of the resulting polymer glass strongly depend on the quenched entanglements. The paper

of Wang and Ge investigates the development and the structure of crazing in deformed ring polymer glass. Making parallels with known crazing properties of linear polymer glasses, they not only explore and explain the mechanical properties of the ring glass (a feat on its own), but make several important discoveries regarding the entanglements of rings.

Upon stretching deformation a solid polymer glass develops cavities interconnected with fibrils of polymer chains (crazing), leading to a plateau in a stress-strain curve. Further straining induces stress increase followed by a drop as the material fails. The stress development and failure mechanism depends on the level of entanglement. If linear chains are long enough ($N \simeq 3N_e$) to entangle substantially, the plateau stress develops and glass fails by chain pullout, and if they are even longer (about $10N_e$) the entanglements cannot be resolved and the glass fails through chain scission. As Wang and Ge show, the rings behave similarly, but the plateau stress develops fully only for much longer chains ($14N_e$) and the glass fails through scission. Two comments are in place: (i) Although it was not investigated in detail, it would be interesting to look if there exists similar threshold between chain pullout and chain scission-dominated failure in rings. (ii) As found *in equilibrium* simulations [7], the length scale above $14N_e$ is the one above which the equilibrium rings start to be strongly impacted by the topological constraints and exhibit a compact size scaling with their length $R \sim N^{1/3}$.

In crazing of linear polymer glass, the ratio of densities in the uncrazed and the crazed regions Λ , is related to the maximum extension the entangled polymers can have, which in turn is related to N_e . In analogy, Wang and Ge implied similar relation holds for the rings. Based on the compact ring scaling, they constructed a geometric argument for the maximum extension of rings. Then measuring and comparing Λ 's for linears and rings allow them to deduce the quantity N_e^R governing the length between entanglements relevant for crazing in rings (analogous to N_e), finding $N_e^R = 4.3N_e$. This finding then reconciles the chain length thresholds for stable craze formation, being $\approx 3N_e$ for linears and $\approx 3N_e^R$ for rings, meaning that a few (about three) entanglements are needed for the formation of the craze and to prevent the chain pullout. The finding of N_e^R was further tested and confirmed by the analysis of the fibril geometry and the plateau stress, both of which are related to the entanglement length scale.

This work finds a nice natural physical way to find the length scale N_e^R , governing some aspects of the ring entanglements. One may argue that its existence is not surprising, because highly stretched rings should resemble highly stretched linear chains. However, when it comes to comparison of the chain *entanglements* such a ring-linear correspondence is not a trivial result at all, because of different initial (equilibrium) ring conformation. Moreover the authors conducted a series of perturbation experiments on the crazed systems to explore the ring entanglements in more detail. First they chopped the glassy rings into linear chains of equal length N_{sub} and showed that (i) stable crazing develops only if $N_{\text{sub}} > 3N_e^R$, hence the N_e^R plays the role of the entanglement length for ring polymer crazing, and (ii) the stress-strain curves for systems with N_{sub} were almost identical to those obtained from rings of length $N = N_{\text{sub}}$, which highlights the self-similar nature of ring conformations. The latter result also implies that the mentioned supramolecular structures (only supported by ring topology) found in extensional flows are not relevant for crazing of ring polymers, as the stress would be different in the cut experiments. In another set of perturbative experiments, the authors pinned a number of monomers on each ring in space and increased the chain

tension. In essence this is a generalization of primitive path analysis (performed on linear chains with just the ends pinned [3]) which reveals the entanglement length as the Kuhn length (in monomer units) of the resulting random walk-like primitive path. The method applied to rings shows: (i) if pinned segments are shorter than N_e^R , they are essentially straight implying no entanglements, and (ii) if longer segments are pinned the scaling of pin-to-pin distance is sub-linear in contour length, but not clearly random-walk-like. These results demonstrate that the length scale N_e^R characterizes both, the topological constraints relevant in crazing and the ones relevant in pulling chains with internal tension. At the same time, the nature of these latter constraints in rings is different from linears, as the resulting “primitive path” is not a standard Gaussian random walk.

In conclusion, the work not only characterizes the mechanical properties of ring glass, but also elucidates the nature of the entanglements in crazing and beyond. The most pertinent question arising is what is the microscopic origin of $N_e^R \simeq 4N_e$ or in other words, why only about every fourth “linear entanglement” is relevant for the crazing of rings, or possibly even in their equilibrium melt? Further, why are the supramolecular structures not relevant in crazing - are they present at all and just subdominant? Can this view of entanglements in rings reveal something about the long-standing conjecture on the existence of topological glass [10]? Irrespective of whether we find answers to these questions, the multi-layered work of Wang and Ge shows that it is worth investing the effort into elucidating the nature of entanglement of polymers with ring topology. Such investigations can not only be of practical consequences (as in the case of ubiquitously used entangled linear polymer glasses), but are also intriguing from the fundamental perspective, i.e. how the topology of the constituents impacts physical properties.

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