# Electronic Supplementary Information: Dynamic-bond-induced sticky friction tailors non-Newtonian rheology

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# S1. Characterization techniques

- Dynamic light scattering (DLS): A dynamic light scattering instrument (Wyatt Technology's Mobius™) was used to measure the hydrodynamic radius of the synthesized thiol-functionalized silica particle and silica seed particle.

- Nuclear magnetic resonance spectroscopy: A Bruker Avance nanobay III HD 400 MHz nuclear magnetic resonance spectrometer was used to characterize the functionalized silica particles and the synthesized Michael-acceptors. The residual solvent $CHCl_3$ peak at $\delta = 7.26$ ppm was used as a reference peak.

# S2. Characterization of the synthesized materials

- Functionalized silica particle characterization

  The functionalized silica particles were characterized with $^1$H NMR following the method reported by Crucho *et al.*[1]. 20 mg of silica particles was dissolved in a solution of 0.5 M NaOD in $D_2O$. To quantify the functional group density, 35 mg of 1,3,5-trioxane was added as an internal standard. The intensity of the $(ONa)_3SiCH_2CH_2C\boldsymbol{H}_2SH$ at $\delta = 2.43$ ppm was compared to that of the internal standard, giving 1.3 SH groups/nm$^2$ surface area of silica particles.

  DLS was used to measure the size of synthesized silica particles suspended in water. The synthesized particle density ($\rho = 1.92$ g/mL) was measured with the bromoform ($\rho = 2.89$ g/ml) and methanol ($\rho = 0.79$ g/ml) mixture at which the particle does not sediment or float.

- Characterization of Michael-acceptors

  The synthesized **1M**, **1H**, and **1N** molecules were characterized with $^1$H NMR (400 MHz, $CDCl_3$ in Fig. S1):

  R=–$OCH_3$ (**1M**): $\delta = 8.23$ (s, 1H, C=CH), 7.67 (d, 2H, Ar-H), 6.91 (d, 2H, Ar-H), 3.82 (s, 3H, Ar-$OCH_3$, 3.42–3.77 (m, -$CH_2$-CH-), 1.25 (m, -$CH_3$) ppm.

  R=–H (**1H**): $\delta = 8.30$ (s, 1H, C=CH), 7.73 (t, 3H, Ar-H), 7.40 (d, 2H, Ar-H), 3.42–3.77 (m, -$CH_2$-CH-), 1.25 (m, -$CH_3$) ppm.

  R=–$NO_2$ (**1N**): $\delta = 8.37$ (s, 1H, C=CH), 8.24 (d, 2H, Ar-H), 7.88 (d, 2H, Ar-H), 3.42–3.77 (m, -$CH_2$-CH-), 1.25 (m, -$CH_3$) ppm.

- Solvent viscosity

  The viscosity of Michael-acceptor endcapped polymer fluids was measured using MCR301 or MCR702 rheometer (Anton Paar). In the measured shear rate range ($1 - 100$ s$^{-1}$), the fluid viscosity exhibited Newtonian behavior.

  $\eta_{\mathbf{1M}_{230}} = 2564$ mPa $\cdot$ s, $\eta_{\mathbf{1M}_{2000}} = 579$ mPa $\cdot$ s, $\eta_{\mathbf{1M}_{4000}} = 1195$ mPa $\cdot$ s

$\eta_{\mathbf{1H}_{230}} = 880\ \mathrm{mPa \cdot s}$, $\eta_{\mathbf{1H}_{2000}} = 528\ \mathrm{mPa \cdot s}$, $\eta_{\mathbf{1H}_{4000}} = 1048\ \mathrm{mPa \cdot s}$

$\eta_{\mathbf{1N}_{2000}} = 980\ \mathrm{mPa \cdot s}$, $\eta_{\mathbf{1N}_{4000}} = 1393\ \mathrm{mPa \cdot s}$

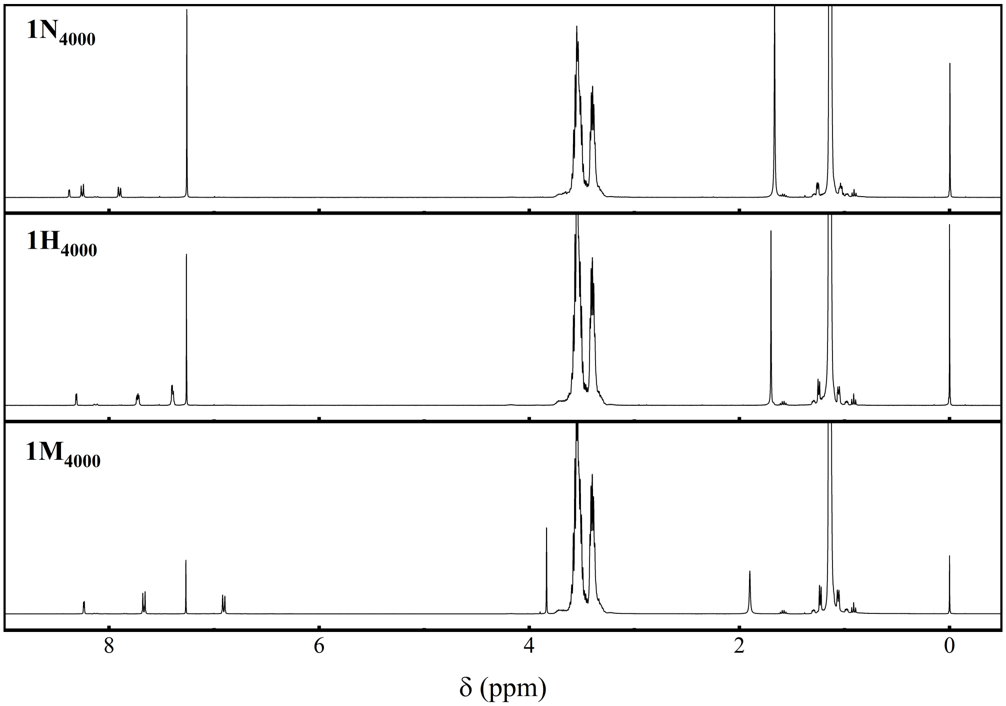
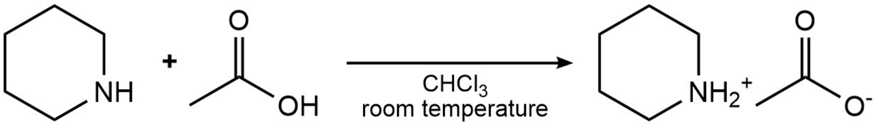


**Fig. S1** $^1$H NMR for $\mathbf{1N}_{4000}$, $\mathbf{1H}_{4000}$, and $\mathbf{1N}_{4000}$ (top to bottom).

## S3. Prepartion of piperidinium acetate

Piperidinium acetate was prepared following the reaction in Scheme S1. 40 mmol of piperidine (Sigma-Aldrich, 99%) and 40 mmol of acetic acid (Thermo Fisher Scientific, $\geq$ 99.7%) were added to a 50 mL round-bottom flask with 12 mL of chloroform. The solution was stirred with a magnetic stirrer for 30 min at room temperature. After the reaction, chloroform was removed from the product using a rotary evaporator.

$^1$H NMR (400 MHz, $CDCl_3$) spectrum for piperidinium acetate: $\delta$ = 8.50 (s, 2H, -C-$NH_2^+$), 3.02 – 2.95 (m, 4H, N-$CH_2$), 1.97 (d, 3H, C-$C_3$), 1.81 – 1.71 (m, 4H, N-C-$CH_2$-C), 1.67 – 1.58 (m, 2H, N-C-C-$CH_2$) ppm.



**Scheme S1** Synthesis of piperidinium acetate.

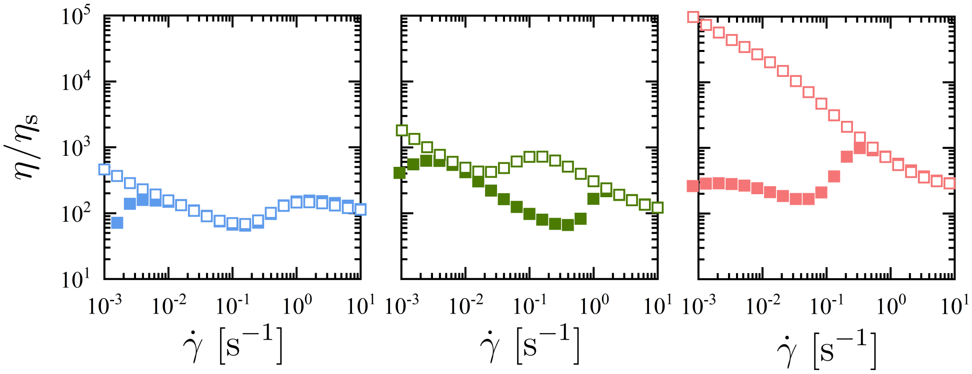


**Fig. S2** Relative viscosity $\eta_r = \eta/\eta_s$ for suspensions in $\mathbf{1M}_{2000}$ (a), $\mathbf{1H}_{2000}$ (b), and $\mathbf{1N}_{2000}$ (c) as a function of shear rate $\dot{\gamma}$. Closed symbols: increasing stress ramp. Open symbols: decreasing stress on the ramp's return cycle.

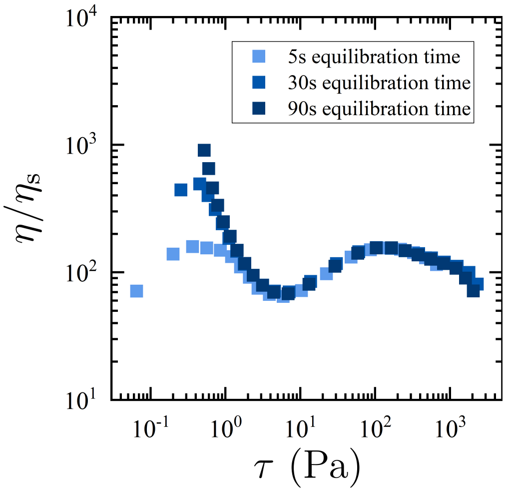


**Fig. S3** Confirmation of steady-state viscosity. Relative viscosity $\eta_r = \eta/\eta_s$ is plotted as a function of shear stress $\tau$ for $\phi = 0.52$ thiol functionalized silica particle suspensions in $1\mathbf{M}_{2000}$. The viscosity is measured at three different equilibrating times (5 s, 30 s, and 90s per each $\tau$).

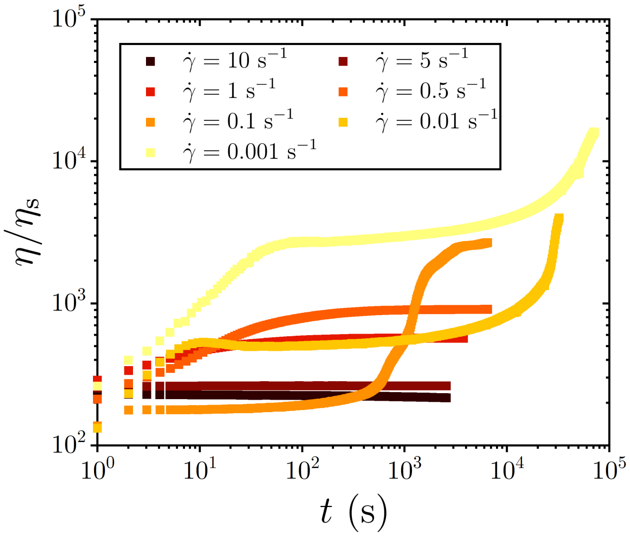


**Fig. S4** Viscosity as a function of time at constant shear rate $\dot{\gamma}$ for the suspension in $\mathbf{1H}_{2000}$.

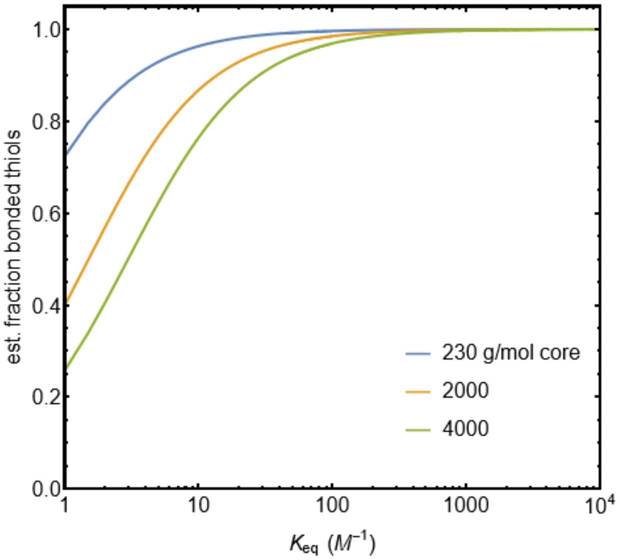


**Fig. S5** The estimated fraction of bonded thiols as a function of $K_{\mathrm{eq}}$ for $M_{\mathrm{PPG}}$=230 (blue), 2000 (orange), and 4000 g/mol (green) at fixed packing fraction ($\phi = 0.52$).

## S4. The fraction of bonded thiols to form thia-Michael bonds

The equilibrium constant of thia-Michael reaction between thiol (–SH) and Michael-acceptor (–MA) is:

$$K_{\mathrm{eq}} = \frac{[\mathrm{tMA}]}{[-\mathrm{SH}]\,[-\mathrm{MA}]}.$$

The fraction of bounded thiol $p$ at equilibrium suggests $[\mathrm{tMA}] = p[-\mathrm{SH}]_0$ and $[-\mathrm{SH}] = (1-p)[-\mathrm{SH}]_0$, where $[-\mathrm{SH}]_0$ is the initial molar concentration of thiol. Then, $[-\mathrm{MA}] = [-\mathrm{MA}]_0 - [\mathrm{tMA}] = [-\mathrm{MA}]_0 - p[-\mathrm{SH}]_0$. Finally, the equilibrium constant is expressed by:

$$K_{\mathrm{eq}} = \frac{p}{(1-p)([-\mathrm{MA}]_0 - p[-\mathrm{SH}]_0)}.$$

Using this equation, $p$ is solved for all Michael-acceptors (Table S1). Based on this expression, we estimated the fraction of bonded thiols as a function of $K_{\mathrm{eq}}$ for all molecular weights in Fig. Fig. S5.

**Table S1** The fraction of thiol reacted for the thia-Michael adduct formation.

| | $M_{\mathrm{MPPG}} = 230$ g/mol | $M_{\mathrm{MPPG}} = 2000$ g/mol | $M_{\mathrm{MPPG}} = 4000$ g/mol |
|---|---|---|---|
| $\mathbf{1M}_{M_{\mathrm{PPG}}}$ | 0.992 | 0.970 | 0.944 |
| $\mathbf{1H}_{M_{\mathrm{PPG}}}$ | 0.999 | 0.996 | 0.992 |
| $\mathbf{1N}_{M_{\mathrm{PPG}}}$ | | 0.999 | 0.999 |

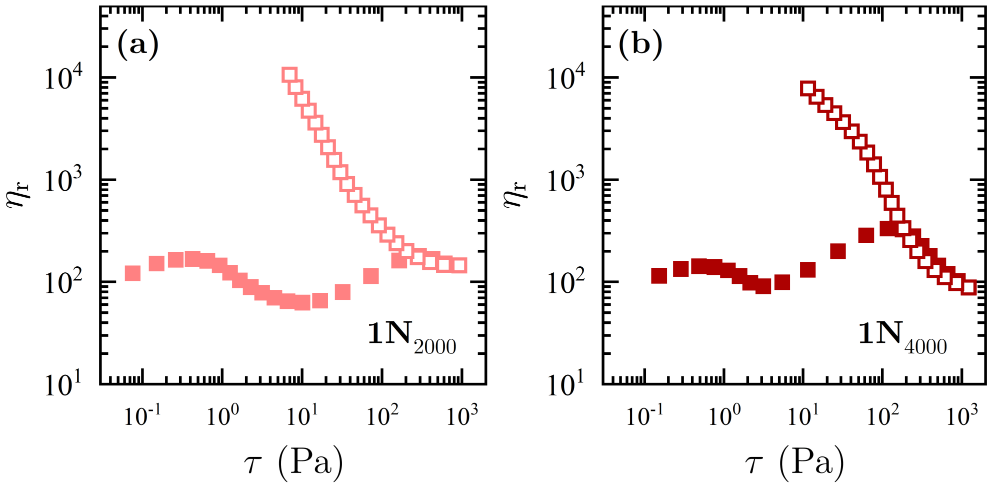


**Fig. S6** Relative viscosity $\eta_r$ versus shear stress $\tau$ of $\phi = 0.52$ thiol functionalized silica particle suspensions in different molecular weight BCAm-endcapped poly(propylene glycol) $\mathbf{1N}_{2000}$ (a) and $\mathbf{1N}_{4000}$ (b).

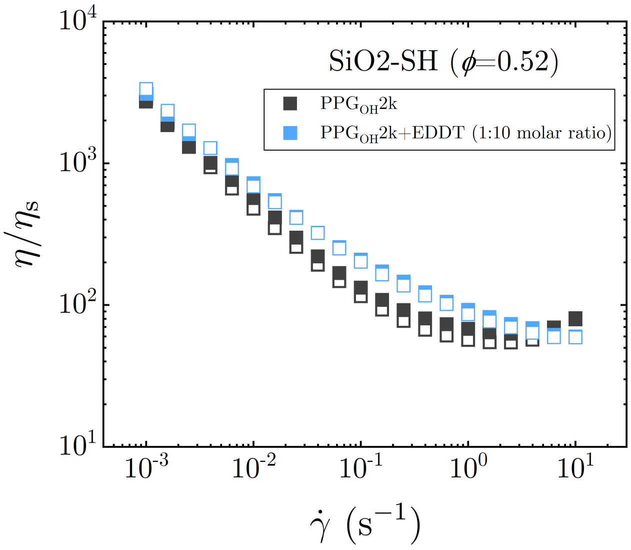


**Fig. S7** Relative viscosity $\eta/\eta_s$ as a function of shear rate $\dot{\gamma}$ of the suspension in hydroxy-terminated polypropylene glycol (2000 g/mol, $PPG_{OH}2k$) and in a mixture of $PPG_{OH}2k$ and 2,2'-(ethylenedioxy)diethanethiol (EDDT) with a 1-to-10 molar ratio. The packing fraction of suspensions is fixed at $\phi = 0.52$.

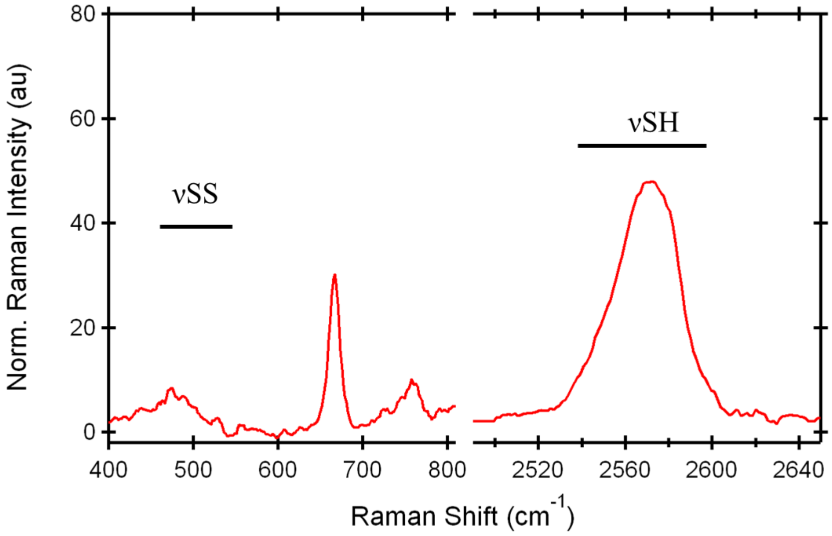


**Fig. S8** A Raman spectrum of thiol-functionalized silica particles suspended in a mixture hydroxy-terminated polypropylene glycol (2000 g/mol, $PPG_{OH}2k$) and and 2,2'-(ethylenedioxy)diethanethiol (EDDT) (1-to-10 molar ratio). The packing fraction of suspensions is $\phi = 0.52$. A free thiol peak clearly appears at 2570 $cm^{-1}$, whereas there is limited-to-no disulfide formation from a peak at 510 $cm^{-1}$.

# S5. Constraint-based Wyart-Cates model fitting

We fitted the experimental rheology curves using the constraint-based model by Guy *et al.*[2,3], which extends an earlier model by Wyart and Cates (WC) that does not account for attractive interactions[4]. This modified WC model includes frictional and adhesive force responsible for the sliding and rolling constraints, respectively. Based on the WC model, the relative viscosity is expressed by

$$\eta_\mathrm{r} = \left[1 - \frac{\phi}{\phi_\mathrm{J}(a, f)}\right]^{-2} \tag{1}$$

with the jamming volume fraction $\phi_\mathrm{J}(a, f)$ that is a function of the fraction of adhesion ($a$) and friction ($f$). These parameters can be expressed by $f(\tau) = \exp\left[-(\tau^*/\tau)^\beta\right]$ with the critical stress $\tau^*$ for dominating friction over particle repulsive interaction and $a(\tau) = 1 - \exp\left[-(\tau_\mathrm{a}/\tau)^\kappa\right]$ with $\tau_\mathrm{a}$, the stress required to break the adhesion between contacting particles. With $a$ and $f$, $\phi_\mathrm{J}(a, f)$ can be interpolated with all four possible constraints,

$$\begin{aligned} \phi_\mathrm{J}(a, f) =& af\phi_\mathrm{alp} + a(1-f)\phi_\mathrm{acp} \\ &+ (1-a)f\phi_\mu + (1-a)(1-f)\phi_\mathrm{rcp} \end{aligned} \tag{2}$$

where $\phi_\mu \equiv \phi_\mathrm{J}(a = 0, f = 1)$, $\phi_\mathrm{alp} \equiv \phi_\mathrm{J}(a = 1, f = 1)$, $\phi_\mathrm{acp} \equiv \phi_\mathrm{J}(a = 1, f = 0)$, and $\phi_\mathrm{rcp} \equiv \phi_\mathrm{J}(a = 0, f = 0)$ are the onset packing fraction for shear jamming of frictional particles in the absence of adhesion, the adhesive loose packing fraction, adhesive close packing fraction $\phi_\mathrm{acp} \equiv \phi_\mathrm{J}(a = 1, f = 0)$, and random close packing for hard spheres, respectively. $\phi_\mathrm{rcp} = 0.64$ was fixed, and the other parameters were used to fit both the shear-thinning and -thickening regimes of the measured rheology curve. Using the fitting parameter, yield stress of each suspension was estimated by setting $\phi_\mathrm{J} = \phi$ where $\eta_\mathrm{r} \to \infty$. Errors were estimated from fits with varied fitting ranges.

## Supplementary References

1 C. I. Crucho, C. Baleizao and J. P. S. Farinha, *Analytical chemistry*, 2017, **89**, 681–687.

2 B. Guy, J. Richards, D. Hodgson, E. Blanco and W. Poon, *Physical review letters*, 2018, **121**, 128001.

3 J. A. Richards, B. M. Guy, E. Blanco, M. Hermes, G. Poy and W. C. Poon, *Journal of Rheology*, 2020, **64**, 405–412.

4 M. Wyart and M. E. Cates, *Physical review letters*, 2014, **112**, 098302.