SI Appendix

1 Viscosities of Glycerol and o-Terphenyl

The plots in Fig. 5 show measurements of the viscosities of glycerol and OTP in the temperature range of interest. The filled circles represent experiments that were conducted with our rheometer during initial cooldown, when both substances exhibited purely liquid-like behavior. The solid lines correspond to literature data measured by the drop method for glycerol [1] and by conventional rheology as well as by the beam-deformation method for OTP [2]. The agreement is very good for glycerol. For OTP, our measurements seem to slightly overestimate the viscosity by a factor of about 1.5, most probably due to systematic differences in the determination of the absolute temperature or other calibration effects. Nevertheless, the temperature dependence of the measured values is in very good agreement with the published data.
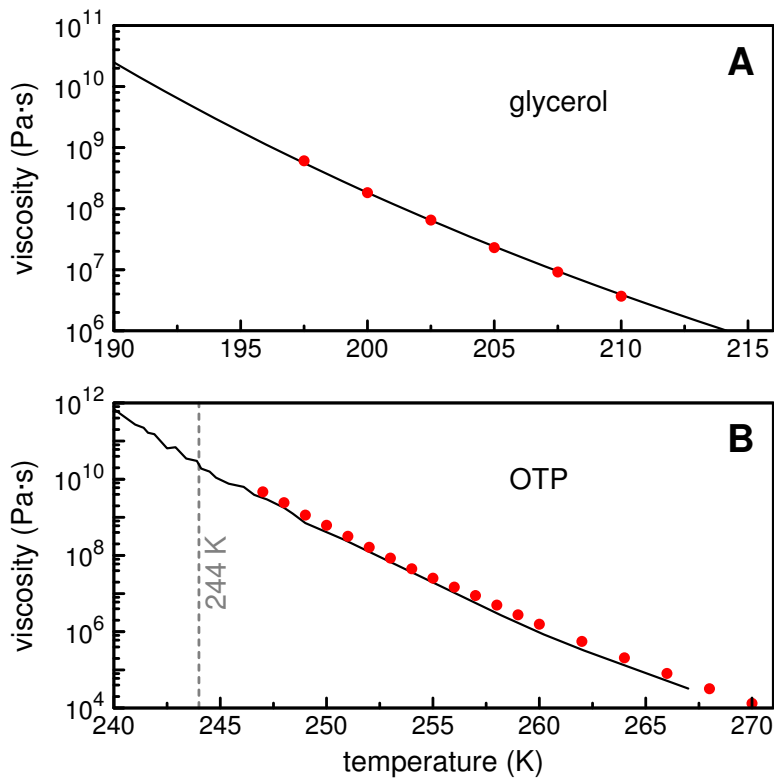

Fig. 5: (A) The viscosity of glycerol ($T_\mathrm{g} = 190\,\mathrm{K}$) as a function of temperature. The solid line represents reference data taken from the literature [1], the circles show the results of our measurements of the liquid response. (B) The viscosity of OTP ($T_\mathrm{g} = 244\,\mathrm{K}$) as a function of temperature (circles: our measurements during the initial cooldown; curve: reference data [2]).

2 Onset of Solid-Like Behavior in Glycerol

An overview of the thermal history of the glycerol sample used in the rheology experiments is given in Fig. 6. Each individual trace starts at or above room temperature with an initial overnight cooldown (at a rate of about 5 K/hour) and presents the subsequent temperature variations with time until we observed the onset of a solid-like behavior. The first detection of a shear modulus at 220 K is indicated by the squares which terminate the curves. From that point on we lowered the temperature to 205 K for the aging study presented in Figs. 3 and 4.

The chronological order of the traces in Fig. 6 is from bottom (oldest) to top (newest) and reflects how we gradually homed in on experimental temperature profiles leading to a solid-like behavior. The thermal history of our previous single-molecule experiments [3] also shows a long period (about 6 days) at 195 K, close to the glass transition, followed by warming up to 205 – 215 K, when the single molecules were measured. (These studies were conducted several months before the rheology experiments.) Comparison to the traces for bulk glycerol strongly suggests that the extended network was also present in the single-molecule sample at the time the temperature-dependent experiments were performed.

The conclusion of this preliminary study is that the growth of the solid network is initiated after a ripening period of at least a few hours at 197 K, seven Kelvin above the nominal glass transition. Note, however, that a more sensitive probing of elastic properties of the supercooled liquid could perhaps detect the onset of the solid network at earlier stages still. Furthermore, it can be expected that single-molecule measurements already reveal structural heterogeneity long before the solid network has become extended enough to influence the mechanical properties of a bulk sample. This suggests that a more sensitive probing of the early stages in the development of the solid-like network is possible in future experiments with individual chromophores.
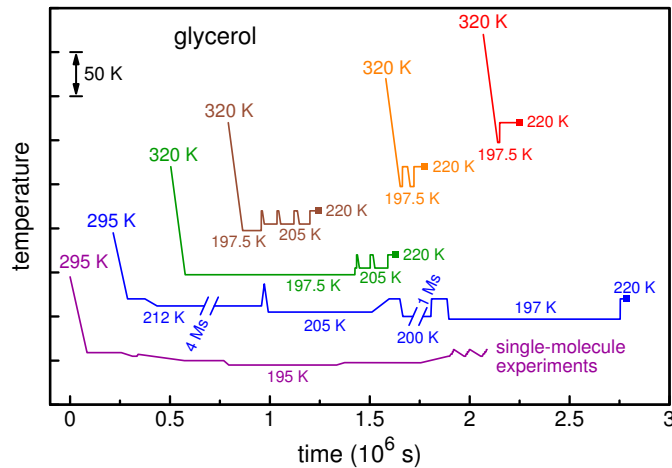

Fig. 6: The thermal history of the glycerol sample in our rheological studies. Each trace is terminated by a square which indicates the first detection of solid-like behavior. The thermal history of the sample in our previous single-molecule experiments [3] is included for comparison (bottom trace).

3 Experimental Details

Design of the Couette Cell.   The design of our rheometer is shown schematically in Fig. 7. A home-built Couette cell was integrated into a variable-temperature cryostat (Janis SVT-200-5). A film of glycerol or OTP, respectively, with a thickness of two millimeters resided between a movable inner cylinder and a static outer cup. Adjustable torque could be applied with a load lever on top of the cryostat via a bronze wire that acted as a torsional spring. The resulting movement of the inner cylinder was inferred from the deflection of a helium-neon laser beam which was retro-reflected by two mirrors rigidly connected to the cylinder and the cup, respectively. This arrangement, with the two mirrors (initially) perpendicular to each other, helps to ensure that the direction of the reflected laser beam is sensitive only to the motion of the inner cylinder relative to the outer cup. The difference signal of a split photodetector was used as an error indicator to control a galvanometer mirror. The current fed into the galvanometer mirror was adjusted by a servo loop to compensate for rotation of the inner cylinder, and therefore provided a direct measure for its rotation. The sensitivity limit of the apparatus was found to correspond to a relative deformation of about 5×10^{-5}.
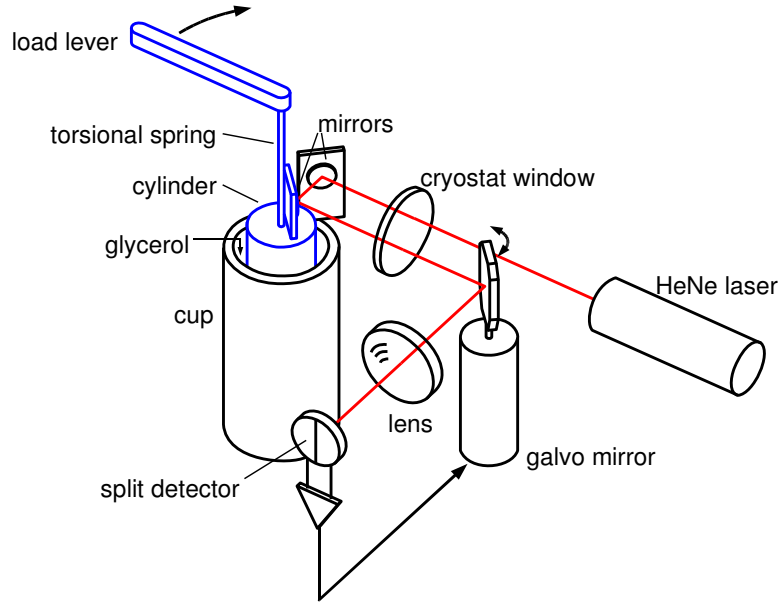

Fig. 7: Schematic drawing of the Couette cell.

Calculation of Shear Modulus and Viscosity.   The (quasi-)static values of the shear modulus G and of the viscosity η relate the elastic stress σ_el and the viscous stress σ_visc to the strain γ and the shear-rate $\dot\gamma$ by:

$$\sigma_\mathrm{el} = G\,\gamma \qquad \text{and} \qquad \sigma_\mathrm{visc} = \eta\,\dot\gamma \quad . \tag{1}$$

The stress and strain are related to the applied torque M and the rotation angle θ of the inner cylinder according to:

$$\gamma = \frac{R\,\theta}{d} \qquad \text{and} \qquad \sigma = \frac{M}{2\pi\,R^2\,h} \quad . \tag{2}$$

The geometrical characteristics of the cell are the average cylinder radius R, the height h of glycerol between the cylinders, and the glycerol film thickness d. We can now relate the intrinsic properties G and η of the material to the experimental parameters:

$$\eta = C\,\frac{M}{\dot{\theta}} \qquad \text{and} \qquad G = C\,\frac{M}{\theta} \qquad \text{with} \qquad C = \frac{d}{2\pi\,R^3\,h} \quad. \tag{3}$$

The torsion constant of the wire, $0.0767\,\mathrm{Nm/rad}$, which is needed to relate the applied torque to the twist angle of the wire, was determined at room temperature by incorporating the wire into a torsion pendulum and measuring the oscillation period of a known, variable moment of inertia.

Because of the slight rotation of the inner cylinder, the torque produced by the torsion wire was not kept exactly constant during the deformation. However, the maximum rotation angle of the inner cylinder was very small compared to the twist angle of the wire, less than $0.7\,\%$ for the weakest shear moduli in Fig. 3. Even for the qualitative demonstration of the solid-like behavior of OTP (blue trace in Fig. 1 B), the deformation remained below $10\,\%$ of the applied twist angle. Therefore, to a good approximation, the applied torque can be considered as constant during each individual measurement.

The smallest shear stress that could be applied reproducibly was about $55\,\mathrm{Pa}$. Conducting control experiments under these conditions to check for the presence of solid friction in our apparatus, we could not detect any friction effects above our sensitivity limit.

References

[1] Schröter K, Donth E (2000) Viscosity and shear response at the dynamic glass transition of glycerol. *J Chem Phys* 113:9101–9108.

[2] Laughlin WT, Uhlmann DR (1972) Viscous flow in simple organic liquids. *J Phys Chem* 76:2317–2325.

[3] Zondervan R, Kulzer F, Berkhout GCG, Orrit M (2007) Local viscosity of supercooled glycerol near T_{g} probed by rotational diffusion of ensembles and single dye molecules. *Proc Natl Acad Sci U S A* 104:12628–12633.