Supporting Information

Linear and nonlinear shear rheology of a marginally entangled ring polymer

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Linear viscoelastic spectrum of PS-198k ring/PS-450k linear blend

A highly entangled blend with 99.9% PS-198k ring (molar mass of ring, $M_{w,ring}$ = 198 kg/mol) and 0.1% PS-450k linear (molar mass of linear, $M_{w,linear}$ = 450 kg/mol) was under step strain test at 170 ^{o}C for comparison with responses of pure linear and ring samples. The linear viscoelastic spectrum of this mixture at reference temperature T_{ref} = 170 ^{o}C is shown in Figure S1.

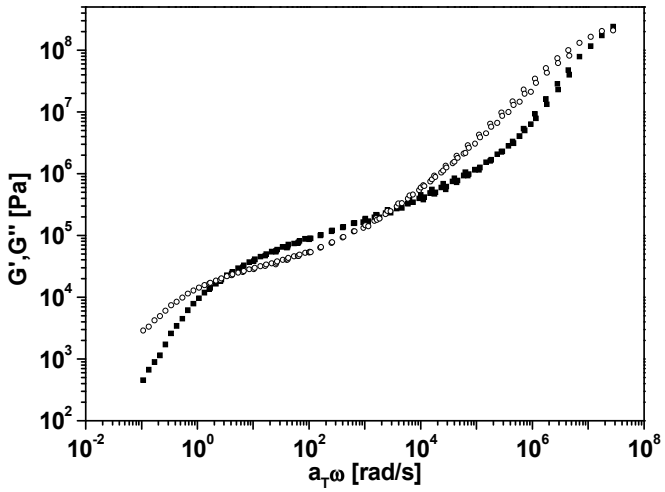
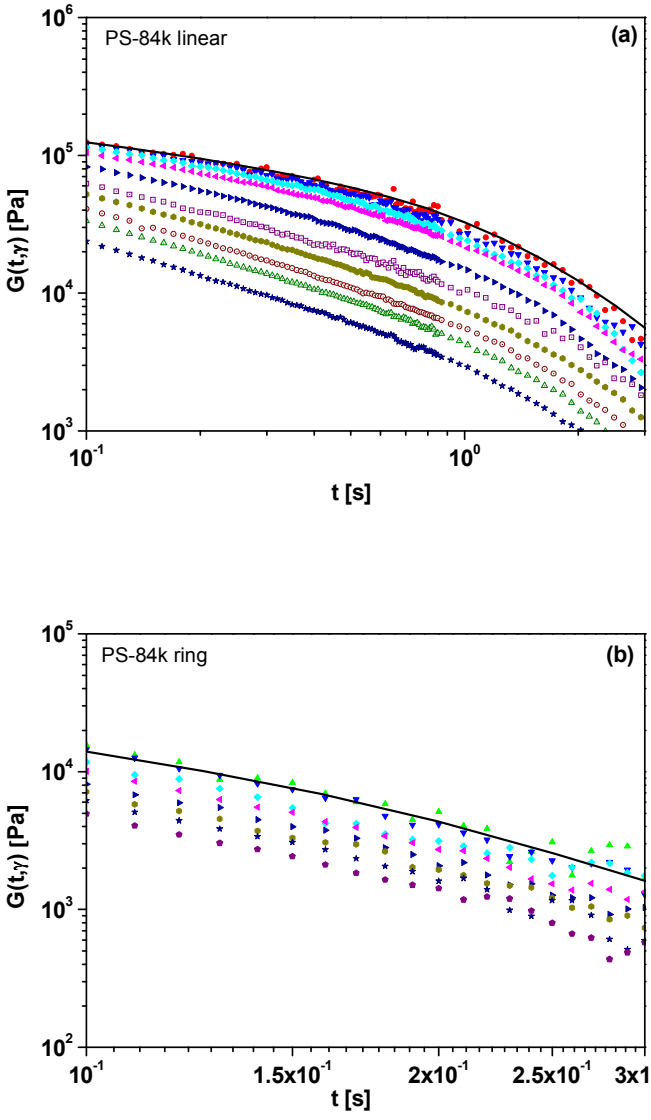


Figure S1. Master curves for the storage G' and loss G'' moduli as function of the shifted frequency for a ring/linear mixture with $M_{w,ring}$ being 198 kg/mol, $M_{w,linear}$ being 450 kg/mol, and linear fraction ϕ_L being 0.001. The reference temperature T_{ref} = 170 ^oC.

The relaxation moduli after nonlinear step shear

Figure S2 depicts the relaxation moduli as function of time after step strain for the PS-84k linear, the PS-84k ring, and a ring/linear mixture ($M_{w,\ ring}$ = 198 kg/mol, $M_{w,\ linear}$ = 450 kg/mol, and ϕ_L = 0.001), respectively. The solid lines are the G(t,γ) envelopes when γ→0, converted from their master curves. The LVE envelope can overlap G(t,γ) at small γ very well, implying the linearity of these small-γ data. The relaxation moduli drops progressively with the increasing γ. A narrow relaxation process has been observed for the PS-84k linear and the PS-84k ring due to their relatively low-M_w. In contrast, the relaxation process of the ring/linear mixture span a wide time scale because the ring is well entangled and penetrated by even larger linear chains. Two factors affect the quality of the data. One is the start-up of the motor, which essentially restricts the reliable data to t >60 ms. Another is the torque

resolution. At longer times, the low torque combined with low modulus values result in a poor signal-to-noise ratio. The moduli at long time scale were vertically shifted to overlap with the LVE envelopes. The good collapse of curves in Figures S3 indicates that the time-strain separability is applicable for both linear and ring polymers. The damping functions $h(\gamma)$ were extracted and plotted in Figure 8 of main text.



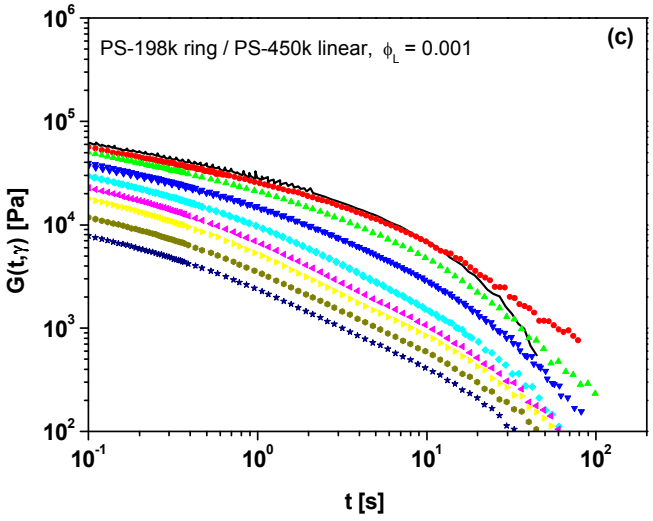
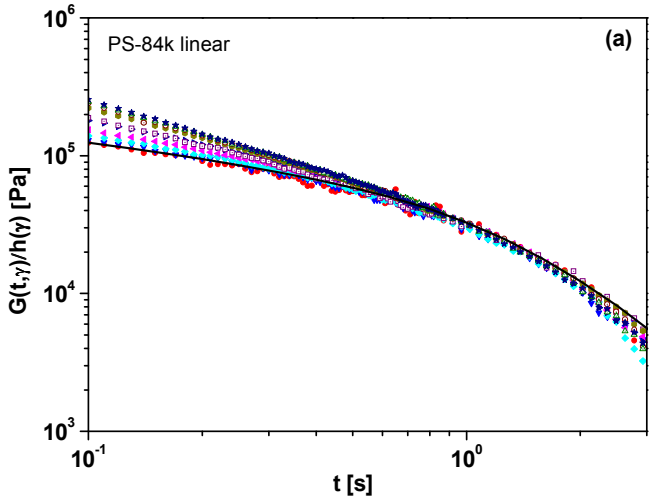


Figure S2. The stress relaxation moduli for (a) the PS-84k linear at 150 °C with applied strains from top to bottom γ = 0.316, 0.562, 1 ,1.78, 3.16, 4, 5.62, 7, 8, and 10, (b) the PS-84k ring at 150 °C with applied strains from top to bottom γ = 1 ,1.78, 3.16, 4, 5.62, 7, 8, and 10, and (c) a ring/linear mixture ($M_{w,\,ring}$ = 198 kg/mol, $M_{w,\,linear}$ = 450 kg/mol, ϕ_L = 0.001) at 170 °C with applied strains from top to bottom γ = 1, 2, 3 ,5, 7, 8, 10, and 12. The solid lines are the G(t,γ) curves when γ→0.



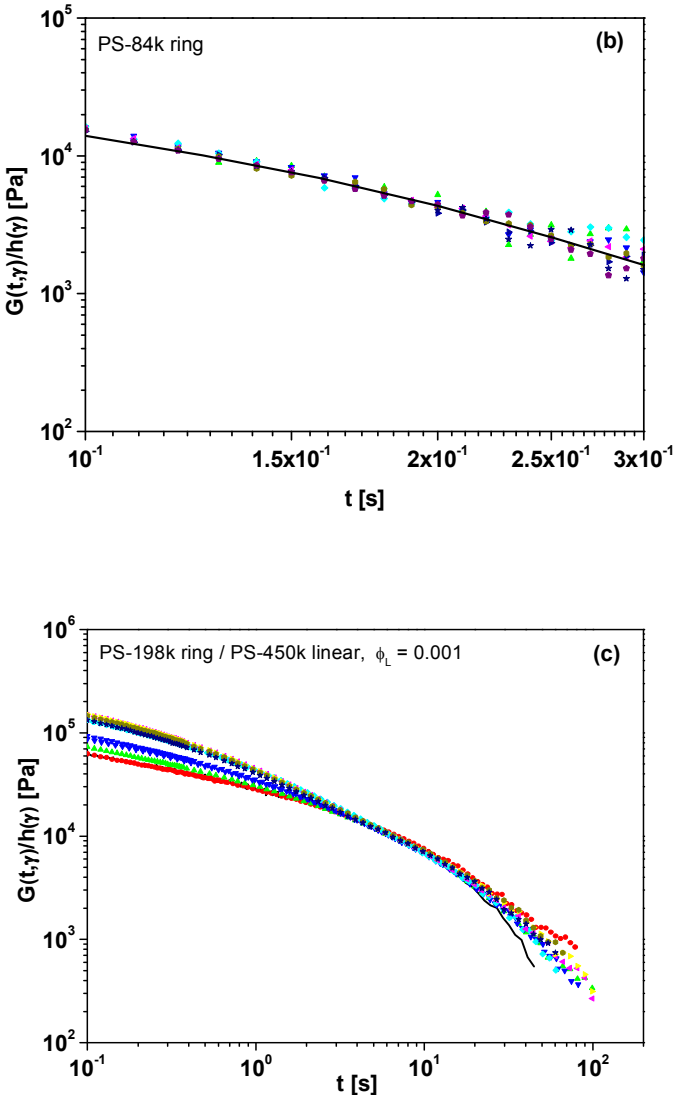


Figure S3. The superposed relaxation moduli after vertical shift (time-strain separability applied) from different strains for (a) PS-84k linear at 150 ^{o}C, (b) PS-84k ring at 150 ^{o}C, and (c) a ring/linear mixture ($M_{w,\ ring}$ = 198 kg/mol, $M_{w,\ linear}$ = 450 kg/mol, and ϕ_L= 0.001) at 170 ^{o}C. The solid lines are the unshifted G(t,γ) curves when γ→0.