Electronic Supplementary Information

Critical behaviour of confined supramolecular soft materials in microscopic scale

Bing Yuan[a,b], Jing-Liang Li[a,c], Xiang-Yang Liu*[a,d], Yu-Qiang Ma[b] and Hong-Yao Xu[d]

1. Experiments

Materials

Gelator N-lauroyl-L-glutamic acid di-butylamide (GP-1, as shown in Scheme 1, >98%) was obtained from Aijnomoto, solvent ethylene glycol (EG, >99%) and propylene glycol (PG, >99%) were bought from Sigma-Aldrich. All of them were used as received.

Rheological Measurements

The rheological measurements were performed on an Advanced Rheological Expansion System (ARES, Research Instruments), using a parallel plate geometry with a diameter of 25 mm. The sol-to-gel transition process occurred between the plates with a fixed gap as specified in the main text. A high cooling rate of 30 ºC per minute was employed for the gel to form. A dynamic temperature ramp test was carried out *in situ* to monitor the change of storage modulus G' and loss modulus G'' during the gelling process, with a constant frequency of 0.1 Hz and a strain of 0.05%. A cover was used to avoid the solvent evaporation or water absorption during the whole measurements.

Optical Observation

The optical micrographs of the network structure of the material were taken in situ from the gel formed within a sealed cell. The gelling system was sandwiched between two pieces of parallel cover glasses with a spacer of a given thickness. The hot solution was quenched to the gelling temperature at a cooling rate of 30 ºC per minute with a temperature controlling system (Linkam Scientific Instrument, THMS600) for the network structure to form. The in-plane morphology of the obtained material was observed using an optical microscope (Olympus BX50).

2. Formulas

The primary nucleation rate J, defined as the number of nuclei successfully generated per unit time unit volume, is determined by the height of the free-energy barrier ΔG^* as[12]

$$J \sim Nf''f^{1/2}B\exp(-\Delta G^*/kT) \qquad (1)$$

where

$$\Delta G^* = \frac{16\pi\gamma_{cf}{}^3\Omega^2}{3(kT)^2(\Delta\mu/kT)^2}f \qquad (2)$$

where N denotes the number of active nucleating centres, f'' and f are factors describing the correlation between the substrate (i.e., nucleating centers), and the nucleation phase, B is the kink kinetics coefficient, k is the Boltzman constant, γ_{cf} denotes the interfacial free energy between the crystal and fluid phases, Ω denotes the volume of the growth units, and $\Delta\mu$ denotes the chemical potential difference between the mother and crystalline phases. The thermodynamic driving force $\Delta\mu/kT$ for the nucleation process can be described as

$$\Delta\mu / kT \cong \frac{\Delta H_{diss}(T^{eq}-T)}{kT^{eq}} \qquad (3)$$

where ΔH_{diss} denotes the molar dissolution enthalpy of the nucleating phase, T^{eq} and T denote respectively the equilibrium and actual temperature at which nucleation occurs. As a result**,** the formulas can be written as

$$\Delta G^{*} \cong \frac{16\pi\gamma_{cf}{}^{3}\Omega^{2} f}{3(kT)^{3}\Delta H_{diss}{}^{2}} / \left(\frac{T^{eq}-T}{T^{eq}}\right)^{2} \sim 1/\left(\frac{T^{eq}-T}{T^{eq}}\right)^{2} \qquad (4)$$

With a given solute concentration, the nucleation rate J can be controlled by changing Tg. An elevated Tg means a lower degree of supercooling and a lower nucleation rate. This will give rise to the formation of fewer but larger fiber networks in a fixed volume.

3. Figures

Fig. S1 Typical micrographs of the network structure of GP-1/EG (1 wt%) gel formed within two spaces of 0.1 mm (A) and 0.2 mm (B). No obvious difference can be obtained in the spherulitic size between the gels formed within these two spaces.

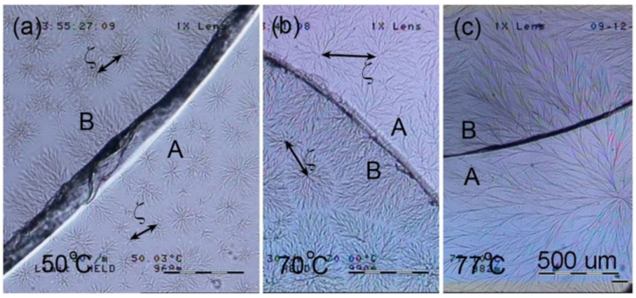
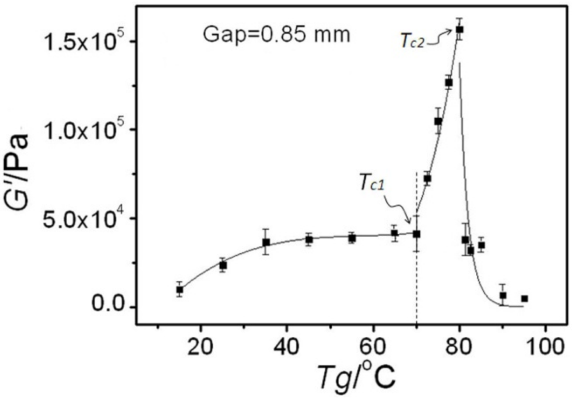


Fig. S2 The storage modulus (G') of the gels formed at different gelling temperatures (T_g), obtained from the dynamic rheological measurements. An elevated T_g (decreased supercooling) corresponds to an increase of G' as a result of the decreased boundary effect within the material. This is determined by two facts. One is the decreased nucleation rate at a lower degree of supercooling (cf. Eqs. 1-3 in the main text), leading to the formation of fewer and larger spherulitic networks in a fixed volume. The other fact is the reduction of the sharpness of the boundary between adjacent fiber networks gives rise to the interpenetration of the fibers from one network to the neighboring networks. This will consequently enhance the elasticity of the material as the fiber networks are integrating into one.



(From reference 13)

Fig. S3 (a-d) Optical micrographs of GP-1/PG (3 wt%) gel formed within a confined (A, 0.1 mm) or unconfined (B, ≥0.2 mm) space. The gelling systems are: (a) 2 wt%, (b) 3 wt%, (c) 4 wt% and (d) 5 wt%. The temperatures for gel formation in all the systems are set at 30 °C. (e) The obtained ζ-solute concentration plots within both spaces. Within a confined space of 0.1 mm, the size of the spherulitic network has been regulated to 210 ± 30 μm (~2.1 times of the space value) for all the solute concentrations (a-b). This regulation effect was applicable until the solute concentration was elevated to larger than 4 wt% (c-d), at which a 0.1 mm space seems to be incapable of adjusting the spherulitic size to the regular value any more (e).