## **Electronic Supplementary**

## Poly(*N*-isopropylacrylamide) Microgels at the Oil-Water Interface: Temperature Effect

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**Fig. S1** The typical hydrodynamic radius distribution of 3.2%BA microgels at 293 and 323 K, respectively, as measured by dynamic laser light scattering.



Fig. S2 The typical image of the 3.2%BA microgels measured by TEM.



**Fig. S3** The typical pendant droplet used for the investigation of PNIPAM microgel behaviors at the heptane-water interface, at 294 K.



Fig. S4 The NaCl salt concentration dependence of the heptane-water dynamic interfacial tensions ( $\gamma_t$ ) in the presence of PNIPAM microgels at 298 K.



Fig. S5 The effect of NaCl on  $\gamma_m$  in the presence of  $5 \times 10^{-3} g/mL$  PNIPAM microgels at 298 K.



Fig. S6 Temperature dependence of  $\gamma_t$  in the presence of PNIPAM microgel dispersed in 0.5 mM NaCl solution.



Fig. S7 Three dimensional plots of the heptane-water  $\gamma_t$ -time-temperature in the presence of PNIPAM microgel dispersed in 0.5 mM NaCl solution (Note the minimum was observed at 304 K).



Fig. S8 Three dimensional plots of the heptane-water  $\gamma_t$ -time-temperature in the presence of PNIPAM microgel dispersed in 2.75 mM NaCl solution (Note the minimum was observed at 305 K).



Fig. S9 Temperature dependence of  $\gamma_t$  in the presence of PNIPAM microgels dispersed in 10 mM NaCl solution.



Fig. S10 The appearances of heptane-water interface of 3.2%BA PNIPAM microgels dispersed at various NaCl solutions. Note that aggregates were only found when microgels were dispersed in 10 mM NaCl solution after heating the temperature above VPTT (50 °C).



**Fig. S11** The appearances of 3.2%BA microgel aggregates at the heptane-water interface and at the water-air interface with microgels dispersed in 10 mM NaCl at 50  $^{\circ}$ C (right box). Note that these aggregates were still observable after the temperature cooled to room temperature and stayed for 24 hours (left box).

For all the single droplet experiments, the temperature was also well controlled with an external cryostat. The first single droplet experiment was carried out as following, as shown in Fig. S12. 1, the droplet was created at 295 K. 2, the droplets were hung in heptane for two hours to let microgels adsorb fully onto the heptane-water interface, and then measured the dilatational rheology properties. 3, the temperature was raised to 320 K, in the heating process, the temperature change rate was  $\sim 1$  K/min. The interfacial tension was tracked during the whole heating process, as shown in Fig. 12. After reaching 320 K, the droplet was hung in 320 K for half an hour and at 320 K to reach thermal equilibrium, and then measured the dilatational rheology properties. 4, the temperature was cooled back to 295 K, the initial temperature, in the cooling process, the temperature change rate was  $\sim 1$  K/min. The interfacial tension was also tracked during the whole cooling process, as shown in Fig. 12. 5, after equilibrating for half an hour at 295 K, the dilatational rheology properties were further probed. All the interfacial dilatational rheology properties were summarized in Table 1 for the first single droplet experiment. The second single droplet experiment was carried out as

following, as shown in Fig. S13. 1, the droplet was created at 320 K. 2, the droplets were hung in heptane for two hours to let microgels adsorb fully onto the heptane-water interface, and then measured the dilatational rheology properties. 3, the temperature was reduced to 295 K, in the cooling process, the temperature change rate was  $\sim 1$  K/min. The interfacial tension was tracked during the whole cooling process, as shown in Fig. 13. After reaching 295 K, the droplet was hung in 295 K for half an hour and at 295 K to reach thermal equilibrium, and then measured the dilatational rheology properties. 4, the temperature was raised back to 320 K, the initial temperature, in this heating process, the temperature change rate was  $\sim 1$  K/min. The interfacial tension was also tracked during the whole heating process, as shown in Fig. 13. 5, after equilibrating for half an hour at 320 K, the dilatational rheology properties were summarized in Table 2 for the second single droplet experiment.





320 K

**Fig. S12** Single droplet experiment starting from 295 K: the droplet was heated to 320 K and then cooled back to 295 K.



320 K, initial

295 K

**Fig. S13** Single droplet experiment starting from 320 K: the droplet was cooled to 295 K and then heated back to 320 K.