

Viscosity of ring polymer melts

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1. Power law stress relaxation

The melts of rings exhibit a power law stress relaxation.

Table S1 below presents the absolute values of the fitted power law slopes of $G(t)$ for polyisoprene and polystyrene rings data of Figure 2 of the main manuscript. Scaling exponents (slopes) obtained from the molecular dynamic simulations data¹ are shown as well. There seems to be a general tendency for the stress relaxation exponent to decrease as the degree of polymerization N increases. The lattice animal has a fractal exponent $D=4$ and suggests a constant power-law slope of -0.4 .^{2,3} However, recent theoretical developments and in particular the loopy globule model⁴ indicate that $D=3$ and a limiting slope of -0.375 for large N .

Table S1. Power-law stress relaxation indices for rings

Samples	Stress relaxation scaling exponents
PI ₃₈	-0.47 (±0.0008)
PI ₈₁	-0.48 (±0.002)
PS ₁₆₀	-0.48 (±0.004)
PS ₁₉₈	-0.42 (±0.003)

N=100 See ref. (1)	-0.52 (±0.01)
N=400 See ref. (1)	-0.47 (±0.04)

2. Analysis of lattice animal and loopy globule models

The lattice animal^{3,5} (loopy globule)⁴ models of self-similar stress relaxation of a ring in an array of fixed obstacles (in melt of other rings), predict the longest relaxation time $\tau_{ring} \approx \tau_e Z^{5/2}$ for lattice animal ($\tau_{ring} \approx \tau_e Z^{8/3}$ for loopy globule) and terminal modulus of kT per chain similar to Rouse model⁶⁻⁸ $G_{ring} \approx G_N/Z$, which yield $\eta_{0,ring} \sim N^{3/2}/N_e^{1/2}$ for lattice animal model ($\eta_{0,ring} \sim N^{5/3}/N_e^{2/3}$ for loopy globule model). If we assume for simplicity pure reptation model^{9,10}, then melt viscosity of linear polymers is $\eta_{0,linear} \sim N^3/N_e^2$. Hence, we obtain for the viscosity ratio $\eta_{0,linear}/\eta_{0,ring} \sim (N/N_e)^{3/2} = Z^{3/2}$ for lattice animal model ($\eta_{0,linear}/\eta_{0,ring} \sim (N/N_e)^{4/3} = Z^{4/3}$ for loopy globule model). If we consider contour length fluctuations corrections^{9,10}, the result becomes $\eta_{0,linear}/\eta_{0,ring} \sim Z^{1.9}$ for lattice animal model ($\eta_{0,linear}/\eta_{0,ring} \sim Z^{1.7}$ for loopy globule model).

3. Determination of zero shear viscosities

In order to obtain the ratio $\eta_{0,linear}/\eta_{0,ring}$, the zero-shear viscosities of the ring and linear polymers for PI have been calculated with three different methods: by fitting the data with the Cross model, taking a value for the viscosity at the lowest reliable frequency and by fitting the data with the Carreau model¹¹. This procedure has been applied at three different temperatures. An example for the calculation of the ratio $\eta_{0,linear}/\eta_{0,ring}$ is shown in Table S2, for the case of $M_w=81\text{kg/mol}$.

Table S2. Example of calculation of the mean viscosities (in Pas) for linear and ring polyisoprenes with $M_w=81\text{kg/mol}$

T[°C]	Linear PI				Ring PI				$\eta_{0,linear} / \eta_{0,ring}$
	Cross	Carreau	Fixed freq	Mean	Cross	Carreau	Fixed Freq	Mean	
30	273 (±2.5)	263 (±2)	263.5	266 (±5)	16.1 (±0.5)	15.7 (±0.58)	13.2	15 (±1)	17.8 (±1.2)
0	2.2×10^4 (±202)	2.2×10^4 (±191)	2.1×10^4	2.1×10^4 (±388)	1286 (±38)	1200 (±42.7)	1312.6	1266 (±82.5)	17 (±1.4)
-30	4.3×10^7 (± 3.8×10^5)	4.1×10^7 (± 3.6×10^5)	41×10^7	4.2×10^7 (± 3.7×10^6)	2.4×10^6 (± 7.2×10^4)	2.4×10^6 (± 9.2×10^4)	2.2×10^6 (± 9.2×10^4)	2.4×10^6 (± 9.7×10^4)	17.7 (±1.7)

Figure S1 shows the complex viscosities as function of frequency at three different reference temperatures for the linear (left) and the ring (right) polymers with $M_w=81\text{kg/mol}$. Figure S2 shows an example of fitting at a reference temperature of -30°C. The red lines are Cross model fits through the data, the green lines are Carreau model fits. The arrow indicates the fixed frequency at which the viscosity values are taken.

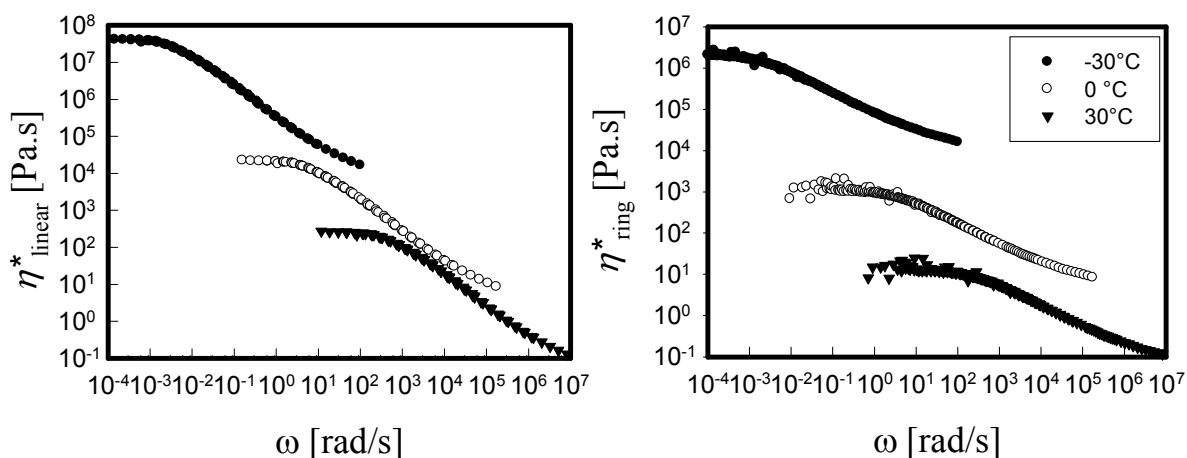


Figure S1. Complex viscosities as function of frequency for the linear polymer (left) and the ring polymer (right) with $M_w=81\text{kg/mol}$ at different reference temperatures (see legend, valid for both graphs, for details).

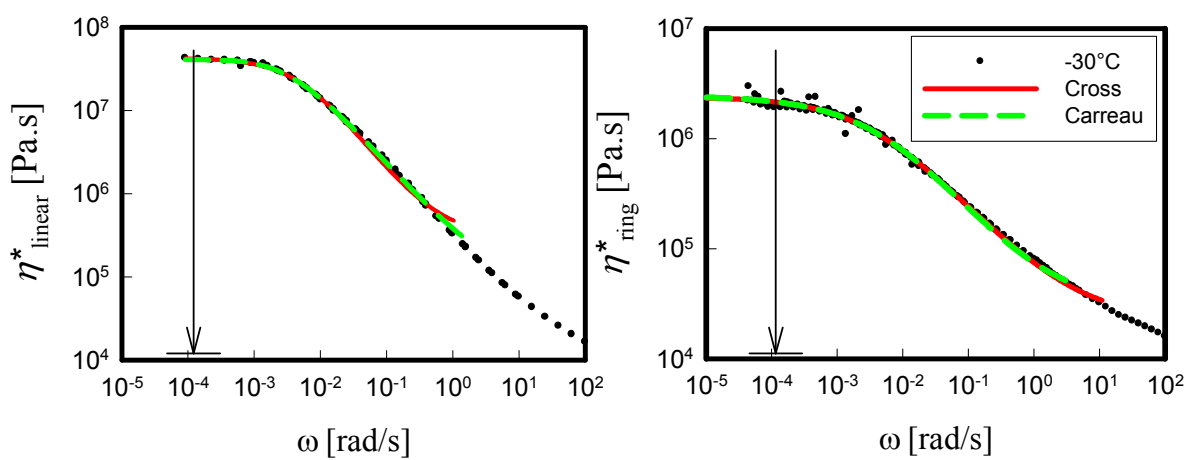


Figure S2. Example of fitting at -30°C for the linear (left) and ring (right) polymers with $M_w=81\text{kg/mol}$. The legend is valid for both graphs.

Table S3 shows details of fitting at a fixed reference temperature for PI samples with different molecular weights. Clearly, the error is larger for rings in comparison to linear polymers, due to the fact that terminal slopes were not reached, which is reflected in an uncertainty in the determination of the zero-shear viscosity.

As a further example, Figure S3 shows the comparison between the shear viscosities for linear and ring polystyrene samples at 170°C . Table S4 summarizes the fitting parameters for the data shown in Figure S3.

Table S3. Viscosities for linear and ring polyisoprene polymers with different molecular weights at 30°C

Mw [kg/mol]	Linear PI				Ring PI			
	Cross	Carreau	Fixed frequency	Mean	Cross	Carreau	Fixed frequency	Mean
24	80.1 (± 0.24)	78.9 (± 0.18)	80.5	80 (± 0.4)	74.8 (± 11.6)	61 (± 17.5)	49.2	62 (± 27)

38	3500 (±18)	3400 (±12)	3300	3400 (±29)	180 (±2)	186 (±3.3)	161	176 (±5)
81	273 (±2.5)	263 (±2.4)	263.5	266 (±5)	16.1 (±0.5)	15.7 (±0.58)	13.2	15 (±1)

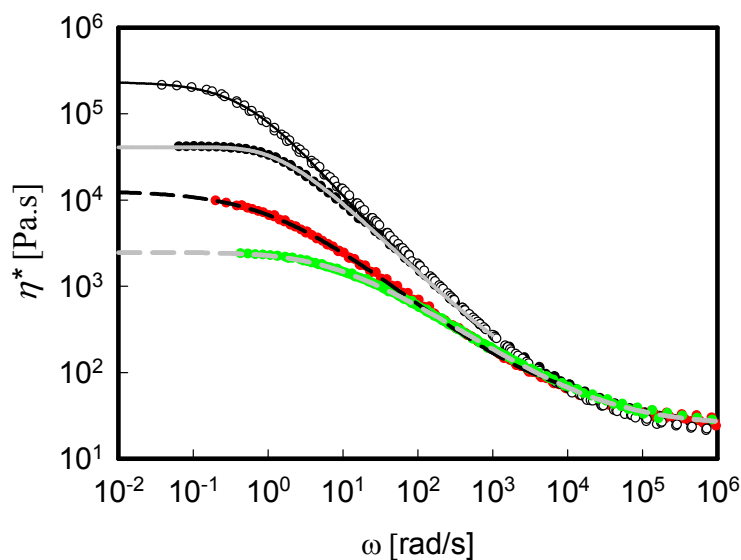


Figure S3. Complex viscosities for polystyrene samples at 170°C. Symbols are experimental data. ○: Ps linear 198k; ◻: Ps ring 198k; ◻: Ps linear 160k; ◻: Ps ring 160k. Lines are fits examples. —: Cross model fit for data on linear Ps 198k; - - -: Cross model fit for data on ring PS 198k; - · - ·: Carreau model fit for data on linear PS 160k; - · - ·: Carreau model fit for data on ring PS 160k.

Table S4. Viscosities for linear and ring polystyrene polymers with different molecular weights at 170°C

Mw [kg/mol]	Linear PS				Ring PS			
	Cross	Carreau	Fixed frequency	Mean	Cross	Carreau	Fixed frequency	Mean
160	43240 (±236)	41460 (±56)	39000	41233 (±2129)	2666 (±11.6)	2555 (±15.2)	2354	2525 (±158)
198	217200 (±1007)	234200 (±1656)	187000	212800 (±23906)	12750 (±133)	11450 (±204)	9709	11303 (±526)

4. Comparison between old data from 1980's and new data with additional details for Figure 3 (main manuscript).

The comparison between new data (fractionated by LCCC) and old data from literature (fractionated by common SEC, often multiple times) is shown in Figure S4. All LCCC-fractionated rings had purity larger or equal to 99.6%.³¹² Table S5 lists references, chemistry and fractionation method for the experimental data on ring polymers shown in Figure S4.

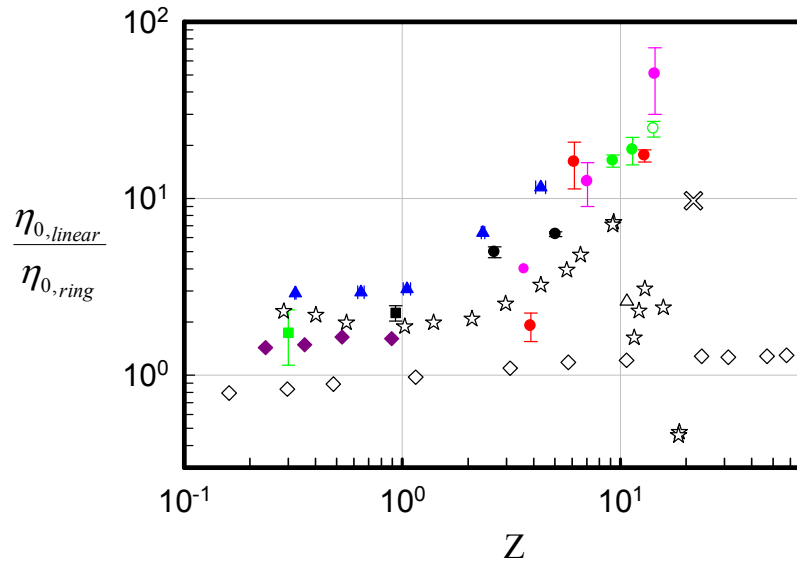


Figure S4. Ratio between the zero shear viscosities of the linear and ring polymers as function of the number of entanglements Z (see also main text). ●: PEO experimental data set; ●: PI experimental data set; ○: PS data, see Ref.(12); ●: PS experimental data set from Ref. (3); ■: PEO experimental data point from Ref. (13); ■: PS experimental data point from ring synthesized in theta solvent conditions, and characterized in Ref. (14); ◆: PEO experimental data set from Ref. (15); ▲: PE atomistic simulations data from Ref. (16); □: molecular dynamics simulations data on coarse-grained bead-spring chains from Ref. (1); ☆: PS data from Ref. (17), reporting synthesis in theta solvent conditions; ◇: PDMS data from Ref. (18); △: PS data from Ref. (19), reporting synthesis in good solvent conditions; ×: PBD data from Ref. (20), reporting synthesis in good solvent conditions.

In the entangled regime, there is a clear scatter of the data. The old literature data were taken on rings purified via SEC, often multiple times^{19,20}, and precipitation¹⁸. They have much higher viscosities, presumably due to insufficient fractionation, which left a non-negligible fraction of linear contaminants in the samples. This leads to lower ratios $\eta_{0,linear}/\eta_{0,ring}$ at high Z , in comparison to the new values based on rings purified by LCCC. Moreover the scatter in the old data is higher as the molecular weight increases, and this is again attributed to the contamination. It is tempting to consider the onset of entanglements, which is known to occur at the critical molecular weight¹⁹. However, to have a firm result, data from many rings over a wide range of molar masses are needed, something that is not yet possible. Hence, we restrict our discussion using the linear polymer entanglement molecular weight as the scaling parameter.

Table S5. Details for ring samples shown in Figure 3 of the main manuscript

	Fractionation method	Chemistry
Current work	LCCC	PI, PEO
Kapnistos <i>et al.</i> ³	LCCC	PS
Nam <i>et al.</i> ¹⁵	Precipitation	POE
Bras <i>et al.</i> ¹³	Multiple SEC	PEO
Roovers and Toporowski ¹⁷	Precipitation	PS
Roovers and Toporowski ²⁰	SEC	PBD
McKenna <i>et al.</i> ¹⁹	Multiple SEC	PS
Orrah <i>et al.</i> ¹⁸	Precipitation	PDMS
Santangelo <i>et al.</i> ¹⁴	Precipitation and LCCC	PS
Cho <i>et al.</i> ¹²	LCCC	PS

5. Conversion of MD units

Plots of stress relaxation moduli for ring polymers are given in (1) as $G(t)\sigma^3/\varepsilon$ as a function of t/τ , with $\varepsilon=k_B T$, $\rho\sigma^3=0.85$ and $\tau=\sigma(m/\varepsilon)^{1/2}$, where m is the mass of a monomer¹⁷. Hence, given the values in (17), the conversion from MD units into Pascal

(y-axis) and seconds (x-axis) is possible by multiplying the y-axis of Figure 6(b) in Ref. (1) by 3.3MPa and the relative x-axis by 3.1×10^{-8} s. A horizontal shift factor has been also used for shifting the data at isofrictional conditions ($aT=0.035$)²².

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