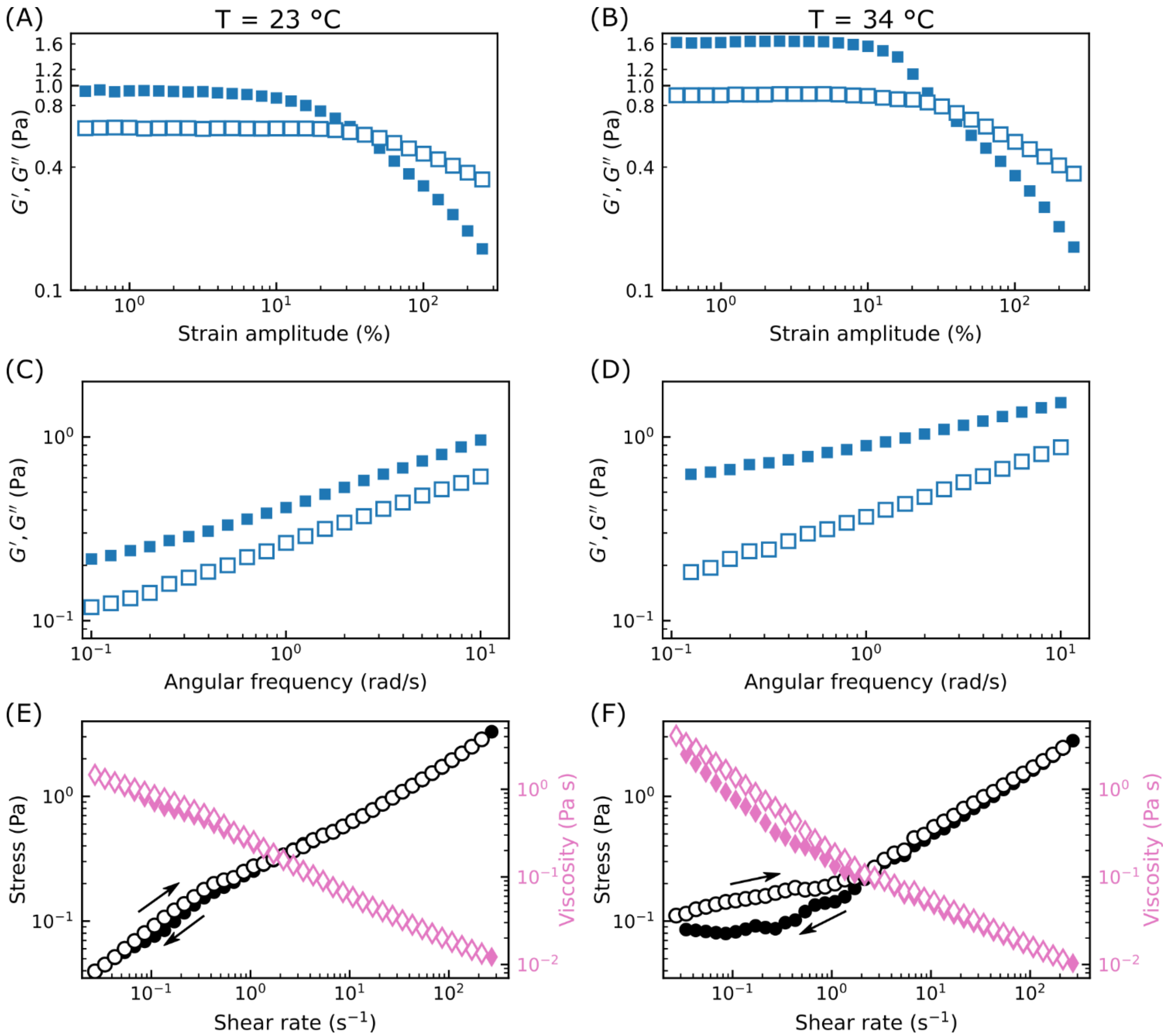
Supplementary Material for "Shear-induced vorticity aligned flocs in a temperature responsive colloid-polymer mixture"

1 Supplementary Table

Symbol	Meaning	Other Notes
$\dot{\gamma}_{T\uparrow}$	Shear rate applied to the sample during the temperature ramp from 23 °C to 34 °C. The temperature ramp is done at 0.5 °C/min.	
$\dot{\gamma}_{hold}$	Shear rate applied to the sample following the temperature ramp to 34 °C while the sample is held at 34 °C (typically for 30 minutes).	For our experiments, we typically set $\dot{\gamma}_{hold} = \dot{\gamma}_{T\uparrow}$.
$\dot{\gamma}_{T\downarrow}$	Shear rate applied to the sample during the temperature ramp from 34 °C to 23 °C.	
$\dot{\gamma}_c$	Maximum shear rate of $\dot{\gamma}_{hold}$ for which we observe stable vorticity-aligned flocs.	
h	Gap height of our parallel plate geometry and approximately 150 μm for all data shown here.	

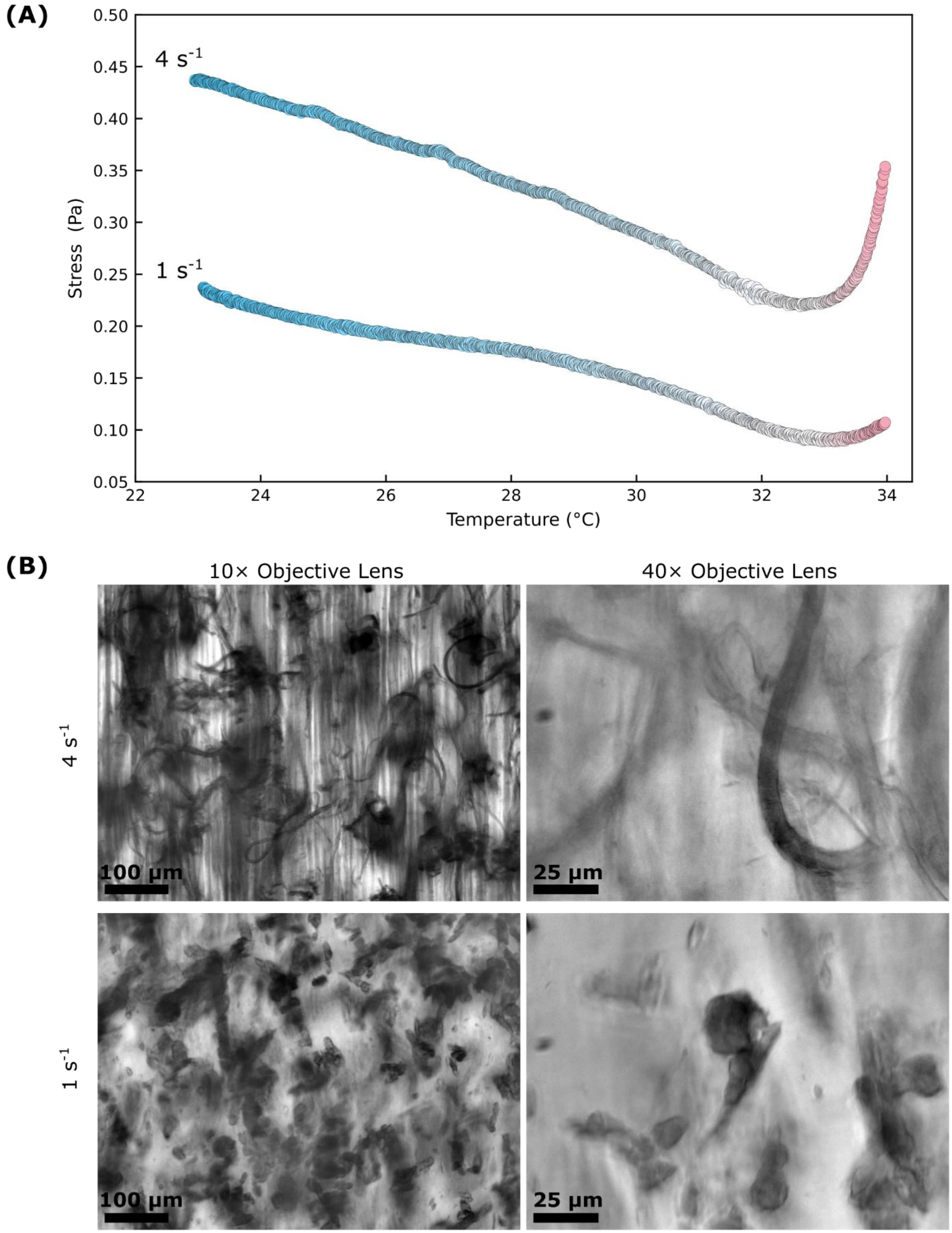
Supplementary Table 1. Variables used in the manuscript are described in this table.

2 Supplementary Figures



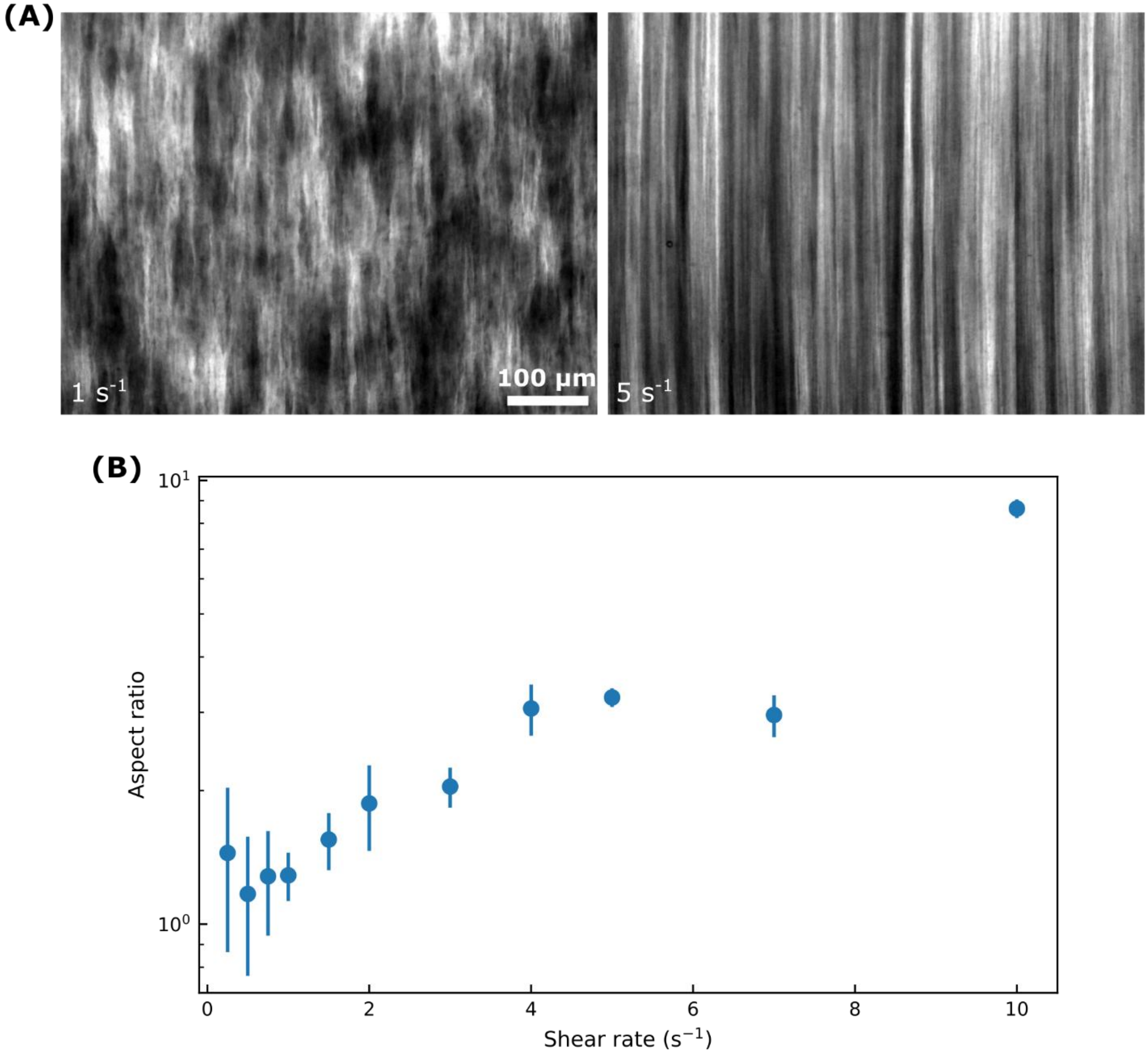
Supplementary Figure 2. Rheological properties of the sample at 23 °C and 34 °C. Before each measurement, we apply a conditioning step where the sample is kept at 23 °C and is sheared at 1000 s^{-1} for 120 s, then sheared at -1000 s^{-1} for 120 s, and then allowed to equilibrate at rest for 180 s. The sample is then either left at 23 °C (left column; A,C,E) or heated to a temperature of 34 °C (right column; B,D,F). Once the set temperature is reached and equilibrated for an additional 180 s, an oscillatory amplitude sweep is performed at a frequency of $\omega = 10\ \mathrm{rad/s}$ for amplitudes of 0.5% to 300% (top row; A,B). After repeating the same conditioning steps and temperature equilibration, we perform an oscillatory frequency sweep (middle row; C,D) for a strain amplitude of 1% and frequencies from 100 rad/s to 0.1 rad/s. The sample at 34 °C (D) shows a more solid-like response than the sample at 23 °C (C). For both the amplitude and frequency sweep data, the filled symbols represent G' and the open symbols represent G''. After repeating the same conditioning steps and temperature equilibration, we perform flow sweeps (bottom row; E,F). The shear rate is first decreased from 300 s^{-1} to 0.03 s^{-1} with 10 points per decade, 20 s of equilibration at each point, and an averaging time of 30 s. Data points for this sweep of decreasing shear rates are shown as filled symbols (circles for stress, diamonds for viscosity). We then perform an increasing flow sweep from

0.03 s^{-1} to 300 s^{-1}, shown as the open symbols. The sample at 34 °C (F) shows more hysteresis than the sample at 23 °C (E).

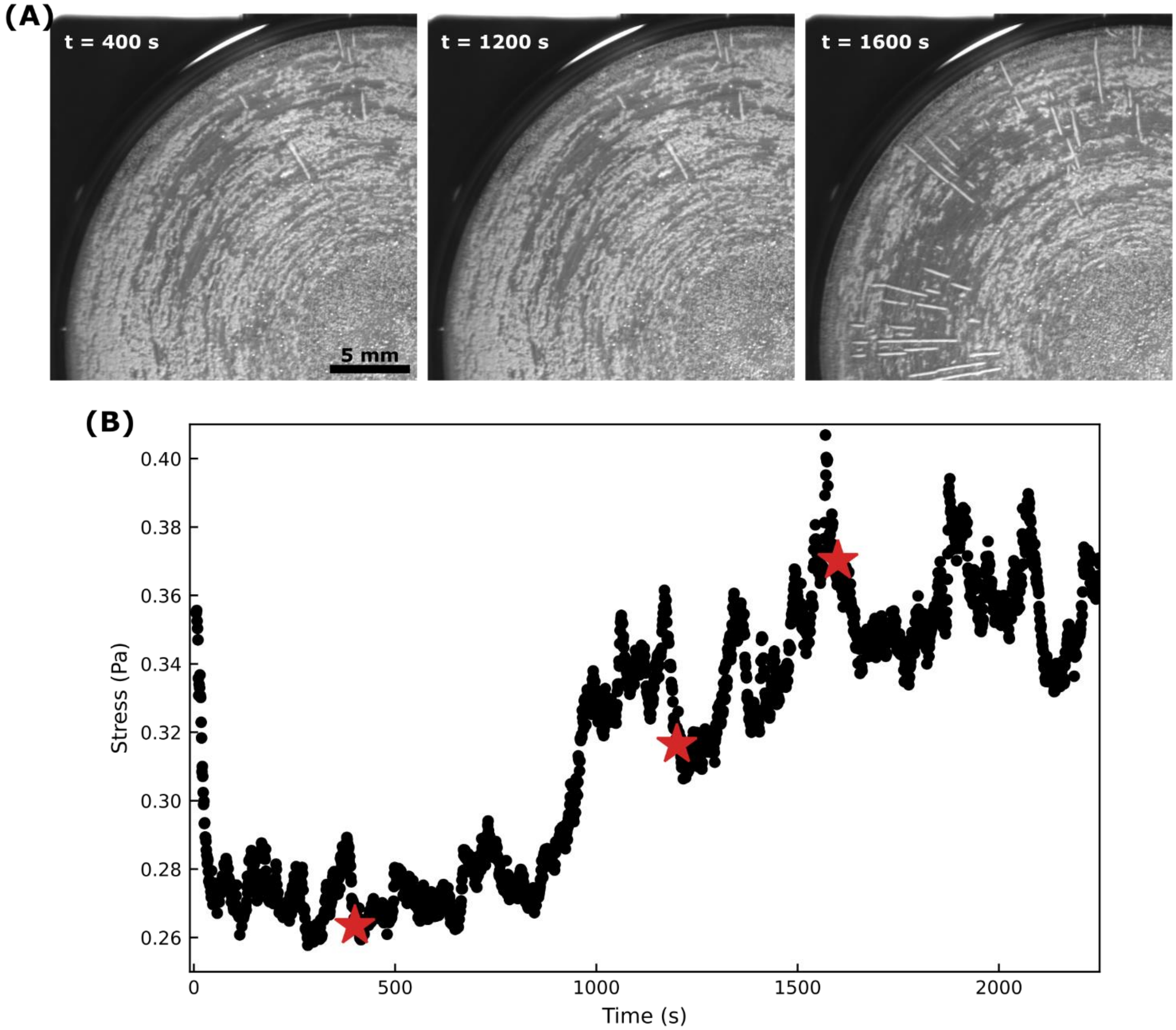


Supplementary Figure 2. The shear rate used during the temperature ramp affects the morphology of mesoscale colloidal clusters. Similar data to that shown in Fig. 2 in the main text is displayed here. (**A**) The stress is measured as a function of temperature as the temperature increases from 23 °C to 34

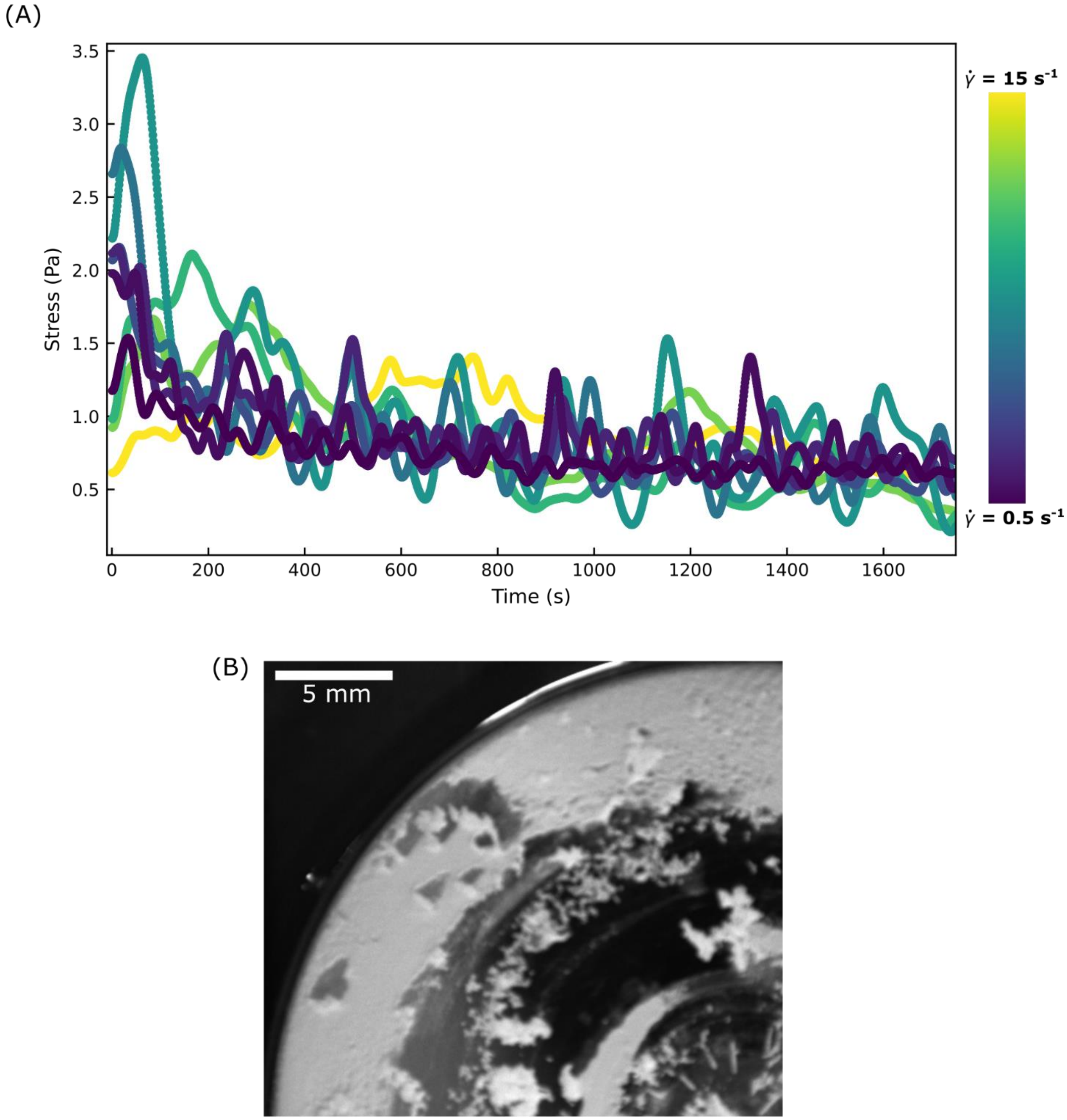
°C at a rate of 0.5 °C/min. During this temperature ramp, we apply a constant shear rate $\dot{\gamma}_{T\uparrow}$. Here, we see data for $\dot{\gamma}_{T\uparrow} = 1\ \mathrm{s}^{-1}$ and $\dot{\gamma}_{T\uparrow} = 4\ \mathrm{s}^{-1}$. (**B**) Images acquired using a 10× (left) or 40× (right) objective immediately after the temperature ramp period where $\dot{\gamma}_{T\uparrow} = 4\ \mathrm{s}^{-1}$ (top) or $\dot{\gamma}_{T\uparrow} = 1\ \mathrm{s}^{-1}$ (bottom). More string-like clusters are observed for samples subjected to the higher shear rate during the temperature ramp to 34 °C.



Supplementary Figure 3. Below the LCST, shear flow elongates the colloid-dense domains along the flow direction. (**A**) Images of the sample while the sample is being sheared and held at 31 °C (below the LCST). At both 1 s^{-1} and 5 s^{-1}, we observe colloid-dense regions elongated in the flow direction. More elongated bands are seen at the higher shear rate. (**B**) We take the two-dimensional autocorrelation of ~500 images at each shear rate. We find a characteristic size in the flow and vorticity directions by locating at what distance the autocorrelation (along the respective directions) decays to 50% (i.e., reaches a value of 0.5 given that the autocorrelation is normalized). We define the aspect ratio as the ratio of this characteristic size in the flow direction divided by the characteristic size in the vorticity direction. The symbols and error bars show the mean and standard error of this ratio for the different shear rates. The aspect ratio shows a roughly monotonic increase with shear rate.



Supplementary Figure 4. Vorticity-aligned floc formation is associated with an increase in the measured stress. (**A**) Macroscale images showing just over a quarter of the parallel-plate geometry. The sample was heated to 34 °C as previously described while a constant shear rate of $\dot{\gamma}_{T\uparrow} = 5\ \mathrm{s}^{-1}$ was applied. The sample was then held at 34 °C with an applied shear rate of $\dot{\gamma}_{hold} = 5\ \mathrm{s}^{-1}$ starting at t = 0 s. Images show the formation of several vorticity-aligned flocs which appear to roll between the bottom and top plate of the parallel-plate geometry. In this case, the bottom glass plate was counter-rotating to allow flocs to remain in the field of view. (**B**) During this period of constant applied shear rate while the sample was held at 34 °C, the stress was measured. The plot shows the stress vs. time with red stars denoting the time points associated with the images seen in (A). See Supplementary Movies 2 and 3 for movies that correspond to this particular experimental run.



Supplementary Figure 5. We performed a set of experiments on a sample identical in composition to what was used in all previous data shown except without xanthan. That is, this sample contains pNIPAM particles at a volume fraction of ~0.3 with 0.05 M NaCl and it contains no xanthan. In this sample, we do not expect particles to form colloid-dense regions at temperatures below the LCST since the depletion attraction induced by the xanthan is no longer present. We perform procedures as described in the manuscript where the sample is placed between parallel plates with a gap of 150 µm and the sample's temperature is increased at 0.5 °C/min while shearing at a rate $\dot{\gamma}_{T\uparrow}$ which was set to a value between 0.5 s^{-1} and 15 s^{-1}. Following this temperature ramp, we continue to shear the sample at a constant rate $\dot{\gamma}_{hold}$ which is set equal to the value used for $\dot{\gamma}_{T\uparrow}$. This period of constant shearing lasts for 30 minutes before we return the sample to room temperature. (**A**) The stress as a function of time is shown for samples sheared at different rates of between 0.5 s^{-1} and 15 s^{-1} while the temperature is held fixed at 34 °C. The shear rate used is indicated by the color. As previously stated, prior to this period of shearing at 34 °C, the sample was sheared (at $\dot{\gamma}_{T\uparrow} = \dot{\gamma}_{hold}$) while the temperature increased from room temperature at a rate of 0.5 °C/min. Unlike the samples which contained xanthan, we do not observe increases in the stress with time. (**B**) We observe the shear induced structures as the sample is sheared while being held at 34 °C. The image shown was taken approximately 18 minutes into the period of constant shear rate with $\dot{\gamma}_{hold} = 4\ \mathrm{s}^{-1}$. We observe what appears to be the colloidal gel breaking into fragments as it is sheared. However, we do not see vorticity-aligned log-like structures which persist. We do sometimes see log-like structures form soon after the sample has reached 34 °C and which are usually near the center of the geometry. But these structures typically do not last more than a couple of minutes.

3 Supplementary Movies

Supplementary Movie 1. This movie corresponds to the image sequence shown in Fig. 3B in the main text. This sample was sheared at a rate of 4 s^{-1} as the temperature increased from 23 to 34 °C. The video shows the sample after this temperature ramp as it is being sheared at 4 s^{-1} while held at 34 °C. Images were taken using a 2× microscope objective. To keep the vorticity-aligned log-like floc in the field of view, we set the bottom glass plate to counterrotate. Scale bar represents 1 mm.

Supplementary Movie 2. This movie corresponds to the image sequence shown in Supplementary Figure 4A. A cropped region of the full field of view shown in Fig. S3A is shown. The sample was heated to 34 °C as previously described while a constant shear rate of $\dot{\gamma}_{T\uparrow} = 5\ \mathrm{s}^{-1}$ was applied. The sample was then held at 34 °C with an applied shear rate of $\dot{\gamma}_{hold} = 5\ \mathrm{s}^{-1}$ starting at t = 0 s. The scale bar represents 2 mm.

Supplementary Movie 3. This movie shows a different region of the sample shown in Supplementary Figure 4A. This is just like Supplementary Movie 2, but we cropped to a different region. The scale bar represents 2 mm.

Supplementary Movie 4. A time series of images of our colloid-polymer mixture was acquired on a Nikon microscope using a 60× objective with differential interference contrast (DIC). Note that this microscope is not the same microscopy setup attached to our rheometer. For this movie, the sample was sealed between a glass slide and coverslip. Images were acquired at 0.5 frames per second as we increased the temperature from room temperature to above the LCST. Temperature was controlled using a Tokai Hit heating stage. We were unable to accurately measure the temperature of the sample as the microscope stage heated. However, from the observed change in the structure of the colloidal gel, we believe that the temperature increased above the LCST of ~33 °C. As the temperature increases, one can observe the colloid-dense regions compressing. Also notice how certain structures in the sample at room temperature look jagged in shape. As the temperature increases, some of those structures become more rounded, indicating that the sample goes from a gel-like state to one more like a fluid-fluid demixed state before finally becoming gel-like again above the LCST. The scale bar represents 20 µm.