Soft Matter

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Control of crystallization in supramolecular soft materials engineering

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As one class of the most important supramolecular functional materials, gels formed by low molecular weight gelators (LMWGs) have many important applications. The key important parameters affecting the in-use performance of a gel are determined by the hierarchical fiber network structures. Fiber networks consisting of weakly interacting multiple domains are commonly observed in gels formed by LMWGs. The rheological properties, particularly the elasticity, of a gel with such a fiber network are weak due to the weak interactions between the individual domains. As achieving desirable rheological properties of such a gel is practically relevant, in this work, we demonstrate the engineering of gels with such a type of fiber network by controlling crystallization of the gelator. Two example gels formed by a glutamic acid derivative in a non-ionic surfactant Tween 80 and in propylene glycol were engineered by controlling the thermodynamic driving force for crystallization. For a fixed gelator concentration, the thermodynamic driving force was manipulated by controlling the temperature for fiber crystallization. It was observed that there exists an optimal temperature at which a gel with maximal elasticity can be fabricated. This will hopefully provide guidelines for producing high performance soft materials by engineering their fiber network structures.

1 Introduction

Supramolecular assembly plays an important role in our life. It governs the formation of many structures (such as cell membranes) in a living organism and the formation of functional materials with important applications in numerous fields. Gels formed by molecular assembly are a class of supramolecular materials.[1] A gel with a three dimensional (3D) fiber network has both the elasticity of solids and viscosity of liquids. The fiber network determines the elasticity and the pore size of the gel. The combination of the network and solvent determines the viscosity, optical properties and applications of a gel. In contrast to conventional polymer gelators, a LMWG has a molecular weight normally less than one kDa. The small molecules self-assemble to form fibers *via* non-covalent forces such as hydrogen bonds, π–π interactions and van der Waals

forces.[2,3] The physical interactions mean that the molecular assembly is reversible upon the change of environmental factors such as temperature,[4] pH and presence of additives.[5–8] Due to the reversible molecular interactions, good degradability, 3D porous architecture and liquid structuring capability, small molecule gels are attracting attention in many fields such as cosmetics,[9] foods,[10] controlled drug release and tissue engineering,[11] nanostructure synthesis,[12] energy transfer and light harvesting,[13] optoelectronics,[14,15] and art conservation,[16] to name a few (Chart 1).

The structure of the 3D fiber network and the macroscopic properties of a material affect its performance and even applicability. Precise control over the fiber network structure is hence essential. For example, it has been proven that for gels formed
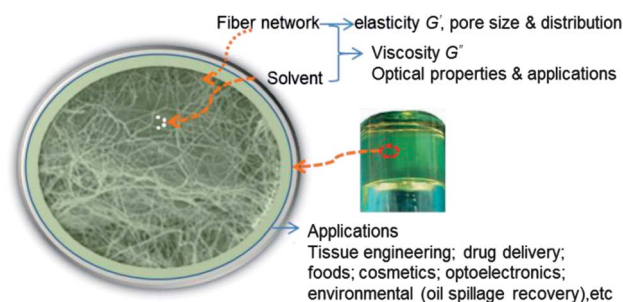
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Chart 1 Illustration of the microstructure of a gel formed by a LMWG and its applications.

by chromophore gelators, precise control over the fiber thickness (on a nanometer scale) and the orientation of the gelator molecules in fibers is essential to the design of an efficient energy transfer and light harvesting system.[13] In order to obtain gels with desired network structures and macroscopic properties, much attention has been focused on the identification of novel gelling agents. Although in recent years a better understanding of the structural properties of molecules required for self-assembly and fiber formation has been acquired, leading to the discovery and design of several new small molecule gelator systems,[17,18] the design of new gelators continues to be largely a trial-and-error process in which successes are often outnumbered by failures.[15,17,19] This is due to the insufficient understanding and strong solvent-dependence of gelling capacity.[20,21] Thus, searching and designing new gelators are generally very time consuming and are inefficient approaches. In particular, in some cases, the strict requirements on the properties of the materials such as biocompatibility are factors limiting the selection of solvents. The solvents generally used for gel preparation are alcohols, alkanes and aromatic hydrocarbons,[21,22] most of which are toxic. Developing gels of biocompatible solvents is essential for the wide applications of this class of materials,[23] and controlling the fiber network structure in such a gel is also important.

2 Mechanisms of fiber network formation and engineering principles

To develop an efficient approach to engineering the 3D fiber network of a gel formed by a LMWG, an understanding of the fiber network formation mechanism is essential. The fiber network formation in such a gel is generally interpreted as a process of molecular assembly through non-covalent forces. While this mechanism is not wrong on a molecular level, it is incapable of addressing several important phenomena, for example, how to control the fiber branching. Fiber branching has a great effect on the rheological properties of a gel. It also determines the pore size, which affects the performance of a gel in many applications. In this context, the self-assembly model cannot provide a global view on the fiber network formation and engineering. Interestingly, it was proven that the fiber network formation in such a gel is a crystallization process, which consists of nucleation and growth of fiber (Fig. 1).[24,25]

On the basis of the nucleation-growth mechanism, in a fixed gel volume, the entire fiber network consists of a collection of individual fiber networks, each originating from a nucleation center. If fiber branching is intense, individual fiber networks with a clear boundary can be identified. A typical example of this is compact spherulitic fiber networks (Fig. 2a). Due to the presence of a boundary, the elasticity of the gel is generally weak. When fiber branching is not intense, fibers from one spherulite can penetrate into the neighbouring spherulites and clear boundaries are not obvious (Fig. 2c). In many cases, a spherulitic pattern is not present and the entire fiber network is formed by the entanglement of fibers with some degree of branching (Fig. 2d). The formation of such a fiber network is due to the non-radial growth from the nucleation centers. A
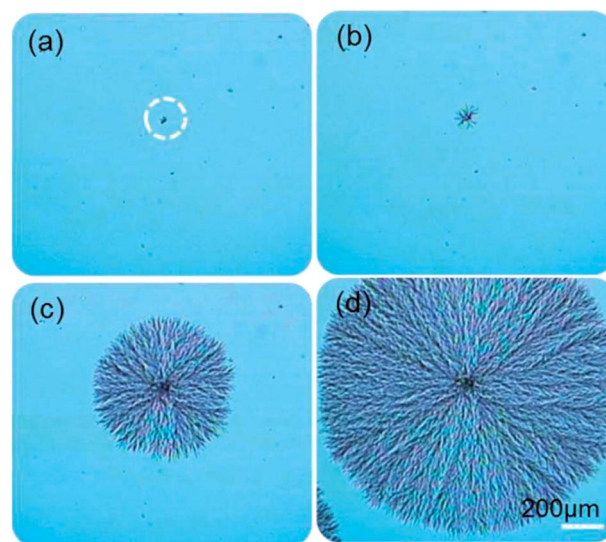

Fig. 1 Real time observation of the nucleation and growth of a spherulitic fiber network of the LMWG N-lauroyl-L-glutamic acid di-n-butylamide (GP-1) (5 wt%) in propylene glycol at 50 °C. During fiber growth, fiber branching occurs due to mismatch nucleation. The images were taken at 12 s, 35 s, 170 s and 360 s. The circled area in (a) shows fiber nucleation and growth starts on a substrate. All the images are on the same scale.

spherulite forms if multiple fiber arms grow from a nucleation center radially. A fiber network similar to that in Fig. 2d forms when a single fiber is generated from each nucleation center, followed by continuous growth and branching.[26]

In our previous work, a network with clear boundaries between individual fiber networks is defined as a multi-domain fiber network and that without boundaries is defined as a single fiber network.[2] Fig. 2a is a typical multi-domain fiber network
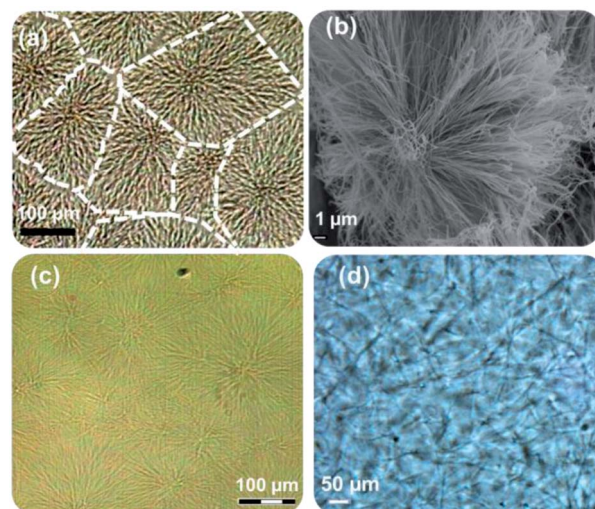

Fig. 2 Typical fiber networks observed in gels of LMWGs. (a) Compact spherulitic fiber networks of GP-1 formed in propylene glycol; areas marked by dashed lines in (a) are individual spherulitic fiber networks, and the boundary between neighboring fiber networks is clear; (b) an SEM image of a spherulite; (c) interpenetrating spherulitic fiber networks formed by 12-hydroxystearic acid in benzyl benzoate; and (d) interconnecting/single fiber network formed by GP-1 in isostearyl alcohol.

consisting of spherulites. As shown in Fig. 2b, each spherulite is a fiber network. Fig. 2d is a typical single fiber network. An interpenetrating spherulitic fiber network, as shown in Fig. 2c, behaves like a single fiber network.[27] Multi-domain fiber networks frequently occur in gels formed by LMWGs. How to engineer the fiber network so as to improve the elasticity of a gel is thus practically significant.

The nucleation-growth mechanism indicates that the fiber network in a gel can be manipulated by controlling the crystallization of the gelator. According to the current nucleation theory, the nucleation rate J can be obtained from:[24,28]

$$J = f''[f]^{1/2} B \exp\left[-\frac{\Delta G^*}{kT}\right] \tag{1}$$

with

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

$$\Delta\mu/kT = \ln(1 + \sigma) \cong \frac{\Delta H_{diss}}{kT^*}(T^* - T) \tag{3}$$

where ΔG^* is the nucleation energy barrier, B is the kink kinetics coefficient, f' and f ($f'' \leq 1$, $f > 0$) are factors describing the correlation between the substrates and the nucleation phase, k is the Boltzmann constant, Ω is the volume of the growth units, γ_{cf} denotes the interfacial free energy between the fibers and the fluid phase, ΔH_{diss} denotes the molar dissolution enthalpy of the nucleating phase, T^* is the equilibrium temperature, $\Delta\mu$ denotes the chemical potential difference between gelator molecules in the fiber state and in the liquid, and σ is supersaturation, defined as $\sigma(T) = (C - C^*(T))/C^*(T)$, where C and $C^*(T)$ are the actual molar fraction and the equilibrium molar fraction of solute in solution at a temperature T, respectively. For a fixed amount of solute, the driving force can also be measured by the degree of supercooling $\Delta T/T^*$ ($\Delta T = T^* - T$).
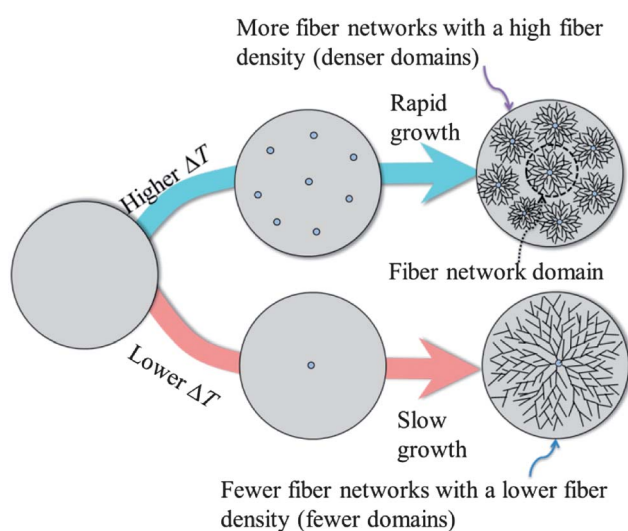
Eqn (1)–(3) indicate that the nucleation rate J is controlled by the thermodynamic driving force (supersaturation or degree of supercooling). By lowering the driving force, a lower nucleation rate will result. This will lead to the formation of a smaller number of spherulites in a certain volume, improving the integrity of the entire network and the elasticity of a gel (Scheme 1). On the other hand, a lower driving force means a lower fiber mass. This compromises the elasticity, which is related to the storage modulus G', of the gel. A combination of the two opposite effects means that an optimal driving force which gives a maximal G' may exist for a gel. Although the primary nucleation and fiber network formation can also be manipulated by using suitable additives to change the correlation between the substrate and the nucleating phase (f and f' in eqn (1)),[27,29,30] temperature control is the simplest approach. Since it does not involve the introduction of new chemicals, it is preferred in many cases. Thus, an experimental investigation of the effects of thermodynamic driving force is significant both fundamentally and practically. It is worth noting that the cooling rate can also affect the nucleation behaviour of a non-isothermal crystallization process. A detailed investigation is available.[31] If the cooling rate is too slow, significant fiber crystallization can take place before a designated temperature is reached, which reduces the supersaturation (thermodynamic driving force). To minimize the impact of cooling rate, a high cooling rate of 30 °C min⁻¹ was used in this work.
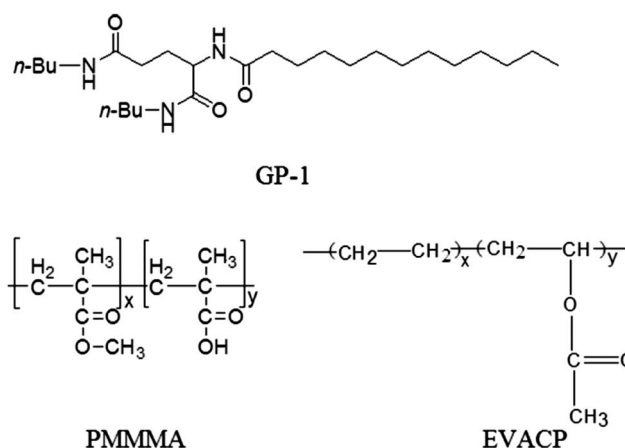
3 Materials and experiments

Chemicals

Polysorbate 80 (Tween 80), propylene glycol (PG), isostearyl alcohol (ISA) and poly(methyl methacrylate comethacrylic acid) (PMMMA) (with a methyl methacrylate to methacrylic acid molar ratio of 1 : 0.016) were obtained from Sigma-Aldrich. *N*-lauroyl-ʟ-glutamic acid di-*n*-butylamide (GP-1) was obtained from Kishimoto Sangyo Asia, and ethylene/vinyl acetate copolymer (EVACP) (M_w 100 000, 40% vinyl acetate) was obtained from Scientific Polymer Products, Inc. The molecular structures of GP-1, PMMMA and EVACP are shown below.

GP-1

PMMMA   **EVACP**

Real time observation of fiber network formation

The microstructures of the gel fiber networks were observed under a microscope. Thin sample films (0.1 mm) were prepared

Scheme 1 Illustration of engineering spherulitic fiber networks by controlling primary nucleation.

by sealing the hot solutions of GP-1 in the solvents in self-made glass cells. A microscope (Olympus BX50) with a heating/cooling temperature controller (Linkam Scientific Instruments, THMS600) was used. The temperature ramp rate was set at 30 °C min^{-1} with an accuracy of ±0.1 °C. The sol-to-gel transition was monitored by a video system. The images from the microscope were converted to digital images through a JVC KY-F55B 3-CCD color video camera.

Rheological measurement

The storage modulus G', a measure of elasticity of a gel, was obtained using an advanced rheological expansion system (ARES-LS, Rheometric Scientific), following reported procedures.[30] In brief, the sol–gel process was performed *in situ* between two circular plates with a gap of 0.85 mm. After a piece of gel was put between the plates, the temperature of the lower plate was increased to 100 °C and kept there for 5 minutes to completely dissolve the gel. Then the temperature was lowered to a certain temperature for gel formation. Both the heating and cooling rates were 30 °C min^{-1}. The samples were subjected to sinusoidal oscillation by moving both the upper (with a diameter of 25 mm) and the lower plate. The amplitude of the oscillation was controlled to obtain a strain of 0.05% in the sample. The oscillation frequency was set at 0.1 Hz.

4 Results and discussion

It is observed that a strong optically clear gel forms when a hot solution of GP-1 in Tween 80 is cooled (Fig. 3a). Tween 80 is an edible surfactant. It is often used as an emulsifier in foods (*i.e.* ice cream)[32] and drug formulations.[33] In Europe and America, people eat about 100 mg of Tween 80 in foods per day.[34] Therefore, the excellent biocompatibility of this solvent makes

Fig. 4 Evolution of the microstructure of GP-1/Tween 80 gel with an increase in temperature. The circled areas indicate individual fiber networks.

it ideal for the fabrication of gels. However, to the best of our knowledge, the gelation of Tween 80 has not been reported. The minimal concentration of GP-1 for gelling Tween 80 at room temperature (*ca.* 20 °C) is as low as 0.1 wt%. The gel is transparent and its light yellow color is from the solvent. Under polarized white light, a spherulitic fiber microstructure with birefringence is shown (Fig. 3c), indicating the crystalline nature of the fiber network. GP-1 also forms spherulitic fiber networks in propylene glycol (PG) (Fig. 3d). PG is generally used in cosmetics and the GP-1/PG gel has been used for controlled drug release.[35] Some of the properties of this gel have been reported in our previous work.[29,36] The minimal concentration of GP-1 to gel PG is 0.5 wt%. The GP-1/PG gel is opaque with a white color (Fig. 3b). As shown in Fig. 4 and 5, the sizes of GP-1 spherulites in both solvents are from a hundred to several hundred micrometers, but the fibers formed in PG are thicker, which is one reason for the color difference. Another major factor in determining whether a gel is clear or opaque is the
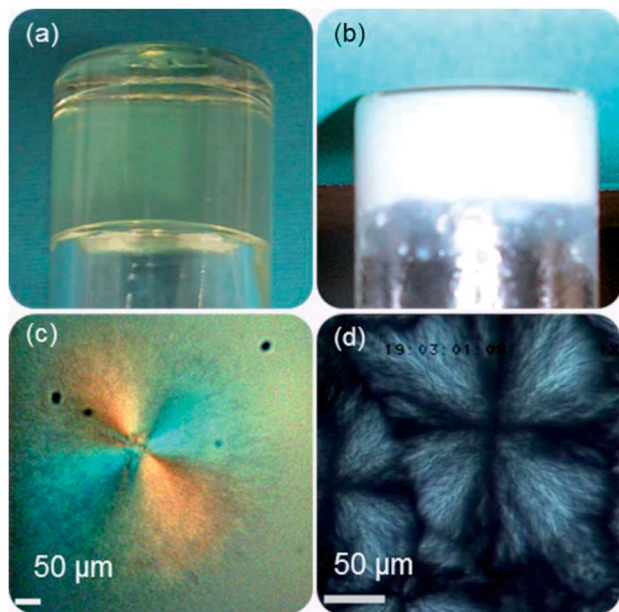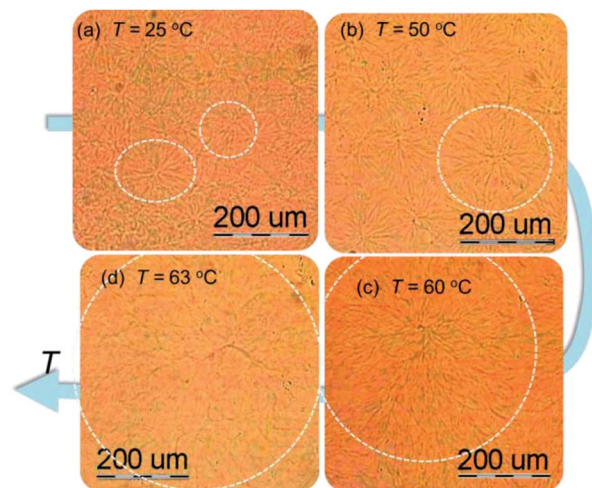

Fig. 3 Optical images of the two gels (a and b) and spherulites of the two gels observed under a polarized white light (c and d). (a) and (c): GP-1/Tween 80 gel, (b) and (d): GP-1/PG gel.
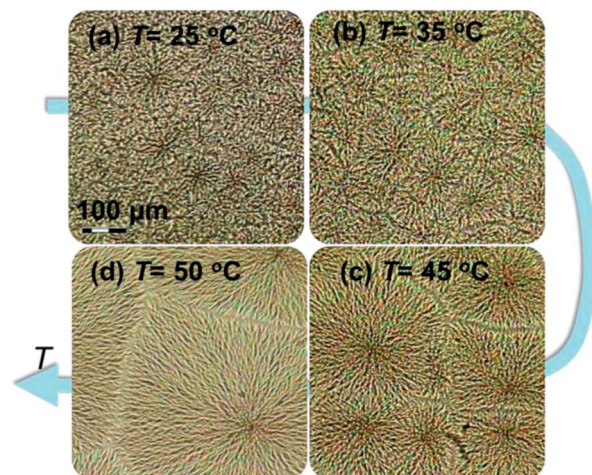

Fig. 5 Evolution of the microstructure of GP-1/PG gel with an increase in temperature. All the images are of the same scale.

difference in the refractive indexes of the solvent and the fibers. A perfect match of refractive index gives a transparent gel.

The influence of supercooling on the fiber network structure of GP-1 in the two solvents was investigated. Due to its lower solubility in Tween 80, the GP-1 concentration was fixed at 1 wt % in this solvent, and in PG, the concentration was fixed at 3 wt %. On the basis of the nucleation-growth fiber network formation mechanism, the number of spherulites in a certain volume of gel can be manipulated by controlling the primary nucleation of a gelator. The primary nucleation rate is determined by the thermodynamic driving force. A higher driving force leads to a higher nucleation rate.[2] The thermodynamic driving force can be correlated to the degree of supercooling $\Delta T/T^*$. When the concentration of a gelator is fixed (T^* is thus fixed), the degree of supercooling is determined by the temperature T at which a gel is formed. In this instance, a higher temperature corresponds to a lower degree of supercooling and a smaller thermodynamic driving force. Therefore, at a higher temperature, the primary nucleation rate is lower and the number of spherulites is smaller.

The images in Fig. 4a–d show the microstructure of 1 wt% GP formed at 25, 50, 60 and 63 °C, respectively. With an increase in temperature, the size of the spherulitic networks increases. A more obvious increase is observed at 60 °C. At 25 °C, the diameter of the spherulites is about 150 μm, which increases to *ca.* 200 and 500 μm, respectively, at the temperature of 50 and 60 °C. With a further increase of temperature to 63 °C, the spherulitic structure can still be identified and the size of the spherulites shows a slight increase, but the fibers are hardly observable due to the smaller fiber mass (Fig. 4d).

A similar trend of microstructure change with temperature was observed for GP-1/PG gel (Fig. 5). The spherulitic fiber networks formed in PG are more compact due to the more extensive fiber branching. This combined with a higher fiber thickness makes the individual spherulitic fiber networks and the boundaries between the networks in PG more easily distinguishable.

The fiber networks of GP-1 formed in the two solvents are typical multi-domain fiber networks. As has been discussed, the elasticity of the gel with such a fiber network is generally weak because of the boundaries between the individual spherulitic fiber networks. Therefore, reducing the fraction of boundary area in a gel volume can improve the elasticity of the gels. To prove this, the effects of temperature/supercooling on the elastic modulus G' of the two gels were studied. The GP-1 concentrations are the same as those for Fig. 4 and 5.

The G' evolution curves of the two gels are shown in Fig. 6. The gel formed in Tween 80 at ambient temperatures (20–40 °C) is weak (Fig. 6a). A slight increase in G' was observed when the temperature was increased from 20 °C to 30 °C and 40 °C. Interestingly, a jump of G' from *ca.* 8000 N m^{-2} to 75 000 N m^{-2} (one order of magnitude increase) occurred when the temperature was increased from 40 to 50 °C, followed by a moderate increase to slightly above 100 000 N m^{-2} at 60 °C. With a further increase of temperature to 70 °C, G' dropped down to a value of about 45 000 N m^{-2}. A similar trend of G' change with temperature was also observed for GP-1/PG gel (Fig. 6b). The G'
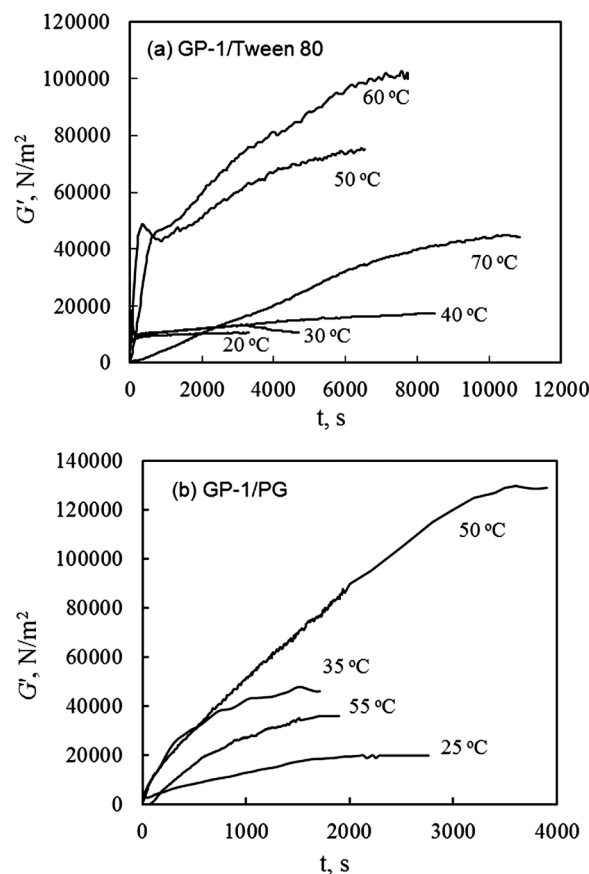

Fig. 6 Evolution of elastic modulus of the two gels at different temperatures: (a) GP-1/Tween 80 and (b) GP-1/PG. The concentrations of GP-1 in the two gels are 1 wt% and 3 wt%, respectively.

increased with temperature from 20 to 50 °C and was reduced with a further increase of temperature to 55 °C. A combination of Figs. 4, 5 and 6 indicates that the elasticity of a gel with a multi-domain fiber network can indeed be improved by reducing the thermodynamic driving force (increasing temperature), giving a more integrated entire fiber network with reduced boundaries. However, an optimal thermodynamic driving force exists for such a gel. Further reducing the driving force compromises the elasticity of a gel.

While reducing the thermodynamic driving force can increase the size of spherulites and reduce the boundary area, it also reduces fiber mass. At a higher temperature, more gelator molecules are dissolved in the solvent, reducing the mass of the gelator in the fiber phase (more obviously shown in Fig. 4d), which compromises the elasticity of the gel. A combination of the two opposite effects determines the elasticity of a gel. Fig. 7 shows the dependence of fiber mass (F_{fib}, the fraction of gelator mass in the fiber phase) and G' on the degree of supercooling and temperature. The fiber mass drops down consistently with a decrease in supercooling (increase in temperature). For both the gels, when the temperature is below a certain value, a temperature increase causes an increase in G', but above this value, the G' drops due to the insufficient fiber mass. When the temperature is increased to T^* (for example, 83 °C for 1 wt%
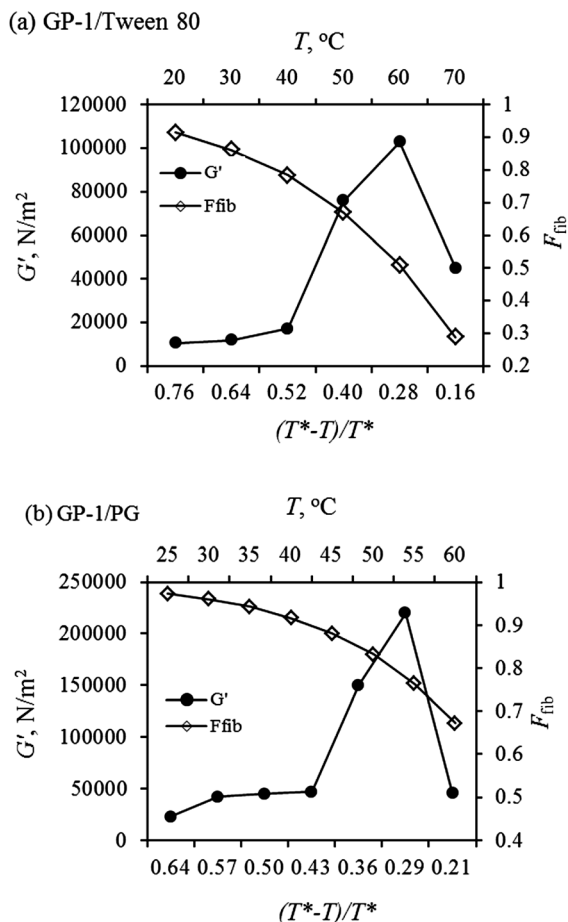
Fig. 7 Elastic modulus and fiber mass fraction as a function of supercooling for the two gels (a) GP-1/Tween 80 and (b) GP-1/PG. With an increase in temperature, more GP-1 is dissolved in the solvent, reducing the mass of GP-1 in the fiber phase. The concentrations of GP-1 in the two gels are 1 wt% and 3 wt%, respectively.

Fig. 8 An optical micrograph of 2 wt% GP-1/PG gel (a) and evolution of the G' of the gel (b) formed at 35 °C.
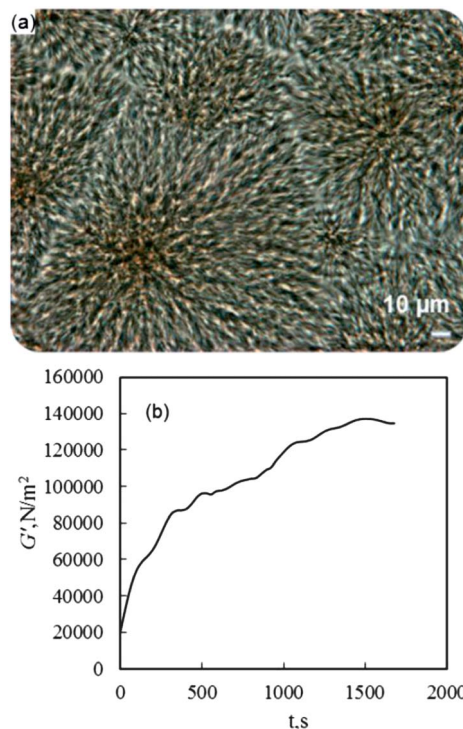
Fig. 9 An optical micrograph of the fiber network formed by 5 wt% GP-1 in PG (a) and evolution of G' of the gel (b) formed at 25 °C.

GP-1/Tween 80), all the gelator molecules are dissolved in the solvent and the fiber mass is zero.

The thermodynamic driving force can also be reduced by using a smaller mass of gelator, which also reduces the nucleation rate and produces larger spherulites. However, a reduction in gelator mass also reduces fiber mass. That is, the G' that results will also be determined by the overall effect of the boundary and fiber mass. For example, at 35 °C, the size of the spherulitic network formed with 2 wt% GP-1 (Fig. 8a) is about five times of that formed with 3 wt% GP-1 (Fig. 5b). However, the G' of the former is 9000 N m^{-2}, which is only one fifth of that of the latter. This means that although the boundary area was reduced significantly by lowering the concentration of GP-1, the elasticity of the gel is compromised due to the lower fiber mass. That is, the G' is also governed by both the boundary effect and fiber mass. Therefore, at a certain temperature, a maximal G' is obtainable by fine-tuning the gelator concentration, which is a subject of further investigation.

It is noteworthy that a gel with higher elasticity can be obtained by forming a gel at a lower temperature but using a higher gelator concentration (to increase the fiber mass).
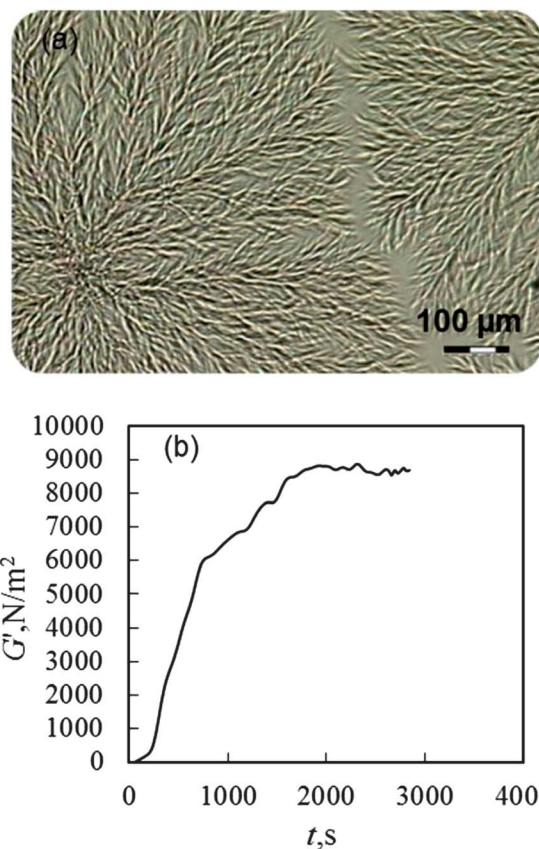
However, this will increase cost and is thus not economically attractive. Instead, using a lower mass of gelator but forming the gel at a higher temperature (a lower thermodynamic driving force) can achieve a gel with similar elasticity. For example, for a gel formed by 5 wt% GP-1 in PG at 25 °C, the G' of the gel is *ca.* 140 000 N m^{-2} (Fig. 9), while with a reduced GP-1 concentration of 3 wt%, a gel with G' above this value can be obtained by forming it at an elevated temperature of 50 °C. This indicates a saving of about half of the gelator dose, which is particularly significant for precious gelators. Nevertheless, the concentration of gelator cannot be reduced without a limit. Lowering gelator mass reduces fiber mass, which compromises the elasticity. In addition, the fiber mass affects not only the elasticity of the gel, but also affects the other properties of the gel such as its optical appearance and pore size. For an application with specific requirements on the properties of a gel, an optimal gelator concentration and temperature need to be determined. This might be more important for some kind of applications
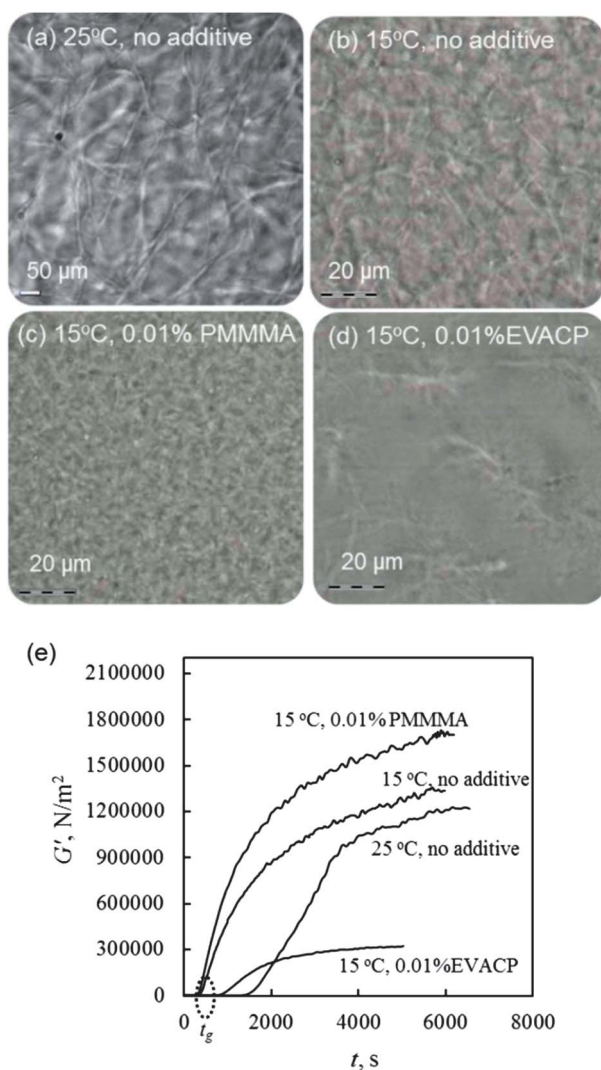
such as optoelectronics, where the fiber mass and network structure may have a predominant influence on the performance of the material. Controlling the formation of multi-domain fiber networks has also been achieved by using additives of copolymer poly(methyl methacrylate co-methacrylic acid) (PMMMA).[29] While the elasticity of a gel can be improved accordingly, the introduction of additives (impurities) may not be feasible in some applications.

It is also worth mentioning that the elasticity of different types of fiber networks is governed by different factors. As observed in this work, both the size (boundary) and fiber mass determine the elasticity of a gel with a multi-domain network. The elasticity of a gel with an interconnecting fiber network, because of the absence of a boundary, is determined by fiber mass and the degree of fiber branching.[26,36] Therefore, in contrast to gels with multi-domain fiber networks, a gel with an interconnecting fiber network has higher elasticity at a lower temperature, due to the larger fiber mass and enhanced fiber branching under the higher thermodynamic driving force. Fig. 10a and b show the fiber networks of GP-1/ISA gels formed at 25 and 15 °C, respectively. A denser fiber network with enhanced fiber branching occurs at the lower temperature, leading to improved elasticity (Fig. 10e). The improvement in elasticity by enhancing fiber branching was also demonstrated when suitable additives were used in gel formation. For example, with the addition of a tiny amount (0.01 wt%) of the copolymer PMMMA, thinner and more extensively branched GP-1 fibers formed (Fig. 10c). The elasticity of the gel was improved from 1.3×10^6 to 1.7×10^6 N m^{-2}, an increase of more than 30%. Suitable surfactant molecules have also been observed to improve the elasticity of this gel by enhancing fiber branching.[37] It is also interesting to notice that another copolymer, ethylene/vinyl acetate copolymer (EVACP), inhibited the primary nucleation and fiber formation of GP-1 molecules in ISA,[30] as evidenced by microscopic observation and the longer gelation time t_g (Fig. 10e). The presence of EVACP compromised the elasticity (which reduced from 1.3×10^6 to 3.2×10^5 N m^{-2}) of GP-1/ISA gel dramatically, due to the conversion of the interconnecting fiber network to a multi-domain network (Fig. 10d). This further proves the important role of boundary in determining the elasticity of a gel. The inhibitory effect of EVACP on fiber crystallization was recently used to purify a heterogeneous fiber network to a homogeneous network.[30]

5 Conclusions

In conclusion, the results show that the elasticity of gels formed by LMWGs with multi-domain fiber networks can be improved by controlling the thermodynamic driving force for the microstructure formation. When the mass of a gelator is kept the same, increasing temperature (reducing thermodynamic driving force) reduces nucleation rate, leading to the formation of a network with a reduced boundary, which improves the elasticity of a gel. However, increasing temperature also reduces fiber mass, which has an opposite effect on the elasticity of a gel. Therefore, an optimal temperature/driving force, which yields a gel with maximal elasticity, exists for a gel. It has been

Fig. 10 Temperature and additive effects on the microstructure and elasticity of GP-1/ISA gel with an interconnecting fiber network. G' data for 15 °C without additive and with 0.01% EVACP are reproduced with permission from ref. 30, copyright 2011 American Chemical Society.

confirmed that the fiber network formation by LMWGs is generally governed by their crystallization. The crystallization mechanism has also been proven for other types of supramolecular materials such as physical polymer gels.[38] The thermodynamic approach reported in this work should be feasible for engineering materials with multi-domain crystalline fiber networks, not limited to the gels studied in this work. The observations may provide general guidelines for cost-effective production of high performance supramolecular materials with 3D fiber networks.

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