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# Bell-shaped sol-gel-sol conversions in pH-responsive worm-based nanostructured fluid

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## Experimental details

### Materials

Palmitic acid (97.5 %, Sipo Chemical Co. Ltd., China), N,N-dimethyl-1,3-propanediamine (Rhodia Feixiang Specialty Chemicals), sodium fluoride (AR, Shanghai Chemical Co. Ltd., China), citric acid (99.5%, Admas) and $H_2O_2$ (30 %, Shanghai Chemical Co. Ltd., China) were used without further purification. All other chemicals used here were of reagent grade, and were used as received. Triply distilled water by a quartz water purification system was used in all the measurements.

### Synthesis of N-(3-(dimethylamino)propyl)palmitamide (PMA)

50 mmol (12.82 g) palmitic acid, 75 mmol (7.66 g) N,N-dimethyl-1,3-propanediamine (DMPDA) and 0.15 g NaF were added into a three-necked flask. The reaction mixture was refluxed 10 h at 155–160 °C under $N_2$ atmosphere, during which the by-product $H_2O$ was absorbed continuously by $Al_2O_3$. The excess of DMPDA was removed and the residue was washed with cold acetone (150 ml×2) (each time 10 ml water was added to remove NaF), followed by drying under vacuum at –45 °C to obtain 15.8 g C16AMPM (yield, 93 %) with the purity of 99.90 % (HPLC).

$^1$H NMR (300 MHz, $CD_3OD$), δ/ppm (Fig.1): 0.89 (t, $J$ = 6.18 Hz, 3H), 1.26 (m, 24H), 1.60 (s, 2H), 1.71 (m, 2H), 2.16 (m, 2H), 2.20 (s, 6 H), 2.40 (t, $J$ = 7.68 Hz, 2H), 3.18 (t, $J$ = 6.81 Hz, 2H).

### Sample Preparation

Specific amounts of PMA, HCA and distilled water were introduced into a glass vial followed by mechanical agitation for several minutes (referred to as "3PMA-HCA"). Lower concentration samples were obtained by diluting the stock solution with distilled water. All the samples were fixed at the same molar ratio of PMA/HCA, 3:1, unless otherwise stated. The concentrations of the solutions are given as the concentration of HCA. All the samples were stayed at 40 °C for about 24 h prior to the measurements. The pH values of the solutions were regulated by adding NaOH and/or HCl aqueous solutions dropwise and determined by a Sartorius basic pH meter PB-10 (± 0.01).

### Rheology

Rheological measurements were performed on a Physica MCR 301 (Anton Paar, Austria) rotational rheometer equipped with CC27 (ISO3219) concentric cylinder geometry with a measuring bob radius of 13.33 mm and a measuring cup radius of 14.46 mm. Samples were equilibrated at 40 °C for no less than 20 min prior to the experiments. Dynamic frequency spectra were conducted in the linear viscoelastic region, as determined from prior dynamic stress sweep measurements. All measurements were carried out in the stress-controlled mode, and CANNON standard oil was used to calibrate the instrument before the measurements. The temperature was controlled by a Peltier device, and a solvent trap was used to minimize water evaporation during the measurements.

### Freeze-fracture transmission electron microscopy (FF-TEM)

The FF-TEM investigation was carried out with a freeze-fracture apparatus (Leica, EM BAF060) on a nitrogen-cooled support and a transmission electron microscopy (JEOL Model JEM-2100). The procedure is composed of the following main steps: sample preparation, freezing of the specimen, fracturing about 30 min at high vacuum of $10^{-5}$ Pa from –115 to –95 °C, replication of the fracture face with Pt–C vapour, and finally transmission electron microscopic investigation of the replicas.

**NMR spectroscopy.** $^1$H NMR spectra were recorded on a Bruker AV400 NMR spectrometer at 400 MHz using $CD_3OD$ as solvent. Chemical shifts (δ) are reported in parts per million (ppm) with reference to the internal standard protons of tetramethylsilane (TMS).

### Dynamic light scattering (DLS)

DLS measurements were performed on a ALV/DLS/SLS-5022F (HOSIC LIMITED, Germany) with a 90° back scattering angle and He–Ne laser ($\lambda$= 633 nm). Samples were filtered with a 0.2-μm filter of mixed cellulose acetate to remove any interfering dust particles. To obtain the apparent hydrodynamic radius ($R_{\mathrm{h,app}}$), the intensity autocorrelation functions were analyzed using CONTIN.

### Surface tension measurement

The surface tension (γ) of the surfactant solutions were measured using the pendant drop method with an optical contact angle tensiometer (OCA 40 micro, Data physics, Germany) at 40 ± 0.1°C. The instrument was checked by measuring the surface tension of distilled water before each experiment. For each concentration, every drop was kept for ten minutes, and equilibrium surface tension were taken from the mean value of five times until the change was less than 0.05 mN·m$^{-1}$.

## Additional Results

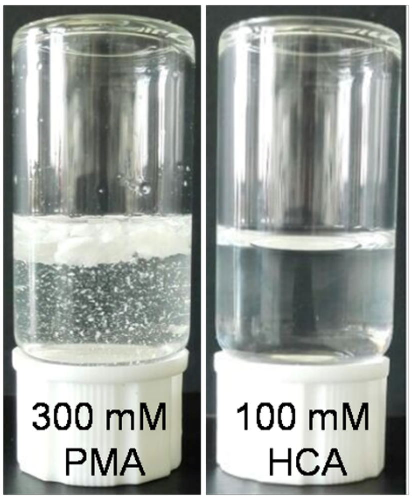

**Fig. S1** Snapshots of single 300 mM PMA and 100 mM HCA solution.

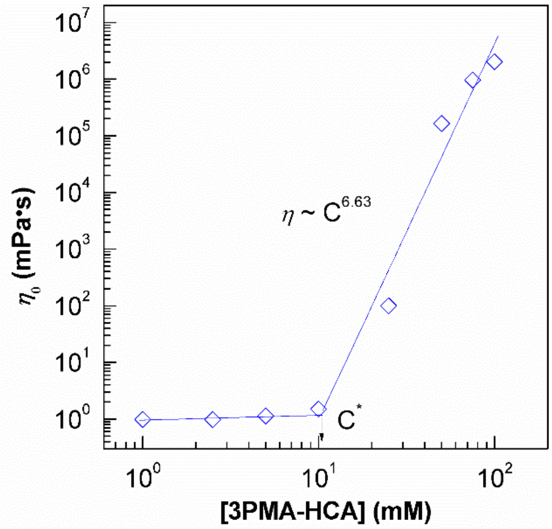

**Fig. S2** Effect of 3PMA-HCA concentration on zero-shear viscosity ($\eta_0$) at pH 6.1.

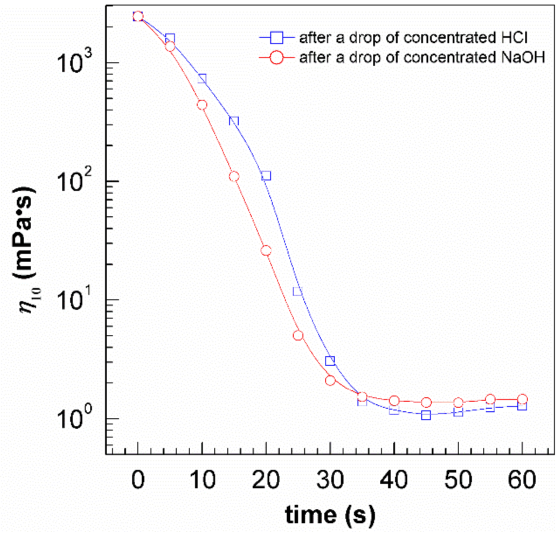

**Fig. S3** The variation of apparent viscosity with time after adding a drop of concentrated HCl or NaOH.

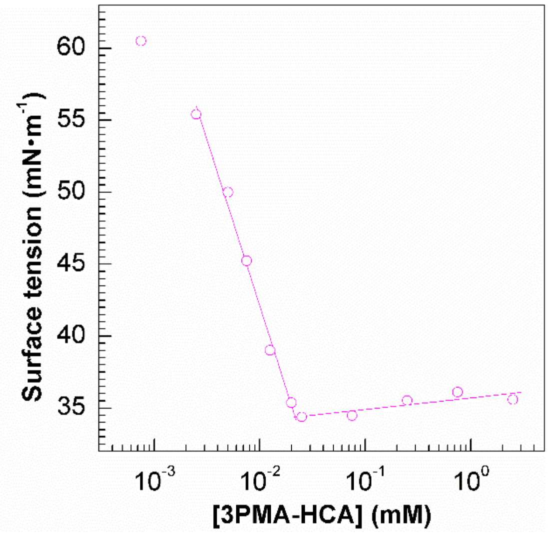

**Fig. S4** The variation of surface tension with concentration at pH 6.1.