Electronic Supplementary Material (ESI) for Soft Matter.

Multiple particle tracking microrheology measured using bi-disperse probe diameters†

Matthew D. Wehrman[a], Seth Lindberg[b] and Kelly M. Schultz*[a]

[a] *Department of Chemical and Biomolecular Engineering, Lehigh University, Bethlehem, PA, USA. Fax: (610) 758-5057; Tel: (610) 758-2012; E-mail: kes513@lehigh.edu* [b] *Process and Engineering Development, Procter & Gamble Co., West Chester, OH, USA.*

1 Supplemental

1.1 Static Error

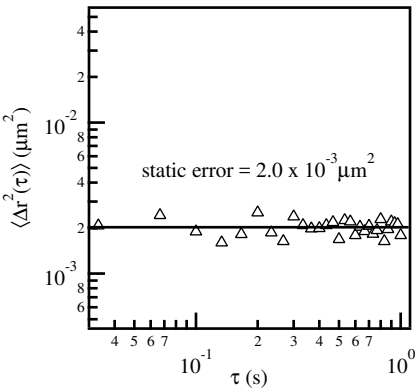

Fig. S1 Measurements of static particle tracking error for 2 μm probe particles. This is a measurements of 2 μm particles that have been crashed out of solution and are stuck on a glass cover slip.

1.2 Time-cure superposition

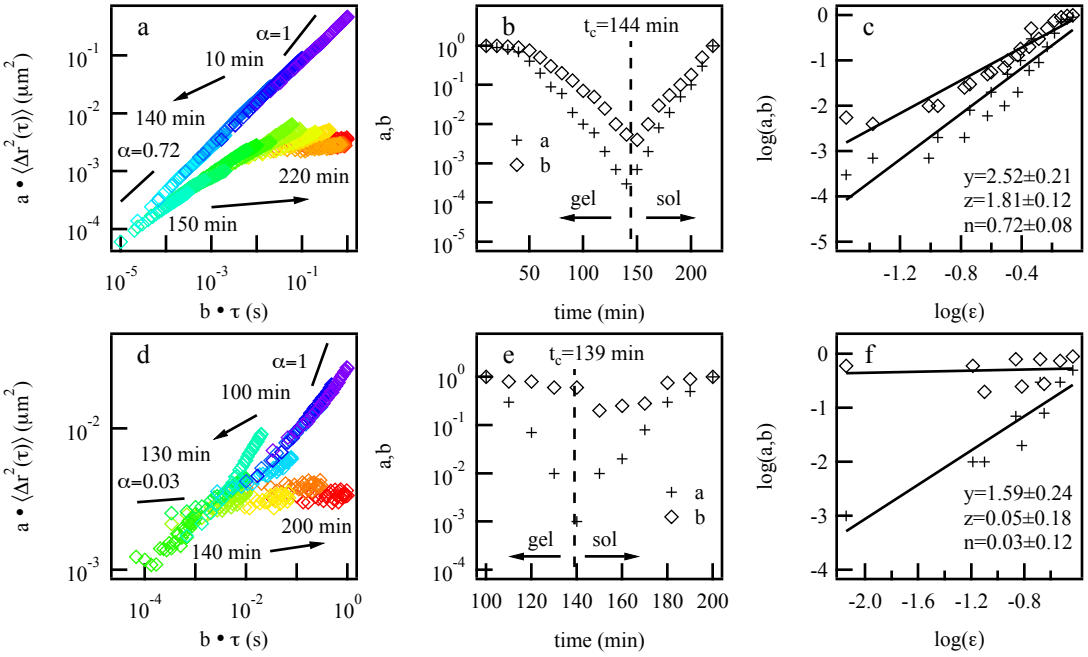

Fig. S2 Time-cure superposition of a HCO degradation using (top row) 0.5 μm probes and (bottom row) 2 μm probes. (a and d) MSD curves from Figure 6a and b in the main text are shifted on the lag time and MSD axes to form sol and gel master curves. (b and e) Shift factors a and b diverge at the critical gel time, t_c. The value of t_c is similar for both probe particle sizes. (c and f) Calculation of the critical relaxation exponent, n. The value of n changes between the two particle sizes because each particle is measuring a different length scale and structure in this heterogeneous colloidal gel.

1.3 Rheological heterogeneity in HCO degradation

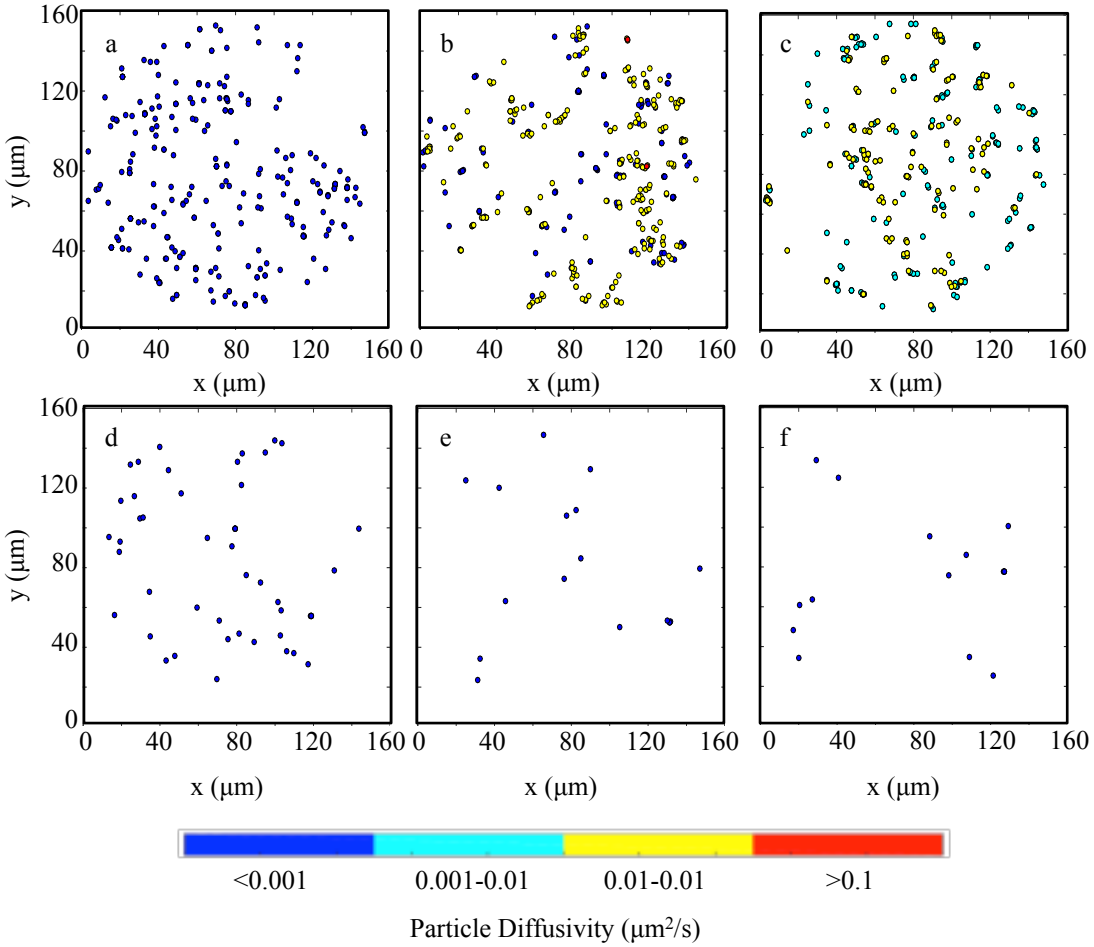

Fig. S3 Rheological heterogeneity of the degradation of hydrogenated castor oil with (top) 0.5 μm and (bottom) 2 μm probes. Heterogeneities are shown in the gel phase (a and d) at the critical transition, $t = 170$ min (b and e) and after degradation is complete (c and f).

The rheological heterogeneity of HCO degradation is calculated at key points throughout the degradation reaction, Figure S3. This is done by comparing the variance of the Gaussian fit to the single particle 1-dimensional van Hove correlation function at a given lag time. Any probes that have the same variance, based on an F-test with a 95% confidence interval, are clustered together[1–4]. Each cluster within a video can then be tracked separately to calculate the ensemble-averaged MSD and the diffusivity. A visual representation of the clusters shows each probes original x location with the color based on diffusivity. The color scale is bounded on the most diffuse side by the diffusivity of a probe particle in water, $D = 1$ μm^2/s and $D = 0.25$ μm^2/s for 0.5 μm and 2 μm probes, respectively. The lower diffusivity is bounded by the limit of our experimental apparatus, calculated from the values of static error, $D = 2.0 \times 10^{-4}$ μm^2/s and $D = 6.2 \times 10^{-4}$ μm^2/s for 0.5 μm and 2 μm probes, respectively.

0.5 μm probes measure a homogenous material with low diffusivity at the beginning of the experiment, Figure S3a. There is very little clustering, and 99% of particles are experiencing the same microenvironment. At the phase transition, Figure S3b, we measure the greatest amount of heterogeneity, with 40% of the particles experiencing a more diffuse microenvironment and 60% of particles experiencing restricted movement. Finally, at equilibrium the structure is homogenous with 93% of particles in the same diffusive microenvironment, Figure S3c. Rheological heterogeneity has been previously quantified for MPT measurements of only 0.5 μm particles. Comparing the bi-disperse MPT and single particle size MPT, we measure the same changes in rheological heterogeneity during HCO degradation[4].

Alternatively, the 2 μm probes show almost no change in rheological heterogeneity throughout the transition, Figure S3d−f. Throughout the dynamic transition there is little change in diffusivity, which is consistently measured at or below

the measurable limit of the apparatus, $D = 6.25 \times 10^{-4}$ μm^2/s. In general, 2 μm probe particles will have 4$\times$ lower diffusivity when compared to 0.5 μm probes in the same medium, based on the difference in probe size. Since the difference in probe particle diffusivities during HCO degradation is much greater than 4$\times$ the structure of the HCO is restricting 2 μm particle movement and it is not simply that the particles are moving slower in the same medium. Due to the low diffusivity of the 2 μm particles they almost all appear in the same statistical cluster. Therefore, the 2 μm probes do not undergo any significant changes in rheological heterogeneity throughout HCO degradation.

References

1 A. Heuer and K. Okun, *J. Chem. Phys.*, 1997, **106**, 6176–6186.

2 A. Rahman, *Phys. Rev.*, 1964, **136**, 405–411.

3 J. C. Crocker, M. T. Valentine, E. R. Weeks, T. Gisler, P. D. Kaplan, A. G. Yodh and D. A. Weitz, *Phys. Rev. Lett.*, 2000, **85**, 888–891.

4 M. D. Wehrman, S. Lindberg and K. M. Schultz, *Soft Matter*, 2016, **12**, 6463–6472.