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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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Thin films of molecular gels formed in confined space have potential applications in transdermal delivery, artificial skin and molecular electronics, etc. The microstructures and properties of thin gel films can be significantly different from that of their bulk counterparts. However, so far a comprehensive understanding of the effects of spatial confinement on the molecular gelation kinetics, fiber network structure and related mechanical properties are still lacking. In this work, using rheological techniques, we investigated the effect of one-dimensional confinement on the formation kinetics of fiber network in molecular gelation process. Fractal analyses of the kinetic information in terms of an extended Dickinson model enabled us to describe quantitatively the distinct kinetic signature of molecular gelation. The structural features derived from gelation kinetics supports well the fractal patterns of the fiber networks acquired by optical and electronic microscopies. With the kinetics-structure correlation, we can gain an in-depth understanding of the confinement-induced differences in the structure and consequently the mechanical properties of a model molecular gelling system. Particularly, the confinement induced structural transition, from a three-dimensional, densely compact spherulitic network composed of highly branched fibers to a quasi-two-dimensional sparse spherulitic network composed of less branched fibers and entangled fibrils at the boundary areas, renders a gel film to become less stiff but more ductile. Our study suggests here a new strategy of engineering the fiber network microstructure to achieve functional gel films with unusual but useful properties.

Introduction

Effects of spatial confinement on soft matter systems have attracted great interest in recent years. Particular attention has been paid to the effects of one-/two-/three-dimensionally (1D/2D/3D) spatial confinement at nanoscale sizes on the assembly, phase transition and crystallization of molecules.^[1-13] For instance, it has been found that molecular packing, orientation, translation, rotation, motion, and reactivity within carbon nanotubes (i.e. 1D confined space) would be dramatically different from that occurring in a free space;^[4] some polymers could undergo fluid-gel phase transition when a 1D spatial confinement reached to the size of a macromolecule.^[6] Besides, a 2D confinement at nanoscale could enable the polymeric crystallization to switch from preferred crystalline orientation to random orientation.^[8] Block copolymer placed inside spherical nanopores (i.e. 3D confined space), could enable new phase formation.^[12, 13] However, in the literature there are very few studies to address the effects of spatial confinement on small molecular gelling systems. Chen et al^[14] demonstrated firstly the dramatic role of 2D confinement in gelation of small molecules. They observed the changes of the fiber network structure and thermal properties of a molecular gel. Later, Yuan and co-workers^[15, 16] revealed an interesting critical behaviour of molecular gelation under 1D

confinement at a micrometer scale, and showed that the microstructure and macroscopic properties of a gel film were different from that of its bulk counterpart. In this work, we aim at understanding how a spatial confinement affects the nucleation and growth kinetics of fiber network, which in turn modifies the structure and properties of a thin molecular gel film.

Nucleation and growth of a fiber network of a small molecular gelator in a solvent governs the formation of a gel.^[17] As demonstrated in previous studies,^[18-24] time evolution of the storage modulus G' during a gel formation can provide important kinetic information of the nucleation and growth of fiber network. Herein we employed the dynamic rheology technique to obtain kinetic data and analyzed in terms of an extended Dickinson model.^[23] This method allowed us to extract the structural parameter, i.e. the fractal dimension D_f , of fiber network from the kinetic data, hence enabling a quantitative description of the effect of spatial confinement on the kinetic feature of molecular gelation. In combination with microstructure characterization by optical and electronic microscopies, we established a direct kinetics-structure relationship and provided a new understanding on the structure-property correlation for the confined gel films.

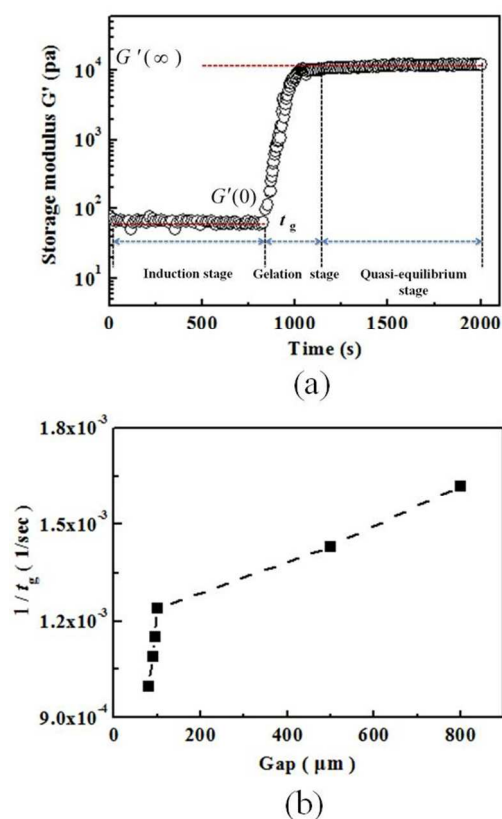


Fig.1 (a) Representative example of dynamic rheological measurements from the gelation process of a 3wt % GP-1/PG system. The gap size was 100 μm . The three-stage of a gel formation is also illustrated. (b) Variation of $1/t_g$ as a function of the gap size for the gelation of 3wt % GP-1/PG.

Materials and Methods

Materials: Gels formed by the H-bonding gelator molecule, *N*-lauroyl-L-glutamic acid di-*n*-butylamide (GP-1, >98 %, Sigma) in propylene glycol (PG, >99 %, Sigma), was chosen as a model system. Such a typical H-bonding gelling system has been well-studied in our previous studies,^[17, 25] which provides a strong basis for the investigation of the space confinement effects on the nucleation and growth of fiber network and structure-property relationship involved in the molecular gelation phenomenon. In a bulk volume of PG, the critical gelation concentration (CGC) of GP-1 molecules at room temperature is ~ 2 wt %. Above this value, GP-1 molecules self-organize into three-dimensional crystalline fiber networks that consist of spherulitic domains.^[25-28]

Microstructure characterizations: For optical observation, gel films were prepared by sealing the hot solutions of GP-1 in PG in home-made glass cells. To examine the effect of 1D confinement on gel microstructures, the gap between the top and bottom glass cover slips was tuned from ~ 800 to ~ 50 μm . An optical microscope (Olympus, BX51) with a temperature-controlled stage was used to acquire images of fiber networks, which were converted to digital images through a color video camera (COOL SNAP 3.3MC). GP-1 xerogels were obtained by a freeze-drier (Linkam Scientific Instrument, FDCS 196), and the microstructure of the xerogels were examined with a scanning electronic microscope (SEM, JEOL JSM-7500F). For a better contrast under the SEM microscopy, the GP-1 xerogels were

coated with gold for 30 s at 30 mA.

Rheological measurements: A rheometer (Physica, MCR-301) with parallel plate geometry (25 mm in diameter) was used to measure the dynamic rheological properties of the GP-1/PG gelling system. In accordance with the above optical microscopic imaging, the gap between the two plates was controlled in between 50 and 800 μm . For the sol-to-gel transition occurring at a gap size in the range from 80 to 800 μm , dynamic rheological measurement was performed to record the time-dependent changes of the storage modulus G' (Fig. 1 a). After G' reached a quasi-equilibrium state (i.e. the completion of gel formation), the strain sweep (from 0.01 to 100%) was conducted to examine the critical strain at which the gel network was ruptured. When the gap size was reduced to 50 μm , it was not feasible to accurately measure the dynamic rheological properties of the gels, due to the instrumental limitation in controlling such a small gap. Thereby, dynamic measurement and subsequently the strain sweep in such cases were conducted after G' of a gelling system reached the quasi-equilibrium state. In all dynamic measurements, the strain and frequency were set at 0.05%, and 1 Hz, respectively. All the GP-1/PG gel samples used in this study were formed at 30 $^{\circ}\text{C}$, with a cooling rate of 20 $^{\circ}\text{C}/\text{min}$. More details of thermal control are referred to Fig. S1 in the ESI.

Results and Discussion

Distinct kinetic pathway in confined gelation

Fig. 1a shows a typical dynamic measurement of G' during the sol-to-gel transition of a 3wt % GP-1/PG system at a gap size of 100 μm . More measurements at other gap sizes (from 80 to 800 μm) are given in the supplementary information (Fig. S1, ESI†). According to previous studies,^[18-24] the dynamic change of rheological property during the sol-to-gel transition is correlated with the nucleation and growth of fiber networks (Fig. 1a). Primary nucleation and growth of crystalline fibers occur mainly at the induction stage. With increase of the volume fraction of fibers to a critical value, the onset of G' appears. We refer to this point as the start point of gelation (t_g). After that, G' increases quickly by a few orders of magnitude, corresponding to a rapid growth of the volume fraction of fractal fibers until a space is filled with fiber networks. After that, G' increases slowly to reach a quasi-equilibrium state, indicating a full presence of the gel phase.

For a given GP-1/PG system (3 wt %) gelled at different gap sizes in the range from 800 to 80 μm , we first investigated the confinement effect on the nucleation and growth of fibers at the induction stage. The raw data of the dynamic rheological measurements at different gap sizes are given in Fig. S2, ESI†. In Fig. 1b, the value of $1/t_g$, which measures the nucleation rate at the induction stage, shows dependence on the gap sizes. One can see a sharp drop of $1/t_g$ when the gap is less than 100 μm . This is an indication of important impact of spatial confinement on the primary nucleation-and-growth kinetics of fibers.^[15] The gap size ~ 100 μm is referred to as the critical point below which the confinement starts to influence significantly the molecular gelation. Herein the gap size above and below 100 μm are defined as the unconfined and confined regimes, respectively, which are used throughout this paper.

To describe the confinement effect on the kinetic behaviours of fiber network formed at the gelation stage ($t > t_g$), we introduced here an extended Dickinson model^[23] to do the fractal analysis of the kinetic data. According to this model, the rheological kinetics of a gel formation can be related to the fractality of the resulting fiber network through

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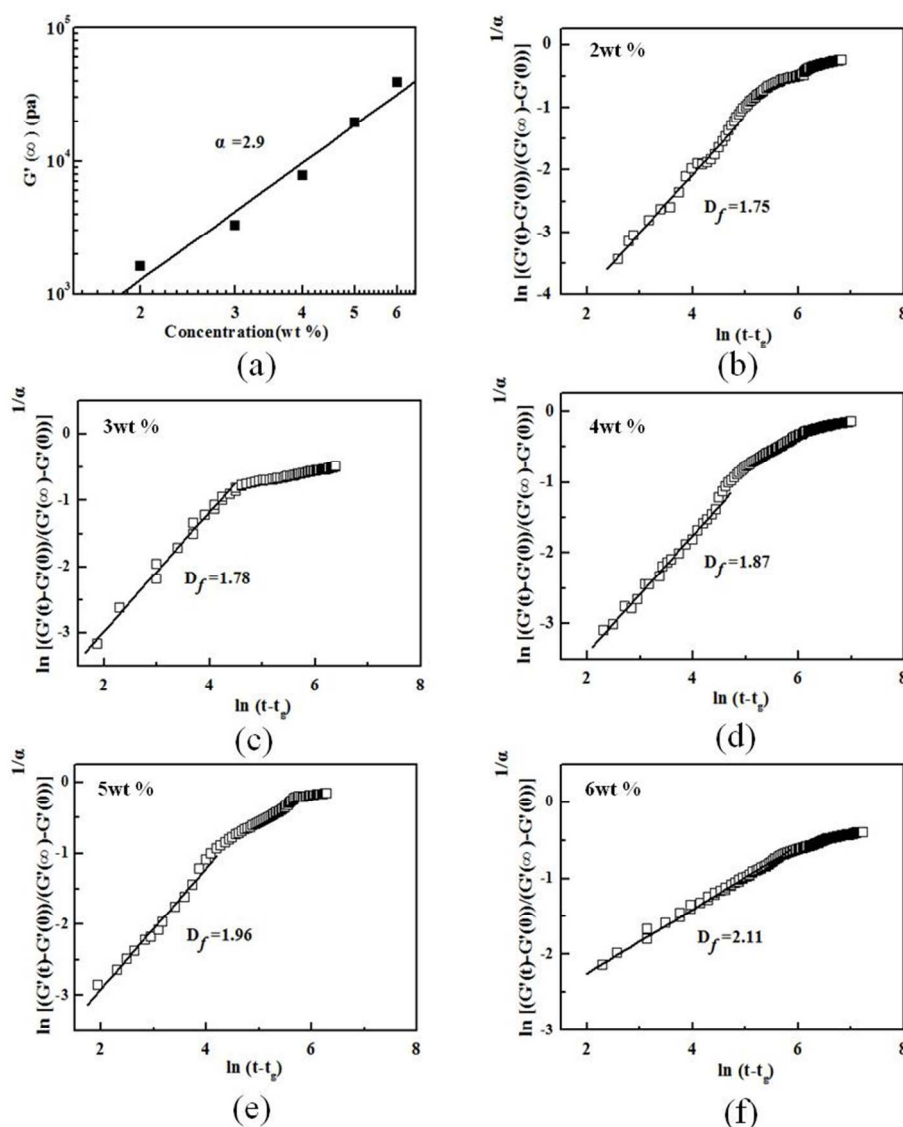


Fig.2 Fractal analysis of the kinetic data acquired by dynamic rheological measurements and in terms of the extended Dickinson model (eqn (1)) for the GP-1/PG gels of different concentrations. (a) power-law behaviours of the storage moduli of the elastic moduli with respect to the gelator concentrations from the GP-1/PG gels. (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 800 μm .

$$\ln \sqrt{\frac{G'(t) - G'(0)}{G'(\infty) - G'(0)}} \propto \frac{3 - D_f}{D_f} \ln(t - t_g) \quad (1)$$

where $G'(0)$, $G'(t)$ and $G'(\infty)$ are the storage moduli at time 0, t , and infinity, respectively (see Fig. 1a). The fractal dimension D_f is a measure of the extent of the compactness of a fiber network microstructure.^[22, 29-33] Here α is the scaling factor, which can be

derived from the scaling law described by $G'(\infty) \propto C_0^\alpha$.^[34] C_0 is the total gelator concentration of a gel. From the linear fit of $\ln[(G'(t) - G'(0))/(G'(\infty) - G'(0))]^{1/\alpha}$ against $\ln(t - t_g)$, D_f can be extracted from the slope of $(3 - D_f)/D_f$. In the calculations, $G'(0)$ is the storage modulus at t_g , and $G'(\infty)$ is the mean value of the last several data points of the quasi-equilibrium stage that shows negligible changes of G' as time increases.

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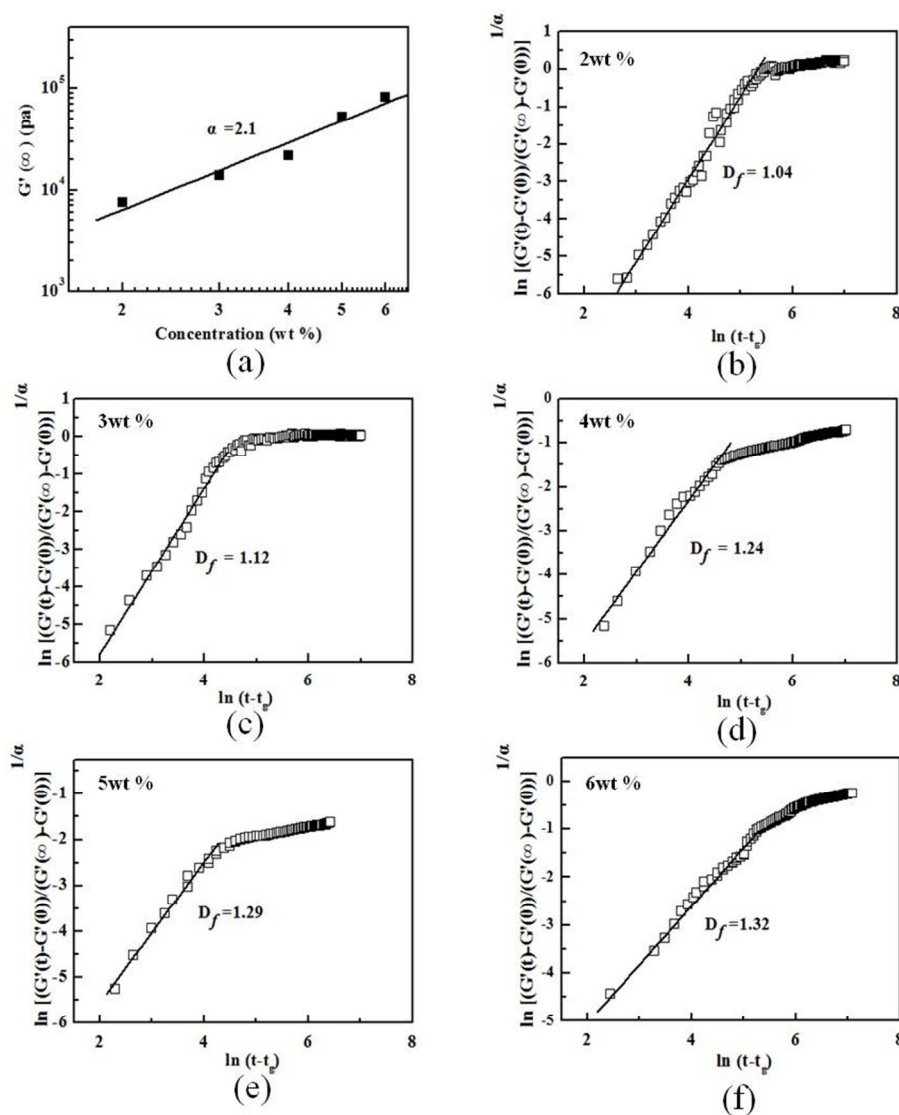


Fig.3 Fractal analysis of the kinetic data acquired by dynamic rheological measurements and in terms of the extended Dickinson model (eqn (1)) for the GP-1/PG gels of different concentrations. (a) power-law behaviours of the storage moduli of the elastic moduli with respect to the gelator concentrations from the GP-1/PG gels. (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 100 μm .

Fig.2 gives the Dickinson-based kinetic analyses for the GP-1/PG gels formed in the unconfined regime (e.g. gap~800 μm). The scaling factor α (~2.9) was derived from the power-law behaviour of the plateau values of the storage moduli ($G'(\infty)$) with respect to the gelator concentrations (from 2 to 6 wt %) (Fig. 2a). In this gelator concentration range, the Dickinson-derived D_f was found to be in the range of 1.75 - 2.11 (Fig. 2b-f). Similar kinetic feature was shown for the gels formed at the gap of 500 μm (see Fig. S3, ESI†). As in previous studies,^[19, 23, 34] here the value of $D_f \sim 2.0$ is a kinetic signature of compact spherulitic

networks composed of highly branched fibers, as demonstrated below.

With decreasing the gap size to the confinement regime ($\text{gap} \leq 100 \mu\text{m}$), the GP-1/PG system exhibited different kinetic feature of nucleation-and-growth of fiber networks. Fig. 3 shows the fractal analyses of gelation kinetics for the gels formed at a gap of 100 μm . While the scaling factor $\alpha \sim 2.1$ was obtained (Fig.3a); the Dickinson-derived kinetic parameter D_f is found to be in the range from 1.04 to 1.32 (Fig.3b-f). Similar results were also obtained for the GP-1/PG system gelled at the gap of 80 μm

(see Fig. S4, ESI †). Such a low value of D_f is a characteristic of open network structures composed of less branched fibers. [19, 23, 34] For the GP-1/PG gelling system with the gelator concentration in the range of 2–6 wt %, tuning the gap size from 800 to 80 μm shows very similar effect of confinement length on the fractal dimension of fiber network (Fig. 4), verifying the distinct kinetic feature of the confined gelation. To the best of our knowledge, the above quantitative description of the kinetic feature for confined gel formations has not been reported in the previous studies.

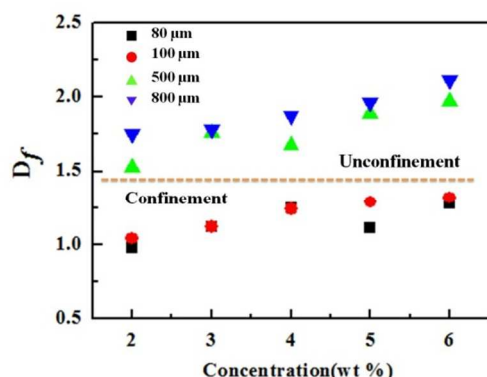


Fig. 4 Distribution of D_f values in the GP-1/PG gels with different gelator concentrations and formed at different gap sizes (■: 80 μm , ●: 100 μm , ▲: 500 μm , ▼: 800 μm). The gelation temperature and cooling rate are 30 $^{\circ}\text{C}$ and 20 $^{\circ}\text{C}/\text{min}$, respectively.

The low D_f values and the slow kinetics of gelation in the confined regime (Fig. 1b) suggest that the primary/secondary nucleation of fibers/branches in the 1D confined space are restricted, leading to the formation of more open and less branched fiber networks. This was verified by the structural characterizations of the gel samples by optical and electron microscopies.

Effect of confinement on gel structures

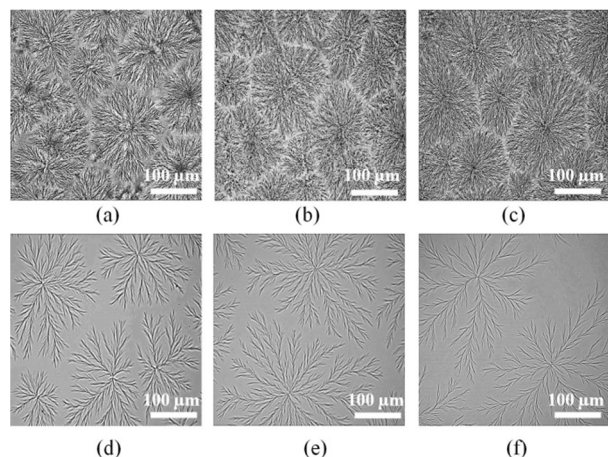


Fig. 5 Optical micrographs of the spherulitic networks of a 3 wt % GP-1/PG gel formed with different gap sizes: (a) ~800 μm ; (b) ~500 μm ; (c) ~200 μm ; (d) ~100 μm ; (e) ~80 μm ; (f) ~50 μm . The scale bar is 100 μm .

Fig. 5 (a-f) shows optical micrographs from a GP-1/PG gel (3 wt %) formed by tuning the gap size from ~800 to 50 μm . One

can see that the space confinement induces a structural transition from 3D to quasi-2D fiber network. At larger gap sizes (from 800 to 200 μm), 3D spherulitic networks (Fig. 5a-c) composed of highly branched fibers are displayed, and the average diameter of the spherulitic domains is ~130 μm . Note that the boundary area between the neighboring spherulites in the 3D network is composed of mutually interpenetrating fibers, which can be clearly seen in the network images obtained at the middle or lower planes of a gel film (see Fig. S5, ESI †). The existence of such a mutually interpenetrating of fibers in the boundary area is also confirmed below in the SEM micrographs (see Fig. 6 and Fig. S6, ESI †). When the gap size was reduced to below the average size of the spherulitic domains, e.g. from ~100 to 50 μm , the formed gels have dramatic different microstructures, as is shown in Fig. 5d-f. Notably, gap ~100 μm is the critical point to show remarkable change of the gel microstructure, which is in accordance with the above rheological measurements.

Several distinct features can be clearly identified from the confinement-induced gel microstructures. Firstly, the spherulitic network appeared to be sparse and quasi-two-dimensional. Secondly, in contrast to the case of unconfinement, the number of the spherulitic domains is much fewer, but the size of the domains can be more than 2 times larger. More strikingly, the spherulites in the confined gels show less branching of fibers. These results support qualitatively the above kinetic analyses, i.e. spatial confinement led to a depressed primary/secondary nucleation of fibers/branches in the gelation process.

According to the earlier work by Chen and co-workers [14], depressed branching of fibers was also observed under a 2D spatial confinement. They reported the occurrence of a structural transition from the spherulitic network to the fibrillar network (consisting of less branched fibers), when a molecular gel was formed in 2D microchannels. Fibrillar structures were also observed in the networks formed in 1D confinement of this work.

We examined the structural details of the fiber networks using SEM technique. In the unconfinement regime, e.g. gels formed at gap ~800 μm , highly branched fibers mutually interpenetrate and interlock to form 3D spherulitic network (Fig. 6a). By contrast, sparse spherulitic network (Fig. 6b) formed in the confined regime (e.g. at gap ~100 μm) are loosely connected through microchannel-like boundary areas (see, e.g. the yellow area in between neighbouring fibers/branches). A closer look into these boundary areas revealed the existence of fibrillar structure—the entangled thin fibrils that grew from the surfaces of thick fibers/branches of the spherulites (Fig. 6c, dashed circles). Such a hierarchical growth of fibrillar network has not been reported in the previous studies. [15, 16] In this regard, our finding here reveals a new facet of the effect of 1D spatial confinement in governing the fiber network structure of molecular gel films.

Furthermore, the fractal patterns displayed in both the optical and the electronic micrographs show a good agreement with the kinetics derived D_f values. The GP-1/PG gels formed in the unconfinement regime show a compact structure of spherulitic network (Fig. 5 a-c) and are hence featured by a D_f value around 2. The confined gels show significantly reduction in the compactness of spherulitic network and particularly the less branched fibers and fibrillar structure (Fig. 5 d-f), thus corresponding a fractality featured by a relatively low D_f value slightly larger than 1. Using an image analysis technique, [35, 36] we estimated the D_f values directly from the fractal patterns of the spherulitic networks formed with and without space confinement (Fig. S7 and Fig. S8, and more details of the fractal analyses are given in ESI †). For the spherulitic network formed without space confinement, distribution of the D_f values is in the

range of 1.75-1.80; whereas for the case of space confinement, distribution of the D_f values is in the range of 1.39-1.44. These fractal features extracted by using image analyses are in a good agreement with that derived from the above rheological measurements.

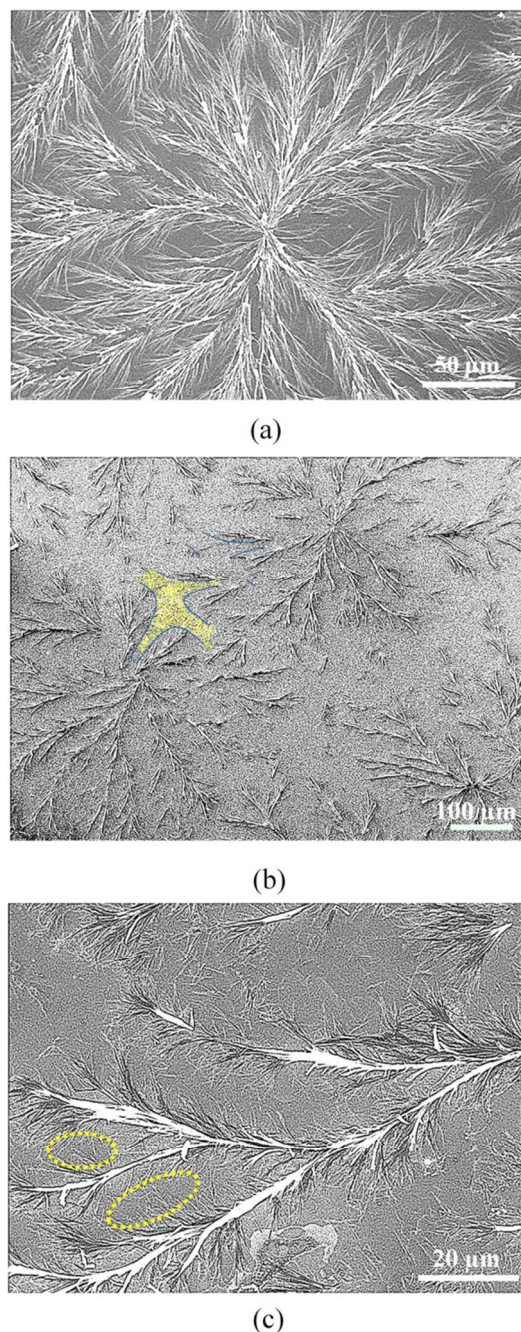


Fig.6 SEM images of 3wt % GP-1/PG gels formed at two different gap sizes: (a) $\sim 800 \mu\text{m}$; (b) $\sim 100 \mu\text{m}$; (c) the enlarged image of (b).

As expected, the aforementioned structural changes induced by spatial confinement would result in a significant modification to the mechanical properties of molecular gels.

Confinement-induced modification of rheological properties

Fig. 7 shows the changes of $G'(\infty)$ and the critical strain (denoted by γ_c) for 3wt % GP-1/PG gel, when tuning the gap size

from 800 to 50 μm . The raw data of the related rheological measurements and the details of calculation of $G'(\infty)$ and γ_c are given in the Supplementary Information (Fig. S9, ESI†). Again, we observed the turning point at gap $\sim 100 \mu\text{m}$, below which the influence of confinement on the rheological properties of a gel is clearly seen. In the unconfined regime, γ_c is less changed, while $G'(\infty)$ shows a slightly increase with the decrease of gap size. By contrast, in the confinement regime both $G'(\infty)$ and γ_c show strong dependence on the gap size. More specifically, as the gap size decreased from 100 μm to 50 μm , $G'(\infty)$ is sharply reduced but γ_c shows a drastic enhancement. Strikingly, γ_c at gap $\sim 50 \mu\text{m}$ is more than 3 times larger than its bulk counterpart (e.g. formed at gap $\sim 200 \mu\text{m}$). Similar phenomena were observed for the gelling system with the GP-1 concentration of 4 wt % (see Fig. S10, ESI†). These results mean that 1D spatial confinement effect renders a strong but brittle gel to be less stiff but more ductile.

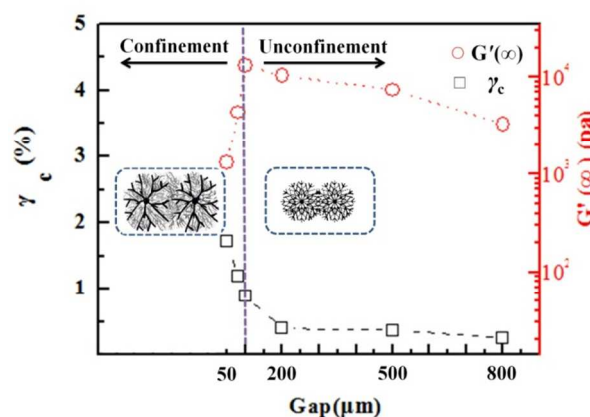


Fig.7 Variation of the storage modulus (\circ) at the quasi-equilibrium state and critical strain (\square) as a function of gap size, acquired from the 3wt % GP-1/PG system. Inset: Illustration of the different structure of the boundary area. Interpenetration of fibers between adjacent spherulitic domains in the case of unconfinement; the entangled thin fibrils in the case of confinement.

Together with the microstructures revealed in Fig. 6, we gained a new understanding of the structure-property relationship in the confined GP-1/PG gels (Fig. 7, more data is referred to Fig. S9 and S10 in ESI†). As mentioned above, without spatial confinement, GP-1/PG gel consists of 3D network of densely compact spherulitic domains, and the interpenetration of fibers between neighboring domains is the mechanically weak part of the gel.^[37] As a result, such a gel shows a high stiffness (large value of $G'(\infty)$) but brittleness (low value of γ_c). By means of confinement effect, we obtained a quasi-2D sparse spherulitic network with a soft fibrillar structure filling in the microchannel-like boundary areas. Although such gel films are less stiff, the presence of loosely entangled thin fibrils at the boundary promotes the mobility of spherulitic domains, thus enabling the soft gel film to possess a good ductility.

As is already known, fragility is an intrinsic weakness of majority molecular gels, which limits their applications significantly. For the brittle GP-1/PG gel that has a small γ_c , we demonstrated here that space confinement effect can provide an effective way for engineering the fiber network structure to improve the ductility of the gel (i.e. with an enhanced γ_c more than 3 times larger). Such an unusual mechanical property of these gel films may find important applications in pharmaceuticals, e.g. the transdermal delivery system.^[38]

In addition, we found that the space confinement can induce very similar changes of the spherulitic network structure and consequently modify the rheological properties of another gelling system. We used here the same gelator molecule GP-1 but with different solvent octanol (the critical gelator concentration is ~ 6 wt% [26]). Similar to the GP-1/PG system, Gelation of GP-1 molecules in octanol also occurred through the spherulitic growth of fiber network. We demonstrate here that applying a space confinement allows us to observe the structural transition of fiber network and consequently to achieve a greatly improved ductility in this GP-1/octanol gel films (see Fig. S11-S13, ESI †). These results verified the reproducibility of the space confinement effects on molecular gelling system. However, more experimental studies are still needed to examine the generality of the above confinement effects, especially for the molecular gelling systems in which the fibrous growth mode, instead of the spherulitic growth mode, is predominant in the formation of fiber networks.

Conclusion

We have identified the distinct kinetic feature of a molecular gel formed in a 1D confinement geometry, and established the kinetics-structure relationship. We have demonstrated that the distinct kinetic pathway toward forming sparse spherulitic network is correlated with the depressed primary/secondary nucleation of fibers/branches in the molecular gelation. The resulting fiber network is featured by less branched fibers and entangled fibrils at the boundary areas. This is in good agreement with the gelation kinetic feature evaluated by D_f in the range from 0.98 to 1.32. These results are different from the situation without spatial confinement, where the gel microstructure displayed as densely compact spherulitic network composed of highly branched fibers, and accordingly the gelation kinetics is featured by the D_f in the range from 1.53 to 2.11. Because of the dramatic differences in the fiber network, the confinement-induced gels are less stiff but more ductile in comparison with their bulk counterparts.

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Notes and references

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† Electronic Supplementary Information (ESI) available: More raw data of the dynamic rheological measurements, the kinetic analyses, and the optical and electron microscopies acquired from the used molecular gelling systems.

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Table of Content

Distinct kinetic feature of the molecular gelation in a confined or unconfined regime, and its relationship with the tailored fiber network structure and mechanical properties.

