Supplementary Information

Distinct Kinetics of Molecular Gelation in a Confined Space and Its Relation to the Structure and Property of Thin Gel Films

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1. The procedure of thermal control used in the dynamic rheological measurements and evolution of the storage modulus in the process of sol-to-gel transition for the GP-1/PG gelling system.

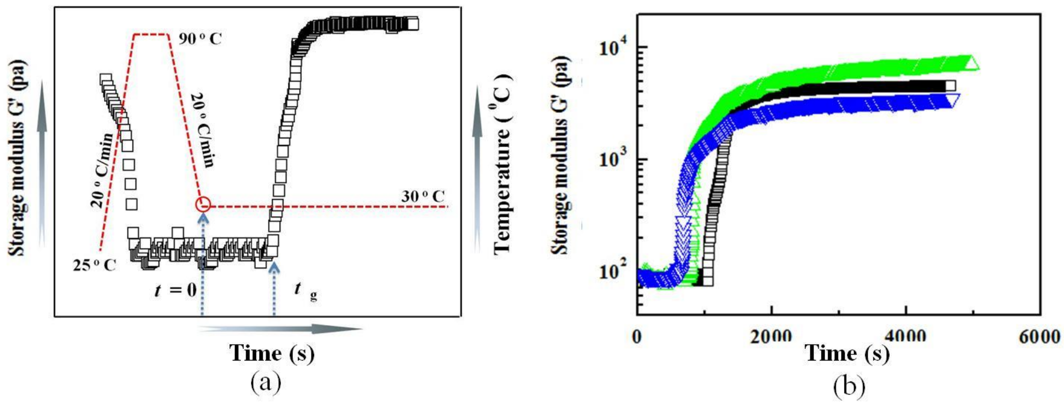


Fig. S1 (a) The procedure of thermal control used in the dynamic rheological measurements for the GP-1/PG gelling system. (b) Evolution of the storage modulus in the process of sol-to-gel transition of a 3 wt % GP-1/PG system at different gap sizes: □: 80 µm, △: 500 µm, ▽: 800 µm.

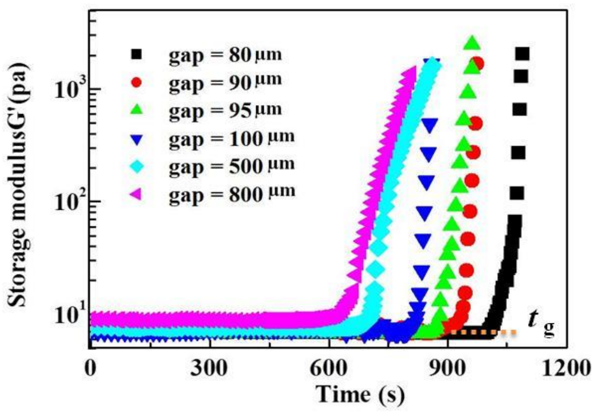
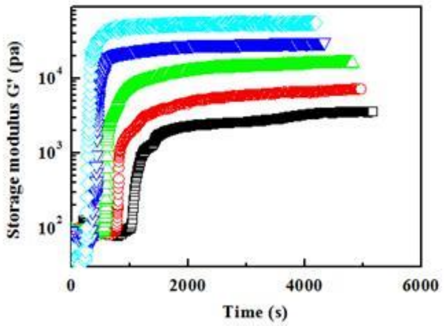
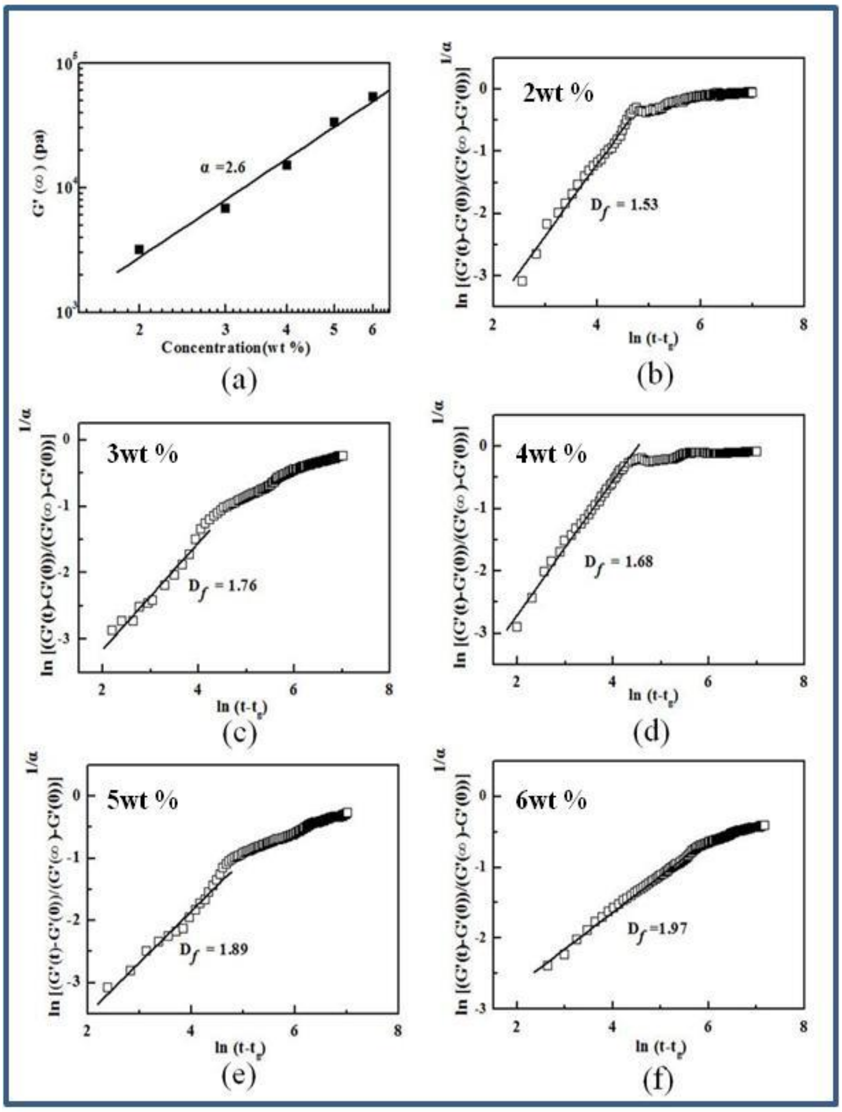


Fig. S2 Evolution of storage modulus at the induction stage of sol-to-gel transition of a 3 wt % GP-1/PG system at different gap sizes.

2. Kinetic analyses of GP-1/PG gel formation

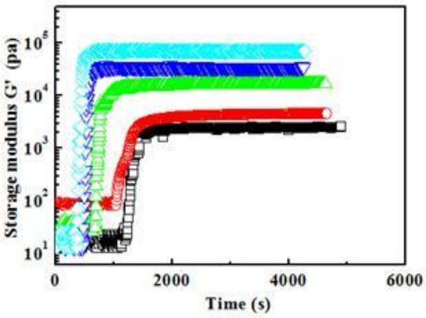


(A)

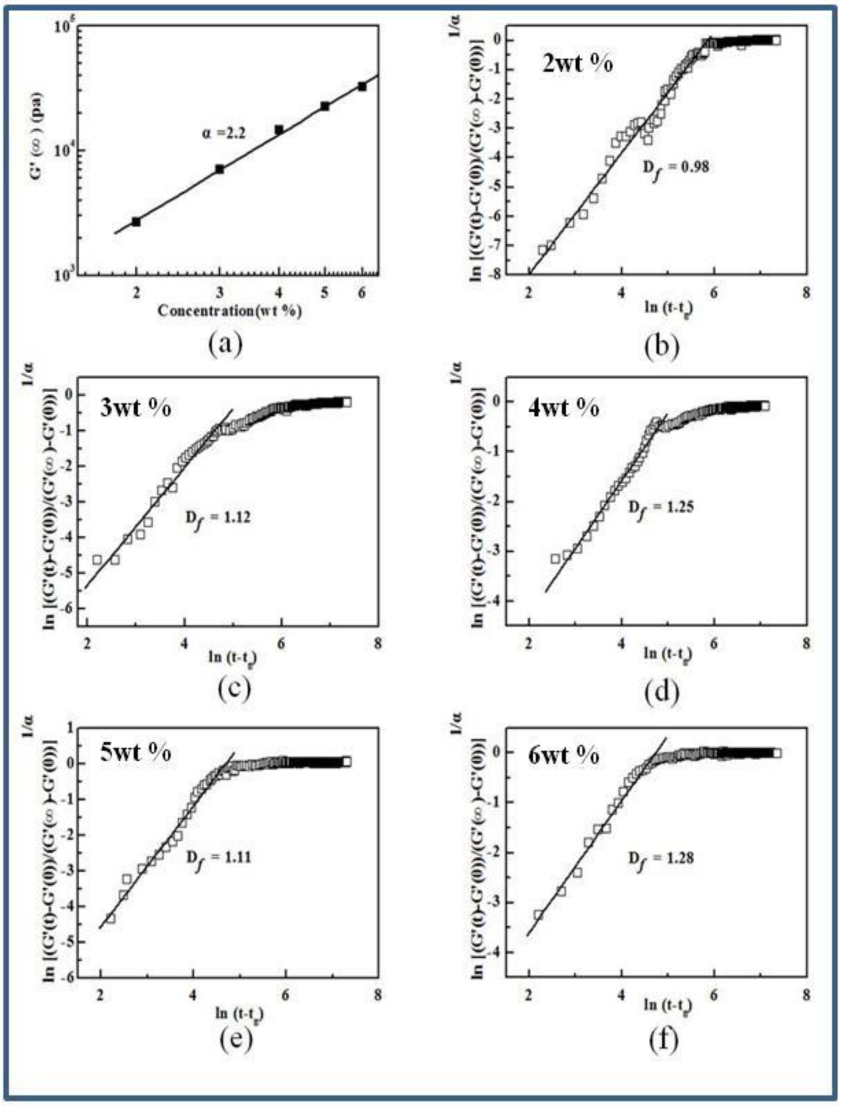


(B)

Fig. S3 A: Evolution of storage modulus in the process of sol-to-gel transition: □: 2wt %, ○: 3wt %, △: 4wt %, ▽: 5wt %, ◇: 6 wt %. B: Fractal analysis of the kinetic data acquired by dynamic rheological measurements and in terms of the extended Dickinson model (eqn (1)) for the GP-1/PG gels of different concentrations. (a) power-law behaviours of the storage moduli of the elastic moduli with respect to the gelator concentrations. (b-e) The linear fits were conducted for the first stage of the kinetic processes to extract the D_f values. All the gels were formed within a gap of 500 μm.



(A)



(B)

Fig. S4 A: Evolution of storage modulus in the process of sol-to-gel transition: □: 2wt %, ○: 3wt %, △: 4wt %, ▽: 5wt %, ◇: 6 wt %. B: Fractal analysis of the kinetic data acquired by dynamic rheological measurements and in terms of the extended Dickinson model (eqn (1)) for the GP-1/PG gels of different concentrations. (a) power-law behaviours of the storage moduli of the elastic moduli with respect to the gelator concentrations. (b-e) The linear fits were conducted for the first stage of the kinetic processes to extract the D_f values. All the gels were formed within a gap of 80 μm.

3. Optical and electron micrographs

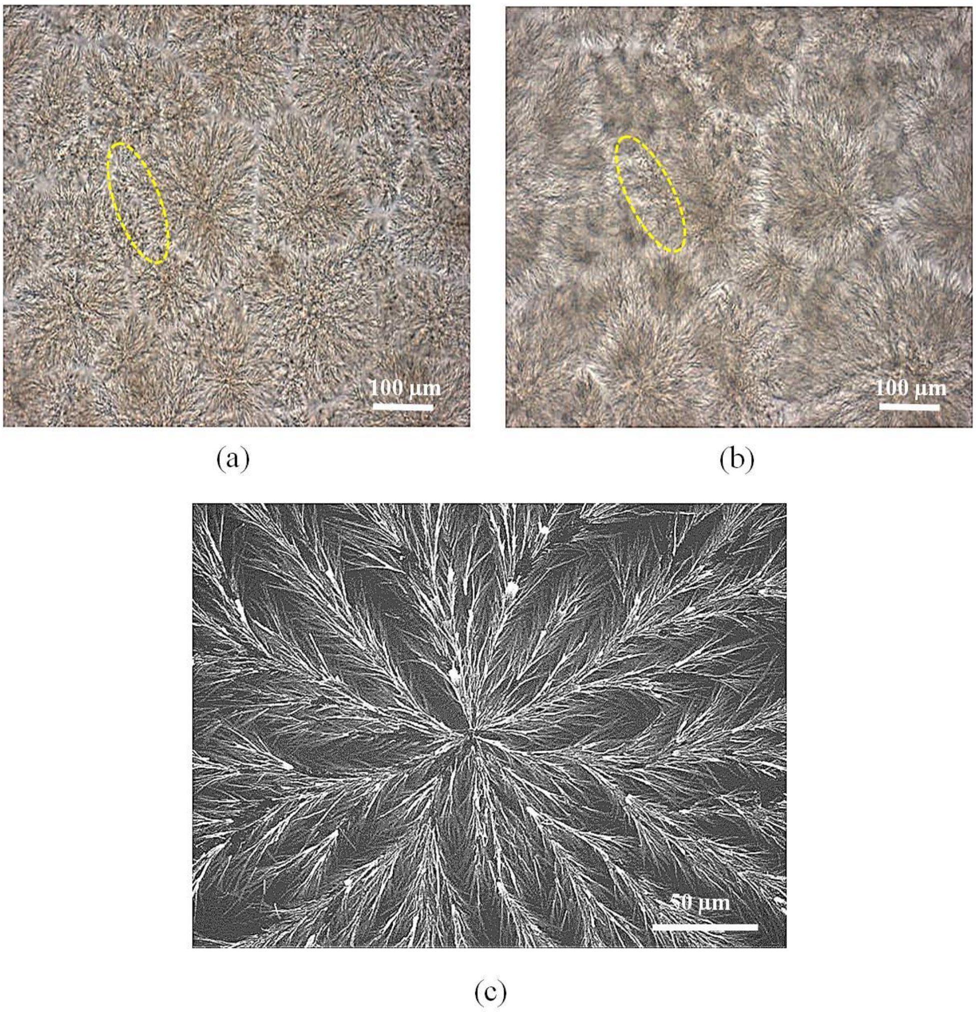


Fig. S5 The microstructures of 3wt % GP-1/PG gel film formed at gap ~ 800 μm. The gelation temperature is 30 ℃ and the cooling rate is 20 ℃/min: Optical micrographs of the 3D spherulitic networks from the middle (a) and lower planes (b), and SEM image (c).

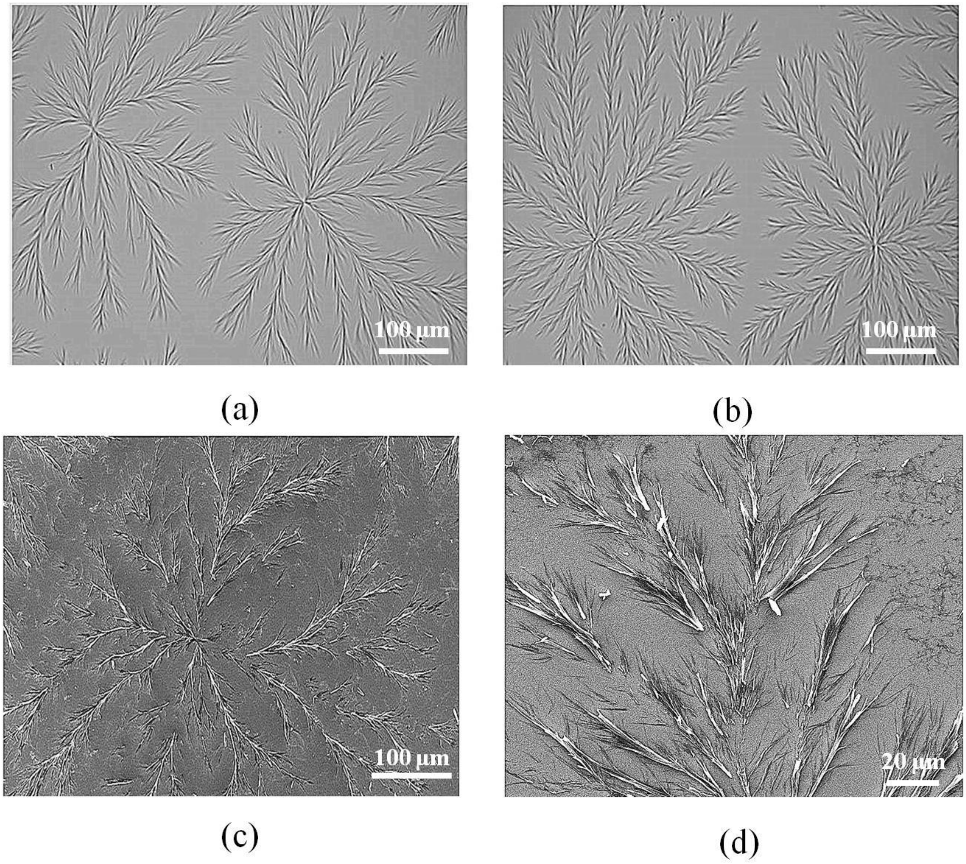


Fig. S6 The microstructures of 3wt % GP-1/PG gel film formed at gap ~ 100 μm. The gelation temperature is 30 ℃ and the cooling rate is 20 ℃/min: (a, b) Optical micrographs; (c, d) SEM images.

4. Estimation of the fractal dimension (D_f) of the spherulitic network by an image analysis method

As in previous studies, [1-4] The fractal dimension D_f of a fiber network can be estimated directly by some image analyses methods, such as the box counting method, Sandbox method and the area - the radius of gyration method. Herein, Box Counting method was used to estimate the values of D_f for the spherulitic networks formed with and without space confinement.

The box counting dimension is computed by superimposing on the object a grid of size ε, counting how many boxes $N(\varepsilon)$ contain the object, and repeating the task for various box sizes ε.

$$N(\varepsilon) \propto \varepsilon^{-Df}$$

where $N(\varepsilon)$ is the number of boxes needed to cover entirely the object and D_f is the fractal dimension. ε is made progressively smaller and the corresponding number of non-empty boxes, $N(\varepsilon)$ are counted.

The logarithm of $N(\varepsilon)$ versus the logarithm of ε, gives a line whose gradient corresponds to D_f. Herein we used a software (FracLac for ImageJ) to do fractal analyses.

For the spherulitic networks formed without space confinement, the SEM micrographs were used to estimate the value of D_f, as shown in Fig. S7.

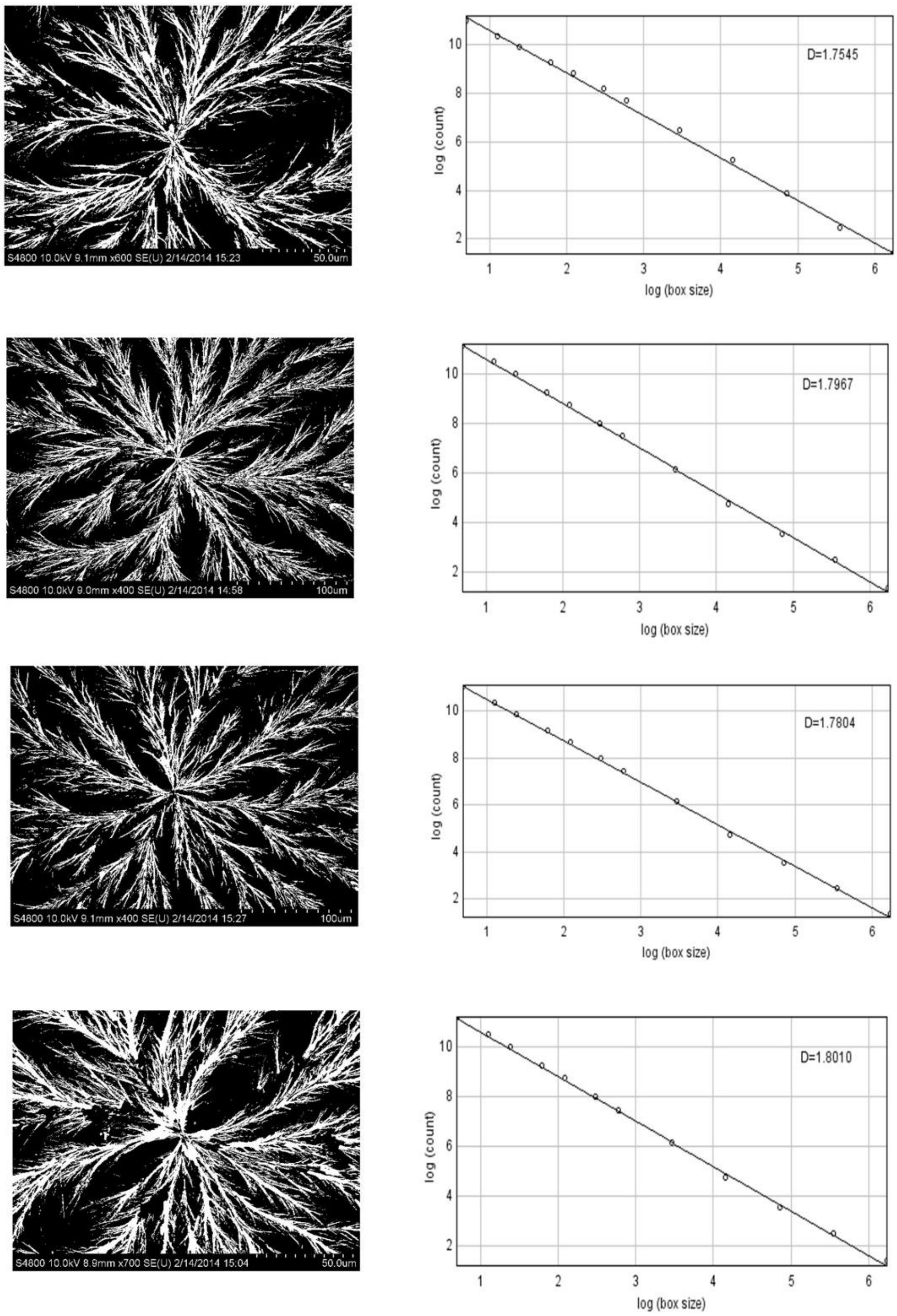


Fig. S7 SEM images (left) and the estimation of D_f by the box-counting method (right, FracLac for ImageJ software) for a 3wt % GP-1/PG gel formed at the gap size of ~ 800 μm.

For the spherulitic networks formed with space confinement, the OM micrographs were used to estimate the value of D_f, as shown in Fig. S8.

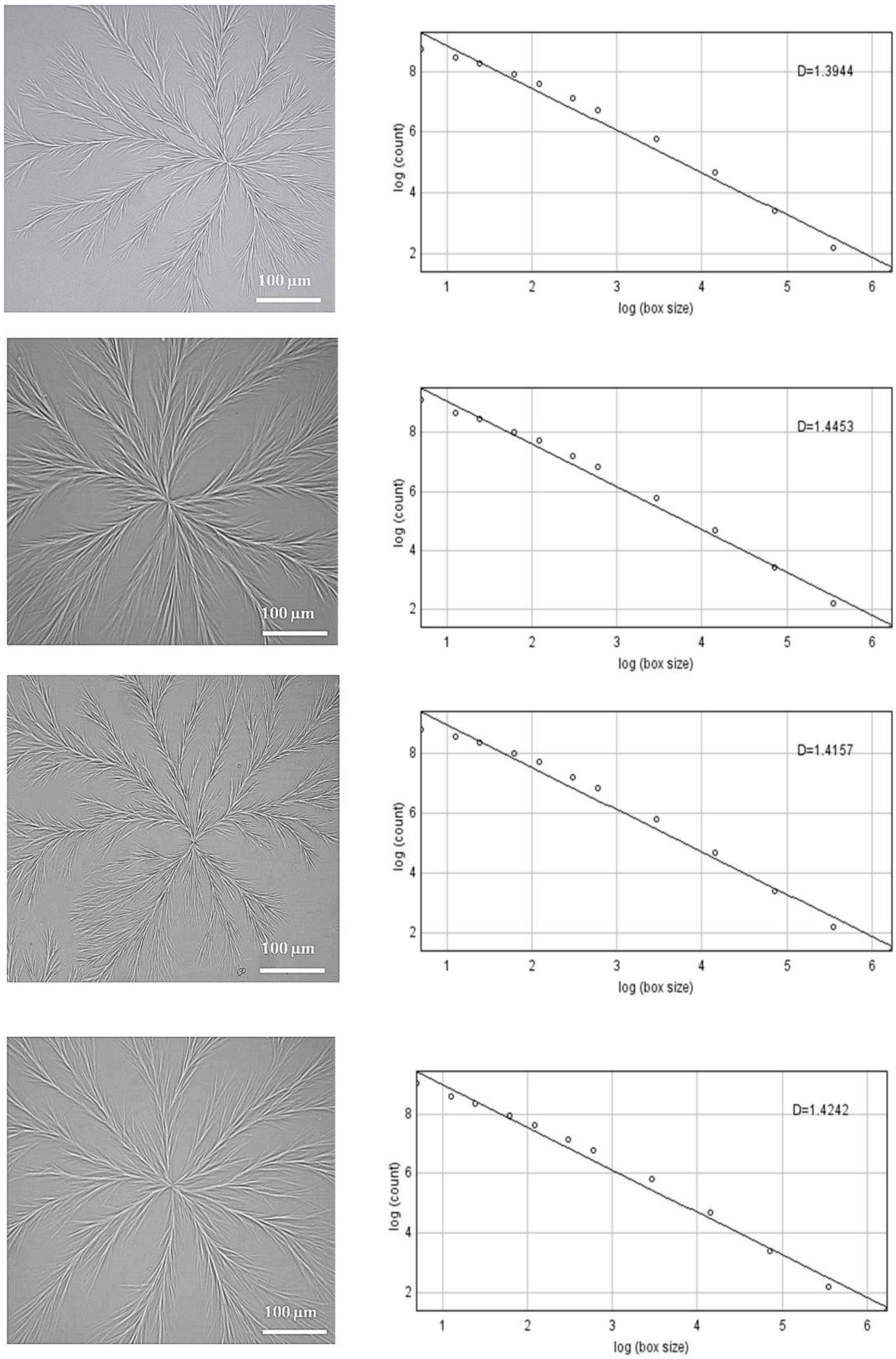


Fig. S8 Optical micrographs (left) and the estimation of D_f (right, FracLac for ImageJ software) for 3wt % GP-1/PG gel formed at the gap size of ~ 50 μm.

5. Rheological properties of the GP-1/PG gels

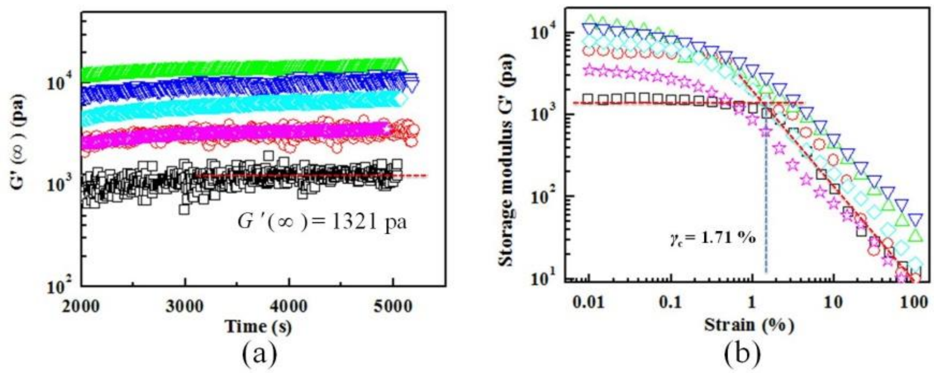


Fig. S9 Raw data of measuring the storage modulus of the quasi-equilibrium state $G'(\infty)$ (a) and the critical strain γ_c (b) of a 3wt % GP-1/PG gel formed at different gap sizes. □: 50 μm, ○: 80 μm, △: 100 μm, ▽: 200 μm, ◇: 500 μm, ☆: 800 μm.

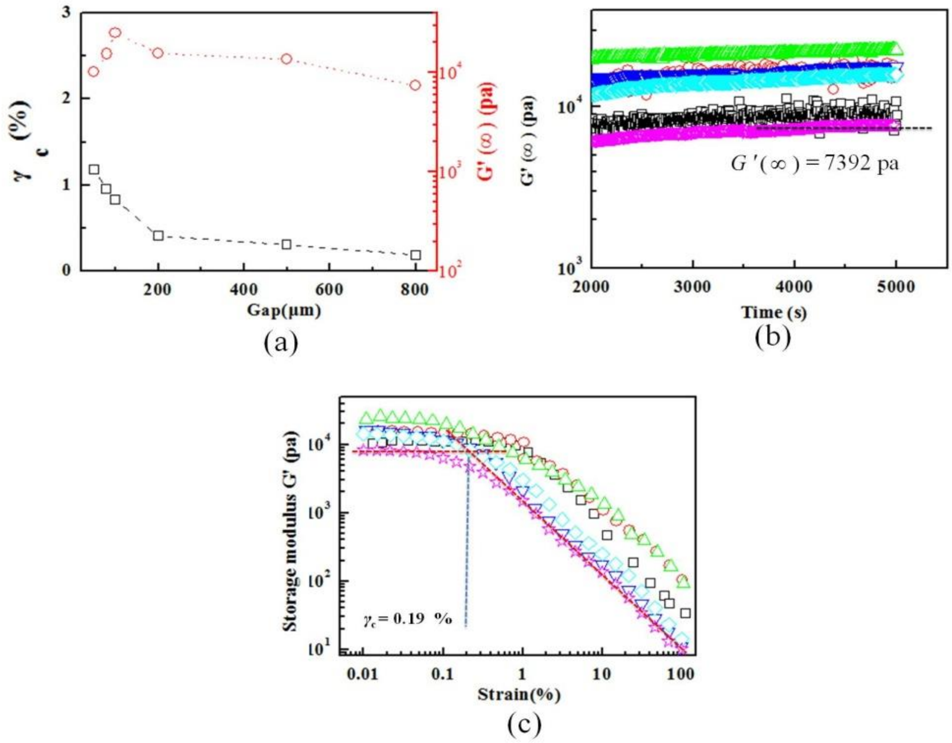


Fig. S10 (a) Variation of the storage modulus (○) at the quasi-equilibrium state and strain (□) as a function of gap size, acquired from the 4 wt % GP-1/PG system. (b,c) Raw data of the measured storage modulus of the quasi-equilibrium state $G'(\infty)$ (b) and the critical strain γ_c (c) from the 4 wt % GP-1/PG gel formed at different gap sizes. □: 50 μm, ○: 80 μm, △: 100 μm, ▽: 200 μm, ◇: 500 μm, ☆: 800 μm.

6. Effects of space confinement on the GP-1/Octanol gelling system

6.1. Structural transition from 3D to quasi-2D fiber network

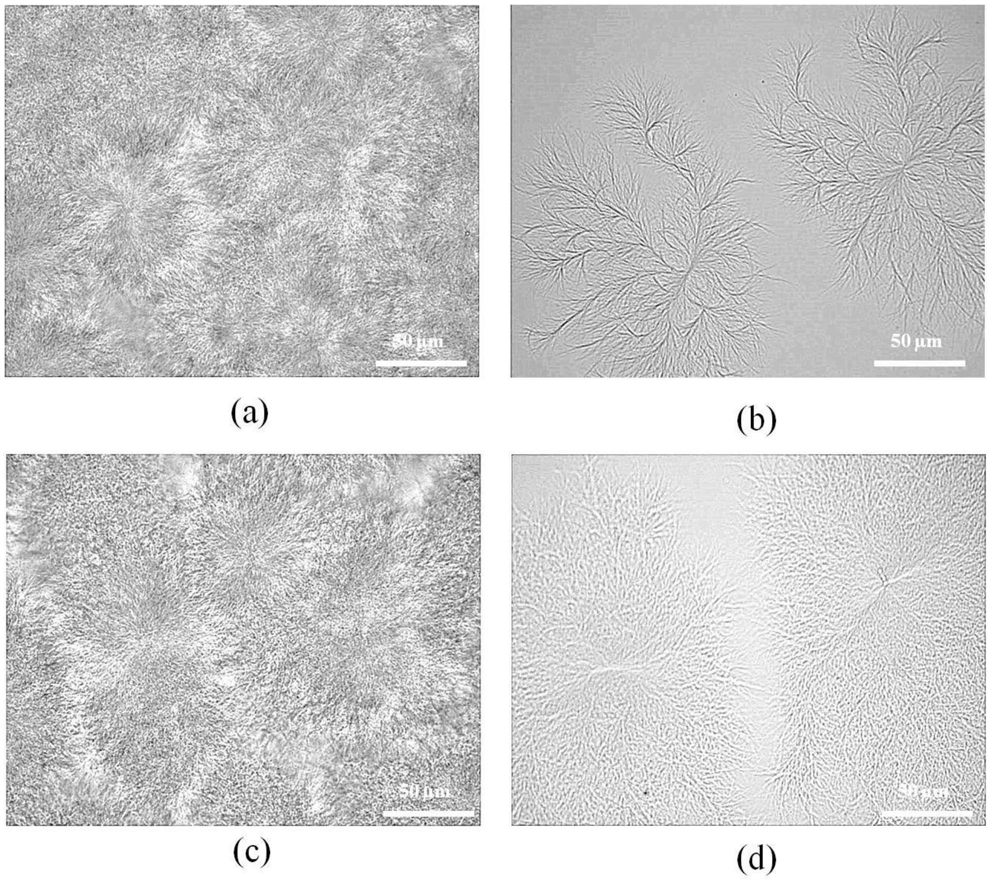


Fig. S11 Optical micrographs of the spherulitic networks obtained from 6 wt % (a, b) and 10 wt % (c,d) GP-1/octanol gels. (a,c) gap ~ 200 μm, (b,c) gap ~ 50 μm. The gelation temperatures for the 6 wt % and 10 wt % GP-1/octanol are set at 15 ℃ and 25 ℃, respectively.

6.2 Modification of the rheological properties of the GP-1/Octanol gel films

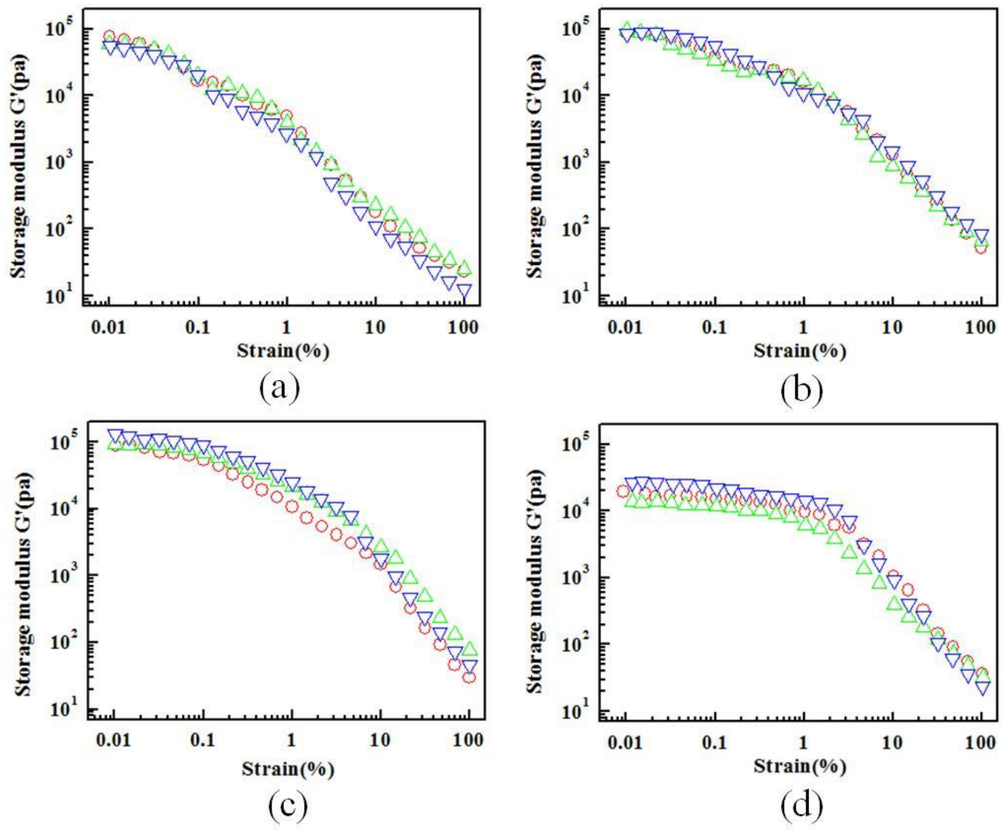


Fig. S12 The critical strain γ_c from the 10 wt % GP-1/ octanol gel formed at the gelation temperature of 25 ℃ with a cooling rate of 20 ℃/min ：(a) gap=200 μm；(b) gap=100 μm；(c) gap=80 μm；(c) gap=50 μm. ○: First measurement; △: Second measurement; ▽: Third measurement.

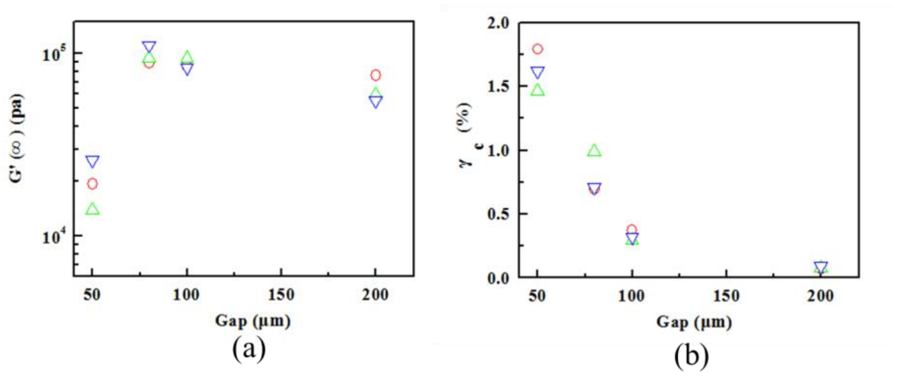


Fig. S13 Variation of the storage modulus (a) at the quasi-equilibrium state and the critical strain (b) as a function of gap size. 10 wt % GP-1/ octanol system is used. The gelation temperature is 25 ℃ and the cooling rate is 20 ℃/min. ○: First measurement; △: Second measurement; ▽: Third measurement.

References

1. E. Fernández, J.A. Bolea, G. Ortega and E. Louis, *J. Neurosci. Meth.*,1999, **89**, 151.
2. G. Landini, P. I. Murray and G. P. Misson, *Invest. Ophth. Vis. Sci.* , 1995, **36**, 2749.
3. T. G. Smith, Jr, G. D. Lange and W. B Marks, *J. Neurosci. Meth.*, 1996, **69**, 123.
4. A. N. D. Posadas, D. Giménez, M. Bittelli, C. M. P. Vaz and M. Flury, *Soil Sci. Soc. Am. J.*, 2001, **65**, 1361.