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Unexpected power-law stress relaxation of entangled ring polymers

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Abstract

After many years of intense research, most aspects of the motion of entangled polymers have been understood. Long linear and branched polymers have a characteristic entanglement plateau and their stress relaxes by chain reptation or branch retraction, respectively. In both mechanisms, the presence of chain ends is essential. But how do entangled polymers without ends relax their stress? Using properly purified high-molar-mass ring polymers, we demonstrate that these materials exhibit self-similar dynamics, yielding a power-law stress relaxation. However, trace amounts of linear chains at a concentration almost two decades below their overlap cause an enhanced mechanical response. An entanglement plateau is recovered at higher concentrations of linear chains. These results constitute an important step towards solving an outstanding problem of polymer science and are useful for manipulating properties of materials ranging from DNA to polycarbonate. They also provide possible directions for tuning the rheology of entangled polymers.

One of the great challenges in polymer science has been the understanding and control of the macromolecular motion that reflects their viscoelasticity. The viscoelastic stress relaxation of short unentangled linear polymer melts exhibits self-similar power-law-like dynamics described by the Rouse model^{1–3}. When the chain size increases, linear polymers entangle

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and are forced to move ('reptate') along their contours⁴ (Fig. 1a). As a consequence, their stress relaxation function exhibits a plateau similar to elastic materials at intermediate times and exponential decay at long times^{2,3,5}. In contrast, stars, the simplest branched polymers, have a logarithmic plateau and relax stress via arm retraction^{2,3,6,7} (Fig. 1b).

Macromolecules with complex branched architectures, such as combs or pom-pom polymers, relax via the so-called hierarchy of modes^{3,8}: different branching generations relax at different timescales in a sequential fashion starting from the outermost dangling ends and moving inwards, often exhibiting a combination of reptation and retraction motions.

One of the remaining challenges is understanding conformations and dynamics of large (entangled) non-concatenated ring polymers, which is the focus of the current work^{9,10}. Several ideas were put forward: one suggestion¹¹ was that rings form double-folded linear conformations (a whole ring being double folded, Fig. 1c), whereas another idea^{12,13} was that the topological constraints of entangled rings force them to adopt 'lattice-animal'-like conformations comprising double-folded loops (Fig. 1d,e); these loops relax stress by sliding along the contour of other loops¹⁴. There is, however, an issue not dealt with in the model of double-folded conformations of entangled rings (which is exact for a non-concatenated ring in an array of fixed obstacles): double folds of neighbouring rings in melts can penetrate each other, open-up the folded structure and temporarily block simple sliding motions of loops (Fig. 1f).

From the above, it is evident that the outstanding mystery remains unresolved: how do entangled polymers without beginning or end relax their stress? To resolve this mystery⁹, the first and foremost difficulty, the preparation of pure ring polymers, has to be overcome. Ring formation by end-linking linear chains was carried out in very dilute solutions¹⁵. Cyclic polystyrenes¹⁶ and polybutadienes¹⁷ were synthesized in good solvents and polystyrene rings were also made near the theta-condition¹⁸. At the theta temperature, polymers are not as extended as in good solvents and therefore, the ring closure reaction is more efficient. Nevertheless, none of the methods leads to pure ring samples and further purification becomes necessary. The standard separation methods (fractional precipitation or preparative size-exclusion chromatography, SEC) turned out to be not very successful for separating cyclic polymers from linear contaminants of similar molecular size^{17,18}. Thus, obtaining pure rings remains a challenge¹⁹, and as we will show below, even trace amounts of linear contaminants remaining after the standard purification dominate the mechanical properties of the samples at low frequencies.

Previous experimental investigations showed that the zero-shear viscosity of ring melts is smaller than that of linear polymers of the same molar mass^{20–23}. In the case of unentangled rings, the iso-free volume zero-shear viscosity was reported to be half that of the linear polymer²⁴. High-molar-mass rings exhibited a plateau modulus with a value between 1/5 and 1/2 that of the corresponding linear polymer²⁵. Moreover, adding linear polymers of the same molar mass affected rheology^{25,26} and diffusion dynamics^{10,27}. However, this past evidence, and in particular the value of a possible plateau modulus and the values of the terminal melt properties of rings (zero-shear viscosity and zero-shear recoverable compliance) as compared with the linear polymers are inconsistent owing to the suspected

contamination by linear chains. As a result, the rheology of entangled rings remains a controversial field.

Recently, the developments of liquid chromatography at the critical condition (LCCC) enabled an efficient separation of rings from linear chains²⁸. This method is a mixed mode of separation mechanisms compensating entropic size exclusion and enthalpic interaction of polymers with the porous packing materials. At the critical condition, all linear chains are eluted at approximately the same time, whereas ring polymers are eluted at longer times depending on their molar mass²⁹.

Following this procedure, we obtained two ‘as pure as currently possible’ ring polystyrene samples (as demonstrated in the inset of Fig. 2) with molar masses $198,000 \text{ g mol}^{-1}$ (code R198) and $161,000 \text{ g mol}^{-1}$ (code R161)²⁹. For comparison, two respective linear polymers (with nominal molar masses of $200,000$ and $160,000 \text{ g mol}^{-1}$) were also studied. All polymers had polydispersity index below 1.1. As the rings were susceptible to degradation at high temperatures (they could ‘open-up’), the condition of some samples was reassessed with chromatography and neutron scattering after the rheological measurements.

Small-amplitude oscillatory shear measurements at different temperatures were used to obtain a master curve after time–temperature superposition with reference temperature $T_{\text{ref}} = 170 \text{ }^{\circ}\text{C}$ (see the Materials and Methods section for more details). A subsequent Fourier transformation yielded the stress relaxation modulus $G(t)$ over several decades in time (Fig. 2). The data for each individual sample can be divided into three regimes: the short-time regime ($t < \tau_e$, for times shorter than the relaxation time τ_e of an entanglement segment as defined for linear polymers^{2,3}); the intermediate times regime ($\tau_e < t < \tau_d$, with τ_d being the sample-specific longest relaxation time); and the terminal regime ($t > \tau_d$). In the short-time regime, all data are nearly identical, implying the same glass-transition temperature, in agreement with calorimetric measurements. The most striking difference between the $G(t)$ of ring and linear samples occurs in the intermediate regime, where unexpectedly the entangled ring polymers do not exhibit the entanglement plateau, but are instead characterized by an extended relaxation regime (Fig. 2). In the terminal zone, the $G(t)$ data follow the expected exponential decay with time. Remarkably, rings relax significantly faster than linear chains of the same molar mass, in agreement with early observations^{20,24,25}, simulation results^{30,31} and diffusivity data³².

These findings are consistent with the model¹⁴ of lattice-animal self-similar conformations of double-folded loops (Fig. 1d,e). However, in a melt of rings, the obstacles are not fixed but formed by double-folded loops of surrounding rings, and therefore appear and disappear as these rings change their conformations. In such a double-folded self-similar tree-like ring structure, diffusion of smaller loops along larger loops proceeds in a hierarchical manner starting from the outermost ‘leaves’, proceeding to larger ‘branches’, finally arriving at the ‘trunk’ (or ‘backbone’) of this lattice animal. The characteristic time $\ell(g)$ for rearrangement of a loop consisting of g monomers is^{3,14} $\ell(g) \approx \tau_e (g/N_e)^{5/2}$, where N_e is the average number of monomers between entanglements. As all loops with the same number of monomers g of all rings in the melt rearrange simultaneously, the memory of the original conformation of these loops is lost at this timescale $\ell(g)$, and therefore the remaining stress

in the melt is kT per section with g monomers. This corresponds to a stress relaxation modulus $G(t) \approx kT[\nu g(t)]$, where ν is the volume of a monomer (this expression implicitly takes into account many-chain effects). By substituting the time dependence of relaxing loop length $g(t) \approx N_e (t/\tau_e)^{2/5}$ into this expression for the stress relaxation function, we obtain $G(t) = G_N (t/\tau_e)^{-2/5}$, where $G_N \approx kT(\nu N_e)$ is the plateau modulus (but the function $G(t)$ does not exhibit a plateau). This self-similar process continues until the longest loop, the whole ring, relaxes at time¹⁴ $\tau_{\text{ring}} \approx \tau_e (N/N_e)^{5/2}$ (N being the ring degree of polymerization), and this ring relaxation time is much shorter than the reptation time of entangled linear polymers^{2,3} $\tau_{\text{linear}} \approx \tau_e (N/N_e)^3$. At longer times $t > \tau_{\text{ring}}$, $G(t)$ decreases exponentially with time and thus the overall stress relaxation for a melt of rings is given by³:

$$G(t) = G_N \left(\frac{t}{\tau_e} \right)^{-2/5} \exp \left(-\frac{t}{\tau_{\text{ring}}} \right) \quad \text{for } t > \tau_e. \quad (1)$$

Note that this scaling argument incorporates constraint release effects via the assumption of complete loop rearrangement and relaxation at the timescale $t(g)$ of a loop. In fact, the same result can be obtained starting from a calculation of the stress relaxation in a single ring in an array of fixed obstacles. Stress is assumed to be supported by the gates of the entanglement lattice (kT per entanglement gate) until all original loops are pulled out of them (see Fig. 1d where the stress in the gate denoted by red bullets would relax after the orange loop is pulled out of this gate). The number density of gates with degree of polymerization m of loops to be pulled out of them is $\sim m^{-3/2}$ (for $1 \ll m \ll N$) (ref. 3). The lifetime of these loops before they are pulled out is $\tau(m) \sim \tau_e (m/N_e)^{5/2}$. Therefore, the stress relaxation function for a ring in the array of fixed obstacles is $G(t) \sim G_N \int m^{-3/2} \exp(-t/\tau(m)) dm \sim G_N (t/\tau_e)^{-1/5}$. Explicit consideration of many-chain effects through tube dilation (squaring the $G(t)/G_N$ expression^{33–35}) yields the result of equation (1). This prediction is distinctly different from stress relaxation of linear or branched polymers that contains an entanglement plateau^{2,3}. The experimentally observed power-law relaxation (Fig. 2) over more than three decades of time is in excellent agreement with equation (1) of the model (without any adjustable parameters) and confirms the self-similar dynamics of entangled rings and the absence of an entanglement plateau. The molecular parameters for the theoretical prediction of the two samples (solid and dotted lines in Fig. 2) were taken from linear polystyrene data³⁶: relaxation time $\tau_e = 4 \times 10^{-4}$ s of an entangled strand, molar mass between entanglements $M_e = 17,500$ g mol⁻¹ and plateau modulus $G_N = 0.18$ MPa. Note that the experimental data in the terminal region do not agree with model predictions, possibly owing to the effects of remaining tiny traces of contaminants (on which this region depends sensitively). Another possibility could be ring penetration by other rings (Fig. 1f)³⁷.

To quantify the effect of the small amount of entangled linear chains in a melt of rings, we purposely contaminated the rings with linear chains of the same molar mass. As can be observed from the data in Fig. 3a, even a tiny fraction of added linear polystyrene strongly affects the linear viscoelastic response by slowing down the ring dynamics. This is further demonstrated in the viscosity plots of the ring/linear polymer mixtures (Fig. 3a, inset), where addition of linear chains raises the purified ring viscosity. Moreover, this plot also shows the tendency of the viscosity towards the zero-linear-fraction limit. We attribute the

behaviour of the mixtures to the entropically driven penetration of rings by the linear chains (local double folds open-up) that is schematically represented in Fig. 4a. The entanglements between rings and linear chains are longer lived than ordinary ring entanglements (double folds) and this explains the enhanced mechanical response of mixtures of rings with linear chains.

The surprisingly low concentration $c_p = 0.0007 \text{ g cm}^{-3}$ at which the linear contaminants significantly modify the rheological response of the melt of rings in sample R198 is approximately 50 times below the overlap concentration³ $c^* = 0.04 \text{ g cm}^{-3}$ of these linear chains. Significant effect of linear chains on the rheology of the mixture at concentration $c^*/50$ implies that the isolated and slower linear chains in a ‘sea’ of much quicker rings have to couple to each other to substantially increase the viscosity of the mixture. We propose that linear chains at a concentration as low as $c^*/50$ are ‘bridged’ by rings as shown in Fig. 4b. Indeed, if these chains were not bridged by rings forming a long-lived percolating network throughout the system, most of the stress in the mixture would relax via the surrounding faster free rings. A detailed estimate of rings bridging between linear chains and formation of a transient network is presented in the Materials and Methods section. We show that the volume in which the linear chains in sample R198 entrap rings is larger than its gyration volume R_g^3 (used for estimating c^*) by a factor of $(l^{1/2}R_e/R_g)^3 \approx 5$ (see Fig. 4 for definition of parameters). This volume is increased by another factor of $((l^{1/2}R_e + R_p)/l^{1/2}R_e)^3 \approx 6$ if the shell around each linear chain spanned by the penetrated rings is included. The product of these two factors accounts for most of the observed 50-fold decrease of the onset concentration at which linear chains significantly modify ring rheology. Thus, trace amounts of linear chains in a melt of rings are bridged by rings and percolate across the sample (Fig. 4c), which substantially alters the rheology of the purified ring melt.

An important conclusion from these contamination experiments is that the uncontaminated ‘as pure as currently possible’ ring samples contain trace amounts of linear chains that cannot be substantially larger than the smallest fraction of added contaminants (about 0.1%), because otherwise the effect of extra linear chains would not be observable. We can in fact estimate the amount of linear contaminants in the original unpurified ring samples using the data on purified ring/linear polymer mixtures. Figure 3b shows the original stress relaxation data of Roovers²⁰ on the ring R198 before purification by LCCC (red line) exhibiting an entanglement plateau that disappears on purification (blue line). Note that all previously reported data (dynamic moduli and recoverable compliance with well-characterized samples at the time of the measurements) exhibited entanglement plateaux^{20,21,23–25}. Mixing the purified R198 rings with linear chains of the same molar mass at a fraction of 0.007 (green line) brings the stress relaxation modulus back to the original unpurified values. Thus, we estimate the contamination level of the original rings by linear chains to be about 1%. LCCC reduces this level of contamination by a factor of 10. The 1% contamination level of the original ring samples is below the overlap concentration of these linear chains ($c^* = 0.04 \text{ g cm}^{-3}$) but above the threshold concentration of the transient network of linear chains bridged by rings ($c_p = 0.0007 \text{ g cm}^{-3}$). The effect of adding a small fraction of linear chains to a melt of fractionated rings was studied by McKenna *et al.*²¹. It was observed that re-fractionation of 180 kg mol^{-1} polystyrene rings raised the recoverable compliance $J_R(t)$, a reciprocal

quantity to $G(t)$, with respect to the original sample in the intermediate time range; on the other hand, addition of linear chains lowered the $J_R(t)$ in this time range²¹. This original observation is consistent with our results of lower $G(t)$ for purified rings as compared with unpurified rings (Fig. 3b) as well as with increasing $G(t)$ on addition of linear chains to purified rings (Fig. 3a). Another observation of ref. 21 is that $J_R(t)$ at long times had the opposite trend to that at intermediate times. Our dynamic data did not reach long enough times to enable a proper comparison. The focus of this work is on the intermediate times, where important differences between ring and linear polymers are evident.

Unlike their drastic effect on rheology, small amounts of linear additives have a much weaker effect on the diffusion of rings. Kawaguchi *et al.*³² reported diffusion data on polystyrene rings purified by the LCCC method. Compared with the linear chains, the ring diffusion coefficients were higher by a factor of about 2, in agreement with simulation results³¹ (M.L. & M.R., manuscript in preparation (2008)). These simulations (M.L. & M.R., manuscript in preparation (2008)) also showed that average diffusion coefficients are almost unaffected by addition of linear chains at very low concentrations. The average diffusion coefficient is controlled by the majority of rings that are unaffected by the linear chains and diffuse fast, in contrast to the stress relaxation, which is controlled by the small unrelaxed fraction of rings penetrated by linear chains percolating across the sample. Consequently, diffusion is not as sensitive as rheology for observing the difference between linear and ring polymers and detecting trace amounts of linear contaminants in ring samples.

An open question is the effect of knots on the properties of a melt of rings. This is particularly relevant in the present polystyrene ring samples, which were synthesized near the theta condition where knot formation is more likely than in good solvents^{38,39}. However, whereas the presence of knots reduces the ring size slightly^{40,41}, we do not expect a change of the power-law nature of stress relaxation. The reason is that diffusion of segments of stored length along the contour of a ring is not affected by the presence of a knot, if the knot is not tight on the scale of an entangled strand. Therefore, we expect the influence of knots on ring rheology to be much weaker than that of residual linear polymers.

As both natural and synthetic polymers can be found or obtained in circular form^{9,10}, the present results are of both scientific and practical significance. For example, the manipulation or micro-processing of ring-shaped DNA will be optimized when its stress relaxation behaviour is known. Furthermore, the extreme sensitivity of ring rheology to added linear polymers can serve as a means for rheology modification. Of the questions that remain unanswered and are currently being addressed, the foremost one is the behaviour of very high-molar-mass rings: investigating their conformations (neutron scattering) and whether there is a transition from the power law to the plateau in stress relaxation (rheology).

MATERIALS AND METHODS

RING POLYMERS

The ring polystyrenes were synthesized as described in refs 18 and 20 and purified with the LCCC procedure²⁹. Further SEC characterization was conducted. The two linear

polystyrenes were obtained from Polymer Source. For the SEC, the polymer passed through two calibrated columns and its elution time was measured. A Thermo Finnigan chromatograph with refractive index and ultraviolet adsorption detectors were used. The elution solvent was tetrahydrofuran and the calibration prototypes were narrow-distribution linear polystyrene with molar masses ranging from 1.31 to 299.4 kg mol⁻¹. All measurements were carried out at 45°C.

RHEOLOGY

Measurements were conducted with a strain rheometer (ARES-2KFRTN1, TA). Temperature varied in the range 105–180(±0.1)°C by means of a nitrogen convection oven for reducing the risk of degradation. Stainless-steel or invar (nickel–steel alloy) parallel-plate geometry was used (diameter 8 or 4 mm, gap 0.5 to 1.5 mm). Before measurements, all samples were press-moulded for 20 min at 180°C into disc-shaped specimens and then slowly quenched to room temperature under vacuum (for 24 h). The ring/linear mixtures were prepared by diluting in volatile co-solvent and then slowly evaporating under vacuum; the temperature and vacuum were sequentially increased over the course of a few days from 22°C and 1 atm, to just above the glass-transition temperature of polystyrene and complete vacuum. Small-amplitude oscillatory shear measurements were carried out at each temperature, preceded by dynamic time sweep and strain sweep experiments (to ensure thermal equilibrium and linear response), yielding the frequency-dependent storage (G') and loss (G'') moduli. With the thermal expansion of the plates being accounted for, the change of polystyrene density with temperature, $\rho(T) = 1.2503 - 6.05 \times 10^{-4} T$ (ρ in g cm⁻³, T in K) (ref. 42), led to vertical shift of data (moduli axis) through $b_T = \rho(T_{\text{ref}}) T_{\text{ref}} / \rho(T) T$. Subsequently, the data were shifted horizontally (frequency axis), and the shift factors for all samples were fitted with a single set of parameters of the Williams–Landel–Ferry function⁴³: $\log a_T = -C_1(T - T_{\text{ref}})/(C_2 + T - T_{\text{ref}})$ with $T_{\text{ref}} = 443$ K, $C_1 = 5.6$ and $C_2 = 120$ K; these values were nearly identical for several polystyrene architectures⁴⁴. The stress-relaxation-modulus master curve $G(t)$ was obtained by Fourier transformation of G' and G'' .

INTERACTION CONCENTRATION IN RING/LINEAR POLYMER MIXTURES

The overlap concentration of linear chains is $c^* = 3M_L / 4\pi N_{\text{Av}} (\sqrt{C_\infty M_L / 6})^3 = 0.04$ g cm⁻³, where $M_L = 200,000$ g mol⁻¹ is the molar mass of linear chains, $N_{\text{Av}} = 6.02 \times 10^{23}$ mol⁻¹ is the Avogadro number and $C_\infty = 0.0047$ nm² mol g⁻¹ is the Flory characteristic ratio³⁶. We observe that addition of linear polystyrene to R198 at a volume fraction ϕ_{linear} of 0.0007 is sufficient to generate a significant change in $G(t)$ (Fig. 3a) and a 90% increase in the zero-shear viscosity. Such an extreme sensitivity to ϕ_{linear} at concentration 50 times below c^* is only possible if there is a mechanism to connect isolated linear chains into a transient network structure that spans the whole system. We propose that this occurs via multiple penetrations of the same rings (Fig. 4b) by linear chains. The main contributing factors that reduce the onset concentration are (1) the change in length scale from R_g to root-mean-square end-to-end distance, R_e , which is relevant for trapping rings, and (2) the increase of the effective capture volume of linear chains by penetrated rings.

The root-mean-square end-to-end distance of linear polystyrene chains with molar mass M_L = 200,000 g mol⁻¹ is $R_e = (C_\infty M_L)^{1/2} \approx 30$ nm and their $R_g = R_e / \sqrt{6} \approx 12$ nm. The average distance between two opposite monomers in a ring with molar mass M_r in its ideal state³ is $R_r^0 = (C_\infty M_r / 2)^{1/2} \approx 22$ nm. In a melt, entangled rings are compressed^{45,46} by a factor $a \approx (M_r / M_e)^{-1/10} \approx 0.8$ and the average distance between two opposite monomers is $R_r = a R_r^0 \approx 17$ nm (Fig. 4b,c).

Only the section of the linear chains that remains unrelaxed at the relaxation time of the ring is able to slow down ring relaxation by penetrating these rings. The fraction of the tube that is abandoned by the chain reptation grows with time t as $(M_e / M_L)^{3/2} \cdot (t / \tau_e)^{1/2}$ and is larger than the tube fraction abandoned by tube length fluctuations at times longer than the Rouse time^{2,3}. Thus, at relaxation time $t = \tau_{ring} = \tau_e (M_r / M_e)^{5/2}$ of rings with the same molar mass $M_r = M_L$, a fraction $f = 1 - (M_e / M_L)^{1/4} \approx 0.46$ of the tube of the linear chain is still unrelaxed. This reduces the spatial extension of the unrelaxed tube to $l^{1/2} R_e \approx 20$ nm for R198. Thus, two neighbouring linear chains that are $l^{1/2} R_e + R_r \approx 37$ nm apart can be dynamically bridged by a ring they both penetrate (Fig. 4b). This reduces the concentration at which this dynamic coupling occurs by a factor of $((l^{1/2} R_e + R_r) / R_g)^3 \approx 30$ for R198 in comparison with the c^* of linear chains. This factor consists of two contributions: the change in volume from R_g^3 to $(l^{1/2} R_e)^3$, which is relevant for trapping rings, $(l^{1/2} R_e / R_g)^3 \approx 5$, and the increase of the effective capture volume of linear chains by penetrated rings, $((l^{1/2} R_e + R_r) / l^{1/2} R_e)^3 \approx 6$. Geometrical factors such as coefficients in the percolation model⁴⁷, definition of c^* and shape distribution of linear tubes account in total for an extra factor of less than two.

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Figure 1. Illustration of entangled polymer conformations and relaxation models

a, Reptation of linear chain. Topological constraints due to neighbours (black dots) force the chain to carry out snake-like motion along its contour (brighter colours show earlier conformations). **b**, Relaxation of star by arm retraction. Diffusion is possible only if arms are completely retracted and pushed around the constraints. **c**, A double-folded ring¹¹ reptating through uncrossable obstacles. **d**, A double-folded ring optimizing its conformational entropy in an array of fixed obstacles^{12–14}. The red bullets illustrate a gate (constraints formed by obstacles). The orange loop has to be pulled out of it (see text). **e**, The shape of this ring can be mapped onto a ‘lattice animal’ structure, exhibiting self-similarity in hierarchy of relaxation: the ring relaxes from outermost towards inner sections. **f**, Mutual penetration of rings increases conformational entropy by opening-up double folds, while simultaneously blocking the gliding of the previously double-folded strands.

Figure 2. Stress relaxation moduli $G(t)$ of entangled polymers

Comparison of the data ($T_{\text{ref}} = 170\text{ }^{\circ}\text{C}$) for two polystyrene rings (R198: open triangles and R161: open squares) with the model predictions (solid and dotted lines) of equation (1) and with their linear counterparts (respectively filled triangles and filled squares). The short straight dashed lines indicate the relaxation times τ_e and τ_d and the plateau modulus G_N of the linear chains (see text). Inset: Characterization of the purified ring polymers. SEC chromatograms of the rings before (mother samples; symbols) and after LCCC fractionation (lines), showing the fraction of the eluted polymer against its elution volume.

Figure 3. Effects of added linear chains on entangled purified ring polymer rheology

Data from mixtures of polystyrene rings with linear polymers of the same molar mass at different added fractions ϕ_{linear} . **a**, Stress relaxation modulus $G(t)$ of the R198 mixtures at $T_{\text{ref}} = 170$ °C. Inset: Extrapolated zero-shear-rate viscosity of mixtures of purified ring and linear chains of the same molar mass, as a function of linear fraction. Data for mixtures with rings R198 (triangles) and R160 (squares) are shown. **b**, Comparison of the $G(t)$ for the same ring R198 before (red line) and after (blue line) LCCC purification. The $G(t)$ of the mixture with $\phi_{\text{linear}} = 0.007$ (green line) and the respective linear melt (black line) are shown for comparison.

Figure 4. Illustrations of conformations of mixtures involving ring and linear polymers
a, Penetration of rings by linear chains in their mixture locally opens the double-folded ring structure. **b**, Multiple ring penetrations prevent rings from relaxing and bridge chains into an effective transient network. Dotted lines show relaxed chain sections up to the ring relaxation time. The root-mean-square end-to-end distance of the unrelaxed fraction f of a linear chain (bold blue line) is smaller than its root-mean-square end-to-end distance R_e by a factor of $f^{1/2}$. The distance between two opposite monomers in a compressed ring in a melt is R_r . **c**, Left: Geometric representation of characteristic sizes of rings and linear chains in **b**. Linear polymer radius of gyration is R_g . Right: Transient network of linear chains bridged by rings. Whereas linear chains (blue circles) are below their percolation threshold, when they are bridged by (yellow) rings the resulting structure percolates through the system, yielding enhanced mechanical response.