ELECTRONIC SUPPLEMENTARY INFORMATION

Steady Shear Microstructure in Dilute Colloid-Polymer Mixtures

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CALCULATION OF THE INTERPARTICLE POTENTIAL AT CONTACT

The interparticle depletion potential, $u_{dep}(r)$, between hard sphere colloids of radius a in the presence of non-adsorbing polymers for a net center-to-center separation, r is given by:

$$u_{dep}(r) = -\Pi\pi\left[\frac{4}{3}\left(a+R_g\right)^3\left(1-\frac{3r}{4\left(a+R_g\right)}+\frac{r^3}{16\left(a+R_g\right)^3}\right)\right],$$ [1-2]

where Π represents the osmotic pressure induced by the polymer and R_g is the polymer's radius of gyration. The osmotic pressure is modeled through a virial equation of state according to:

$$\Pi = nkT(1+B_2 n+\ldots),$$ [3]

where n is the polymer bulk number density, k is the Boltzmann's constant and T is the absolute temperature and B_2 is the second virial coefficient, related to the depletant volume (V_p):

$$B_2 = 4V_p = {}^{16}\!/_{3}\left(\pi R_g{}^3\right)$$

The magnitude of the interparticle electrostatic repulsion, $u_{\mathrm{elec}}(r)$ was estimated by inverting the 2D radial distribution function of a polymer-free suspension, $g(r)$, using the hypernetted chain (HNC) approximation as described in reference [4]

$$u_{elec}(r) = w(r) + nkTI(r)$$

where n is the areal number density of particles, $w(r)$ is the mean potential:

$$w(r) = -kT\ln g(r)$$

and $I(r)$ represents the convolution integral:

$$I(r) = \int\left[g(r')-1-nI(r)\right]\left[g\left(\left|r'-r\right|\right)-1\right]d^2r'$$

The magnitude of the interparticle potential at contact, $|U_{\mathrm{min}}|$, was estimated by extrapolating $U(r) = u_{\mathrm{dep}}(r) + u_{\mathrm{elec}}(r)$ to the particle diameter.

SUPPLEMENTARY TABLES & FIGURES

PS conc. (C_p, mg/ml) → / $\dot{\gamma}$, s^{-1}	**9.0**	**14.4**	**20.8**
0.07	3.76E-03	1.50E-03	7.59E-04
0.14	7.53E-03	3.00E-03	1.52E-03
0.56	3.01E-02	1.20E-02	6.07E-03
2.24	1.20E-01	4.79E-02	2.43E-02
8.96	4.82E-01	1.92E-01	9.72E-02

Table S1. Calculated values of the dimensionless shear rate, $\dot{\gamma}$*, for PS Mw = 97,400 Da over the range of $\dot{\gamma}$ and C_p investigated.

PS conc. (C_p, mg/ml) → / $\dot{\gamma}$, s^{-1}	**4.5**	**7.2**	**10.4**
0.07	7.88E-03	2.55E-03	1.20E-03
0.14	1.58E-02	5.10E-03	2.41E-03
0.56	6.31E-02	2.04E-02	9.63E-03
2.24	2.52E-01	8.16E-02	3.85E-02
8.96	1.01E+00	3.26E-01	1.54E-01

Table S2. Calculated values of the dimensionless shear rate, $\dot{\gamma}$*, for PS Mw = 777,500 Da over the range of $\dot{\gamma}$ and C_p investigated.

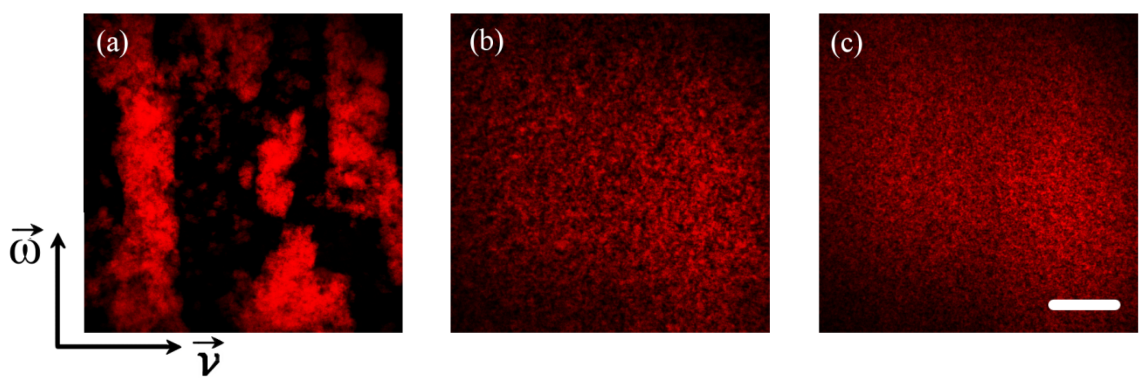

Figure S1. Low magnification confocal micrographs of the terminal microstructure in the flow-vorticity plane at shear rate, $\dot{\gamma}$= (a) 0.14, (b) 0.56 and (c) 2.24 s^{-1}. Scale bar corresponds to 300 µm.

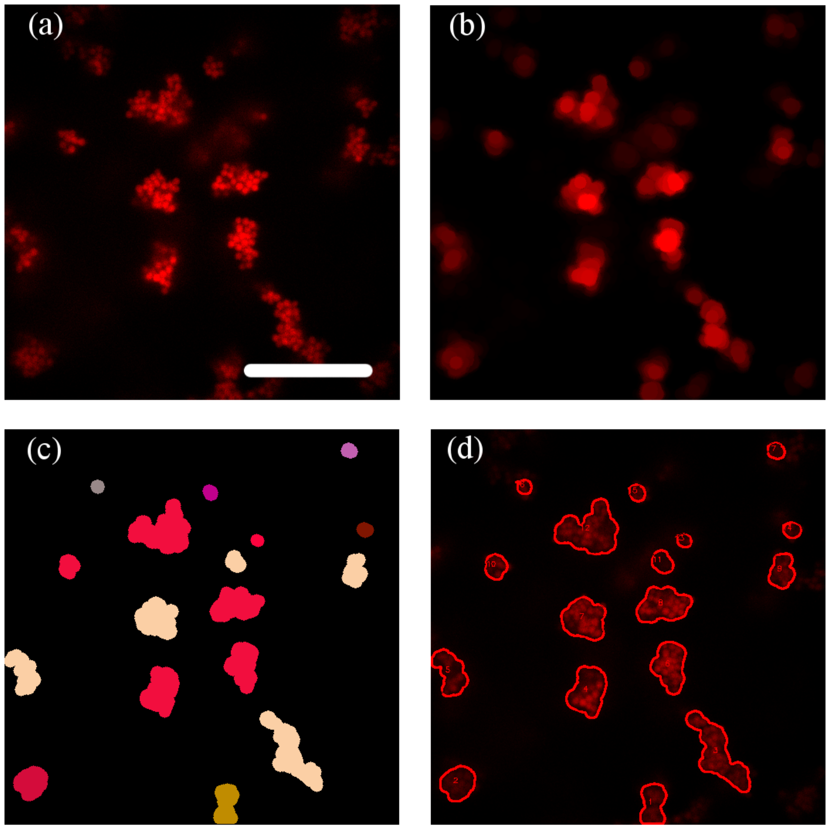

Figure S2. Overview of terminal cluster radius (R_c) quantification: (a) Raw image, (b) processed image after morphing and dilation operations, (c) identification of clusters and (d) overlay of identified clusters. Scale bar represents 20 μm.

Figure S3. Long-range reconstruction of the sheared microstructure at: (a) C_p = 20.8 mg/ml, M_w = 97,400 Da, (b) C_p = 10.4 mg/ml, M_w = 777,500 Da. $\dot{\gamma}$ (from top to bottom) = 0.07, 0.14, 0.56, 2.24, 8.96 s^{-1}. Scale bar represents 100 µm.

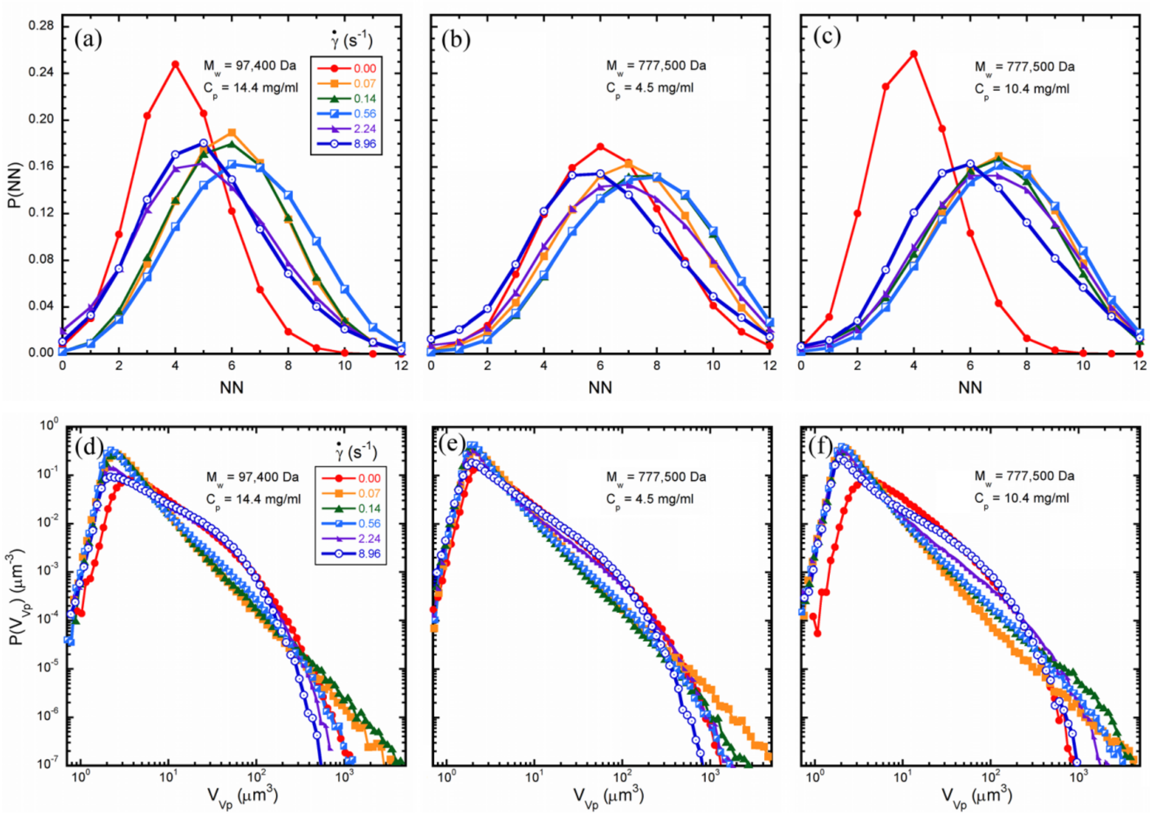

Figure S4. Probability distributions of: (a-c) nearest neighbors (P(*NN*)) and, (d-f) volumes of Voronoi polyhedra (P(V_{VP})) at three representative polymer concentrations. The symbols reported in the legend are common to all the plots.

REFERENCES

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3. A. Vrij, *Pure Appl Chem*, 1976, **48**, 471-483.
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