SUPPORTING INFORMATION

Molecular Weight Dependence of the Viscosity of Highly Entangled Polyisobutylene

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To determine the molecular weight of the fraction used for rheological measurements, a 0.1 g/L THF solution was injected into an SEC instrument consisting of a Waters 515 HPLC Pump, Waters 2487 Dual Absorbance UV Detector, Wyatt OPTILAB DSP Interferometric Refractometer, Wyatt DAWN EOS multi-angle light scattering detector, Wyatt ViscoStar viscometer, Wyatt QELS quasi-elastic light scattering instrument, Waters 717 plus autosampler, and 6 Styragel® columns (HR6, HR5, HR4, HR3, HR1 and H0.5). The columns were thermostated at 35 °C, with THF continuously distilled from CaH2 used as the mobile phase at a flow rate of 1 mL/min. Results were analyzed using ASTRA software (Wyatt Technology) taking dn/dc = 0.108. Note the PIB was close to the exclusion limit of the SEC instrument. The SEC traces are shown in the figure below. Note the absence of second peaks, which affirms there is no "tail" in the molecular weight distribution.

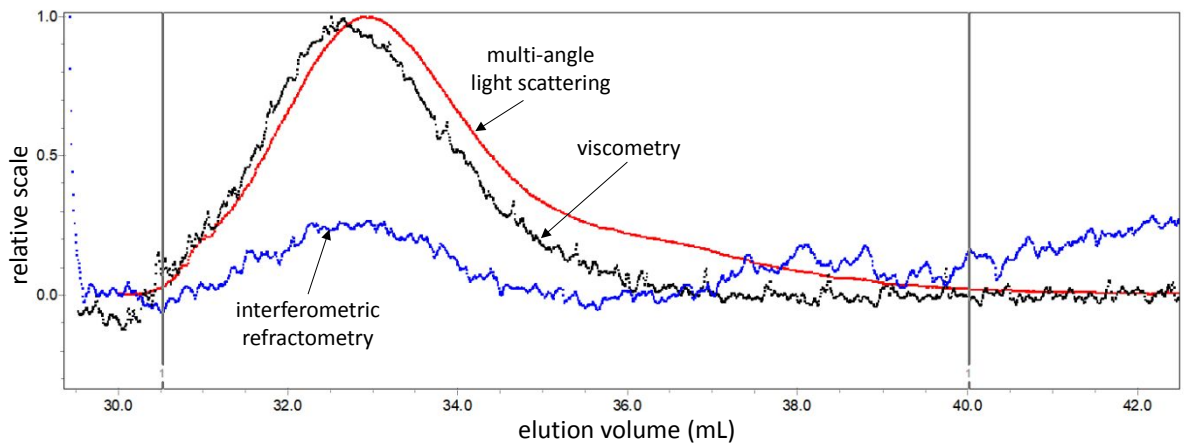

Figure S1. SEC traces of PIB for which M_w =4.5×10^6 Da.

If the creep data in Figs. 2 and 3 did not correspond to steady-state, the zero-shear viscosity would be underestimated. To corroborate the result for 160°C the approximation method due to Ninomiya[25] was applied to the data. There are two equations derived from the definition of the compliance:

$$\eta_0 = \left(J(t)/t - J_S^0/t \right)^{-1} \tag{S1}$$

with the intercept of a plot of *J(t)/t* versus reciprocal time yielding η_0, and

$$\eta_0 = \left(\lim_{1/t \to 0} \left[\frac{J(t)}{t} \frac{d \log J(t)}{d \log t} \right] \right)^{-1} \tag{S2}$$

These two essentially equivalent methods are shown in Figure S2, yielding η_0=34 ± 1 MPa s. This is in good agreement with the viscosity directly obtained from the reciprocal slope of the creep curve, thus verifying that steady-state had been attained in the measurements.

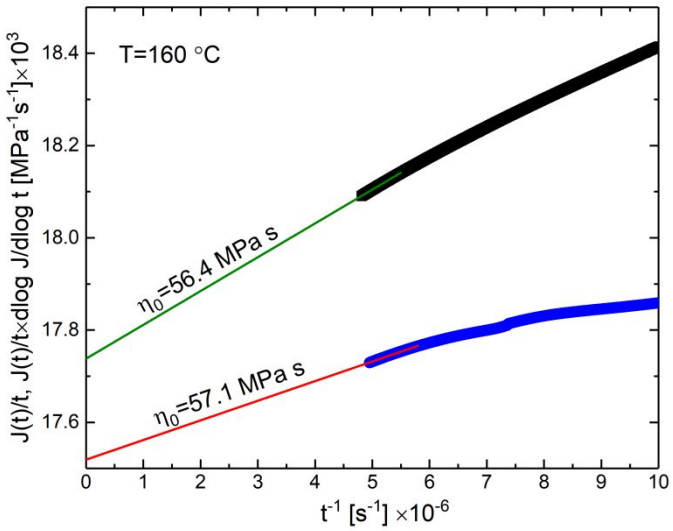

Figure S2. Approximation to steady-state viscosity [ref. 25]. The solid lines are linear fits to last 37 hours of creep, the intercept of which yields the indicated values of η_0.

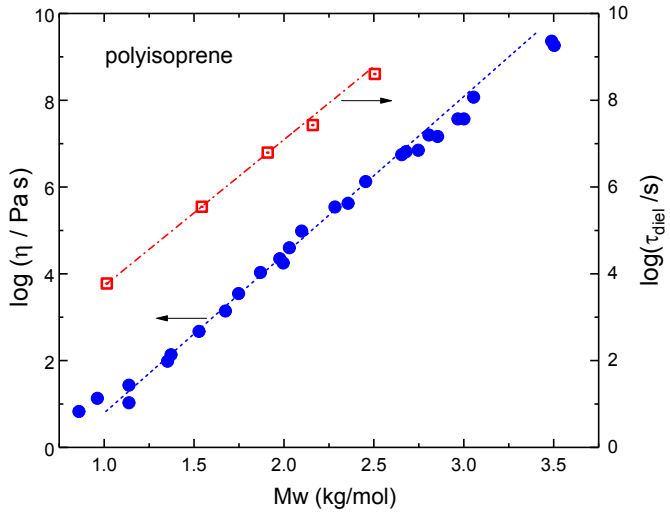

Figure S3. Viscosities [ref. 15] and dielectric normal mode relaxation times [ref. 45] for polyisoprene, with lines intended to represent the behavior prior to the pure reptation regime.