Electronic Supplementary Information (ESI)

Size tenability of fibrous networks of supramolecular soft materials during formation under critical volume confinement

Bing Yuan,[a,b] Jing-Liang Li,[c,b] Xiang-Yang Liu*[b], Yu-Qiang Ma[d,a] and Yingjun Wang[e]

Formulae[1,2]

In a multi-domain network, the initial primary nucleation rate J is governed by the supersaturation σ as :

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

where

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

$$\Delta\mu/kT = \ln(1+\sigma) \cong \frac{\Delta H_{\mathrm{diss}}}{kT^e}(T^{\mathrm{eq}} - T_g) \quad (3)$$

where N denotes the number of active nucleating centres, f'' and f are factors describing the correlation between the substrate, *ie* nucleating centers, and the nucleation phase, B is the kink kinetics coefficient, k is the Boltzman constant, ΔG^* denotes the nucleation energy barrier, γ_{cf} denotes the interfacial free energy between the two phase, Ω denotes the volume of the growth units, and ΔH_{diss} denotes the molar dissolution enthalpy of the nucleating phase, T^{eq} and T_g denote the equilibrium and gelling temperature of the solution, respectively. Here, $\Delta\mu$ corresponds to the chemical potential difference between solute molecules in the fiber state and in the liquid, and $\Delta\mu/kT$ denotes the thermodynamic driving force for the gelation (the degree of supercooling).

Figures

Fig. S1[3] 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.

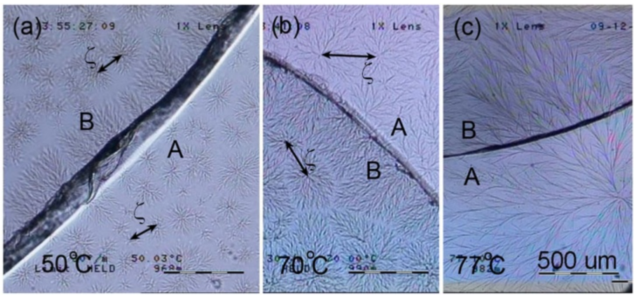


Fig. S2[3] (a-d) Optical micrographs of GP-1/PG gel formed within a confined (A, 0.1 mm) or unconfined (B, ≥0.2 mm) space. The gelling systems are: (a) 2 wt%, (b) 3 wt%, (c) 4 wt% and (d) 5 wt%. The temperatures for gel formation in all the systems are set at 30 ^{o}C. (e) The obtained ζ-solute concentration 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).

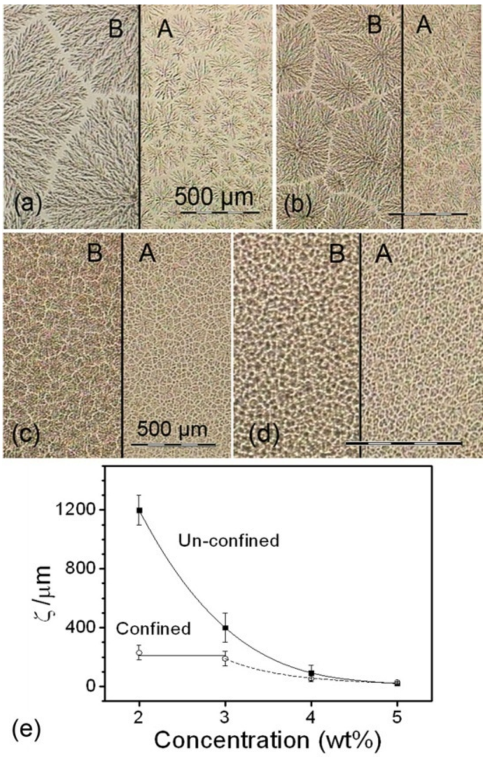


Fig. S3[2] The storage modulus (G') of the gels formed at different gelling temperatures (T_g), obtained from the dynamic rheological measurements. An elevated T_g (decreased supercooling) corresponds to an increase of G' as a result of the decreased boundary effect within the material. This is determined 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.

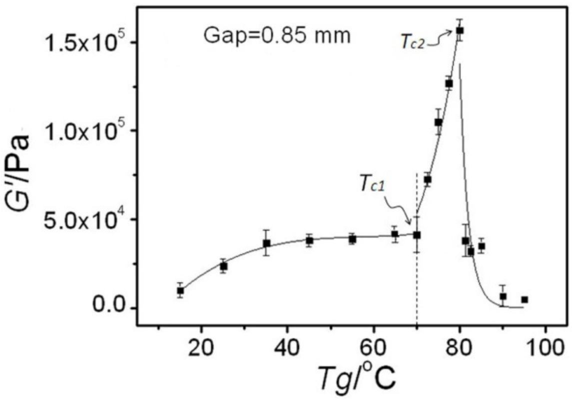
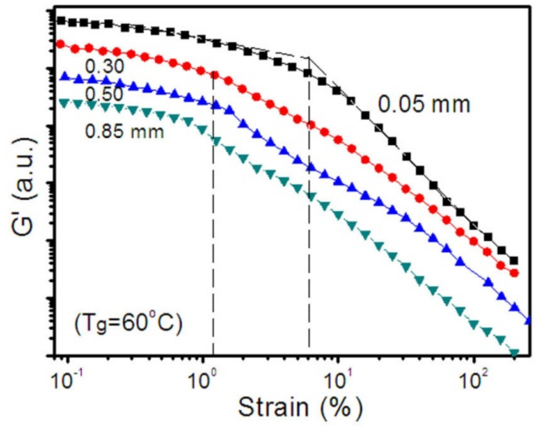


Fig. S4 Strain dependence of *G'* for gels formed within different spaces at 60 °C. γ^c for the gels is displayed with broken lines. From 0.85 to 0.30 mm, γ^c keeps 1.2%; within a much confined space of 0.05 mm, γ^c jumps to ~6.0%. Curves are shifted for clarity.



Reference

(1) J. L. Li and X. Y. Liu, *J. Phys. Chem. B*, 2009, **113**, 15467-15472; X.Y. Liu and P.D. Sawant, *Appl. Phys. Lett., 2001,* **79**, 3518-3520.

(2) B. Yuan, X. Y. Liu, J. L. Li, and H. Y. Xu, *Soft Matter*, 2011, **7**, 1708.

(3) B. Yuan, J. L. Li, X. Y. Liu, Y. Q. Ma and H. Y. Xu, *Chem. Comm.*, 2011, **47**, 2793.