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From kinetic–structure analysis to engineering crystalline fiber networks in soft materials†

Cite this: *Phys. Chem. Chem. Phys.*, 2013, **15**, 3313

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Understanding the role of kinetics in fiber network microstructure formation is of considerable importance in engineering gel materials to achieve their optimized performances/functionalities. In this work, we present a new approach for kinetic–structure analysis for fibrous gel materials. In this method, kinetic data is acquired using a rheology technique and is analyzed in terms of an extended Dickinson model in which the scaling behaviors of dynamic rheological properties in the gelation process are taken into account. It enables us to extract the structural parameter, *i.e.* the fractal dimension, of a fibrous gel from the dynamic rheological measurement of the gelation process, and to establish the kinetic–structure relationship suitable for both dilute and concentrated gelling systems. In comparison to the fractal analysis method reported in a previous study, our method is advantageous due to its general validity for a wide range of fractal structures of fibrous gels, from a highly compact network of the spherulitic domains to an open fibrous network structure. With such a kinetic–structure analysis, we can gain a quantitative understanding of the role of kinetic control in engineering the microstructure of the fiber network in gel materials.

Received 24th October 2012,
Accepted 30th December 2012

DOI: 10.1039/c2cp43747c

www.rsc.org/pccp

1 Introduction

Molecular gels formed by the self-assembly of low molecular-weight organic gelators (LMOGs) are an important kind of soft material with wide applications in bioscience and biomedicine.^{1–7} A molecular gel is composed of a three dimensional (3D) fiber network that entraps a large amount of organic solvent, thus possessing both the elastic properties of an ideal solid and the viscous properties of a liquid. It is believed that capillary forces and surface tension,^{6,7} and osmosis⁸ play a principle role in the solvent holding ability of the fiber network. The nucleation and growth of the fiber network is governed by thermodynamics and kinetics.^{5–7,9–12} Controlling the kinetics in the formation of fiber networks to tailor the microstructure

of a gel material and consequently to obtain its optimized performance/functionality is crucial for various applications. To date, large numbers of molecules that are capable of forming 3D fiber network structures in organic and/or aqueous solutions have been identified or designed,^{5–7} however, the gelation kinetics involved in the fiber initiation, fiber growth and branching, and network development are far from being understood. In fact, so far very few kinetic models are available for describing the kinetics of molecular gel formation, and knowledge on the kinetic–structure relationship is largely based on very limited data.^{13–15}

A molecular gel is formed by the hierarchical assembly of molecules into a fiber network structure, involving very complicated kinetic processes.^{9,10} For the investigation of gelation kinetics, light scattering,^{13–16} fluorescence spectroscopy,^{14,15} CD spectroscopy,^{14,15} and rheology^{13–18} are usually employed. The kinetic data obtained from these techniques can be correlated to the different stages of gel formation, from the initial molecular aggregation (nucleation) and one-dimensional growth of fibrous structures, to the full development of a fiber network.^{14,15}

In terms of kinetic data acquired by means of rheology, Liu and co-workers¹³ advocated the fractal analysis of gel formation kinetics in terms of the Avrami equation. This provides a way to correlate the structural parameter, *i.e.* the fractal dimension, of the crystalline fiber network in a molecular gel to its nucleation

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† Electronic supplementary information (ESI) available: Raw data of the dynamic rheological measurements for various fibrous gels, and details of the fractal analyses based on the original and extended Dickinson models. See DOI: 10.1039/c2cp43747c

and growth kinetics.^{17,18} A major drawback of this method is that the kinetic factor, *i.e.* the Avrami exponent, depends strongly on both the crystal growth dimensionality and the nucleation mechanism.¹⁷ Therefore the Avrami-related structural parameters obtained from gels that have similar fractal dimensionality but different nucleation mechanisms are not comparable.^{13,14} Later, Terech and co-workers¹⁴ proposed that the Dickinson model, which was originally developed to describe the kinetics of weak gelation particles,¹⁹ can be suitable for the fractal analysis of molecular gelation kinetics. For a few model gelling systems, they demonstrated that the fractal dimension derived from kinetic data based on the Dickinson model was consistent with the fractal characteristics of the fiber network observed by optical microscopy.¹⁴ But note that their study focused mainly on the formation kinetics of dilute or semi-dilute gelling systems that presented open or non-compact fiber network structures,¹⁴ and no further work has been reported on concentrated gelling systems.

Practically, concentrated systems with compact fiber network structures are more significant because gels with such structures have superior mechanical properties that are essential for demanding applications. We were motivated in this study to explore a method that is suitable for the fractal analysis of the gelation kinetics occurring in various concentrated gelling systems for the purpose of the applications.

The method reported herein has two features that distinguish it from that in previous studies.^{14,15} Firstly, only the rheological method was chosen to acquire the kinetic data for gel formation, for the following two reasons: (1) in comparison to other techniques, the rheological technique is suitable to characterize the microstructure of gelling systems over a wide range of concentrations from dilute to highly concentrated systems,^{20,21} and (2) rheological measurements are advantageous over other techniques in providing kinetic information of the development of the tertiary structure of a gel, *i.e.* the fiber network, due to their high sensitivity to the connectivity of individual fibers during gel network formation.^{14,15,22,23} In addition, through such a kinetic investigation, a correlation between the rheological properties of a gel and the characteristics of the microstructure of the fiber network can be established,¹⁴ which is of particular significance since it determines the performance of a gel product. Secondly, the scaling behaviours of dynamic rheological properties were introduced in developing an extended Dickinson model to establish a direct relationship between the gelation kinetics of a gel and its fractal network structure. This enabled an extension of the Dickinson model developed by Terech and co-workers¹⁴ (we refer to it as the original model) to be suitable for concentrated gelling systems, in addition to reserving its validity for dilute systems.

This method was used to perform fractal analysis of the formation kinetics for a series of gels in which fibrous networks varying from open to highly compact structures were obtained using different kinetic controls. The fractal features extracted from the kinetic data based on the extended model were consistent with those in optical observations. We demonstrated

that such a kinetic–structure analysis can be used to provide a deeper understanding of the role of various kinetic controls in the microstructure engineering of fibrous gels.

II Material and methods

Gels formed by the H-bonding gelator molecule, *N*-lauroyl-L-glutamic acid di-*n*-butylamide (GP-1, >98%, Sigma) in two solvents, propylene glycol (PG, >99%, Sigma) and isostearyl alcohol (ISA, Kishimoto Sangyo Asia), were chosen as model gels, since gelation of these two solvents by GP-1 have been well studied in our previous work.^{11,24–29} The critical gelation concentrations (CGCs) of GP-1 molecules were *c.a.* 0.5% and 3% (both at 20 °C), in PG and ISA, respectively. In addition, for the GP-1/PG system, a copolymer, poly(methyl methacrylate-*co*-methacrylic acid) (PMMMA) (at a concentration of 0.06%), was used to illustrate the effects of additives on the gelation kinetics and the fractal structure of the GP-1 fibers. All the concentrations are expressed as weight fractions (wt%) throughout this work.

For optical observations, thin films were prepared by sealing hot solutions of GP-1 in the solvents in self-made glass cells with a diameter of 5 mm and a spacing of 0.1 mm. A conventional microscope (Olympus BX50) integrated with a heating/cooling temperature controller (Linkam Scientific Instrument, FDCS 196) at the sample stage was used to control the cooling rate and temperature for gel formation, as well as to observe the microstructures of fiber networks.

Rheological experiments were performed on a Physica MCR301 (Anton Paar) rheometer. The gel samples were sandwiched between two parallel plates (25 mm in diameter) with a gap of ~0.85 mm. Dynamic temperature ramp experiments were performed to monitor the dynamic elastic modulus G' during gel formation. The strain and frequency were set to 0.1% and 0.1 Hz, respectively. For fractal analysis, the time evolution of G' (Fig. S1, ESI†) was used in this work.

III Fractal analysis of gelation kinetics

In the fibrous networks of molecular gels, the fractal patterns are typically displayed as the interconnecting fiber network and the network of the spherulitic domains.^{11,13,15} In both cases, fractal crystalline nanofibers are the major constituents of the gel networks. Such fractal objects can be quantified by the fractal dimension, D_f .^{30,31} The number of nanofiber mass elements (M) contained within a sphere of radius R is described by $M \propto R^{D_f}$.³⁰ Thus, the value of D_f is a measure of the extent of the compactness of the fiber network microstructure. Typically, for linear (open) network structures, $1 < D_f < 1.5$;¹⁴ for less compact network structures, $1.5 < D_f < 2.0$;^{13,14} and for highly compact network structures, $2.0 < D_f < 3.0$.^{23,32,33} By supposing that the individual fractal crystalline fibers in a fibrous gel are analogous to the colloidal aggregates (fractal flocs) in colloidal gels, the influence of the fractal structure of a fibrous gel on its rheological properties can be understood on the basis of the well-known fractal model of scaling theory.^{20,21} In this

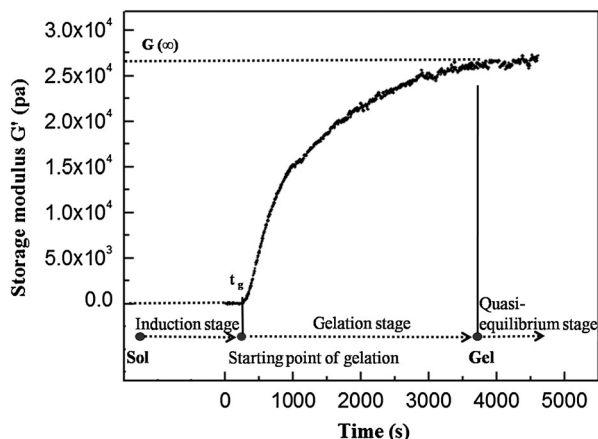


Fig. 1 A typical gelation process acquired by dynamic rheological measurement for a 3% GP-1/PG fibrous gel formed at a gelation temperature of 30 °C with a cooling rate of 30 °C per min. The three stage of gelation in the dynamic rheological measurement of gel formation are also illustrated.

fractal model, the elastic properties of a fractal gel are approximated as a linear chain of springs, and are attributed to two levels of microstructure: intra-microstructure within a fractal aggregate and inter-microstructure due to the collection of fractal aggregates.

During fractal gel formation, the time evolution of the rheological properties, *i.e.* the storage modulus G' , provides important kinetic information for the development of a fiber network.^{14,15,34} Fig. 1 shows a typical kinetic process for gel formation acquired by dynamic rheological measurements. The nucleation and growth of crystalline fibers occurs at the induction stage. Upon the increase of the filler content (the volume fraction of the fibers) to a critical value, the onset of the storage modulus G' appears. We refer to this point as the start point of gelation (t_g). After that, the time evolution of G' can be divided into two stages.³⁴ During the first stage, G' increases quickly by a few orders of magnitude, corresponding to a rapid growth of the volume fraction of the fractal fibers to form a gel network in the solvent till the space-filling of the crystalline fiber network is completed. During the second stage, the reinforcement of the network *via* the rearrangements of fibers and junctions occurs, leading to a relatively slow increase in the elasticity until a quasi-equilibrium state is reached.

According to the Dickinson model, the time-dependent increase of the volume fraction of a gel network in the first gelation stage can be expressed as¹⁴

$$\phi_{\text{gel}}^t \propto kt^{(3-D_f)/D_f} \quad (1)$$

where ϕ_{gel}^t is the volume fraction of the gel phase at time t . For a dilute or semi-dilute gelling system, a simple relationship between the dynamic rheological properties during gel formation was supposed to be¹⁴

$$\phi_{\text{gel}}^t \propto \frac{G'(t) - G'(0)}{G'(\infty) - G'(0)} \quad (2)$$

where $G'(0)$, $G'(t)$ and $G'(\infty)$ are the storage moduli at time 0, t , and infinity, respectively. By combining eqn (1) and (2), the fractal

dimension D_f of a fibrous gel network can be extracted from the kinetics data acquired by dynamic rheological measurements.

For concentrated gelling systems, however, the direct use of such a fractal analysis would produce underestimated D_f values. For instance, the kinetic data of 3% GP-1/PG shown in Fig. 1 gives a Dickinson derived D_f of 1.24 (Fig. S2a, ESI†), indicating an open/linear fiber network structure.^{14,35} This obviously deviates from the compact fiber networks displayed in the optical micrograph (Fig. 2a). To address this issue, we developed herein an extended model by taking into account the scaling behaviour of the dynamic rheological properties with respect to the transformed volume fraction of the gel phase.

As is well-known, for a gel well above the gelation threshold, the scaling law of the equilibrium elastic modulus can be described by $G'_e \propto (C_0)^\alpha$.²⁰ C_0 is the total gelator concentration in a gelling system (supposing that all gelator molecules are within fibers at a gel quasi-equilibrium state). α is the scaling factor. This scaling behaviour of the elastic modulus is dominated by the fractal nature of the crystalline fibers that are the building blocks of the gel networks.^{20,21} Assuming that the fractal nature of the crystalline fibers, once they are formed, would change negligibly, the scaling behaviour of the elastic modulus $G'(t) \propto (C_{\text{fiber}}^t)^\alpha$ would apply throughout the gelation process when t is well above t_g . C_{fiber}^t is the gelator concentration within the fibers at time t . As such, the transformed volume fraction of the gel network at a given time during the gelation stage could be related to its dynamic rheological properties through

$$\phi_{\text{gel}}^t \propto \frac{C_{\text{fiber}}^t}{C_0} \propto \left[\frac{G'(t) - G'(0)}{G'(\infty) - G'(0)} \right]^{1/\alpha} \quad (3)$$

By combining eqn (1) with eqn (3), an extended Dickinson model to describe the gelation kinetics of a gel is given by

$$\ln \sqrt[\alpha]{\frac{G'(t) - G'(0)}{G'(\infty) - G'(0)}} \propto \frac{3 - D_f}{D_f} \ln(t - t_g) \quad (4)$$

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 following calculations, the time zero point is defined as $t - t_g = 0$, $G'(0)$ is the storage modulus at t_g , and $G'(\infty)$ is the average of the last few data points of the quasi-equilibrium state (Fig. 1) that show negligible changes in G' as time increases.

Note that a single kinetic process was reported in the previous study on the fractal analysis of dilute gelling systems,¹⁴ such a case was usually not encountered here, probably due to the fact that more complicated kinetic processes are involved in non-dilute gelling systems. Typically, the concentrated gelling systems showed a curve consisting of two zones with different slopes in the fractal analysis of the kinetics data, either by using the original Dickinson model (Fig. S2, ESI†) or the extended one (see below). Note that the Dickinson model held in describing the kinetic processes at the first gelation stage. In the following, the linear fits using eqn (4)

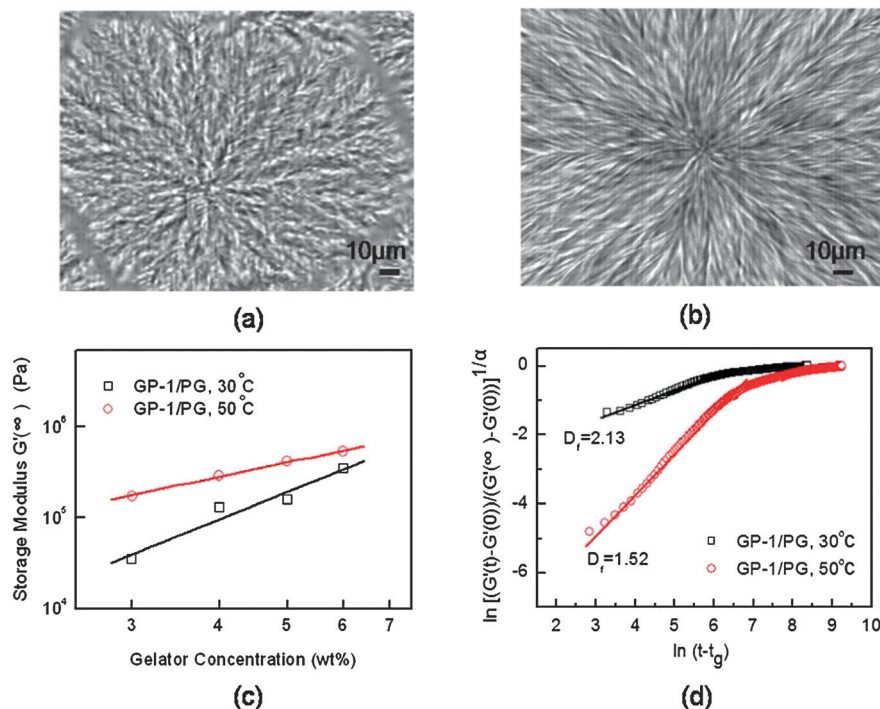


Fig. 2 Optical micrographs of the spherulitic networks of the GP-1/PG gels (3%): (a) compact structure with highly branched fibers formed at $T_g = 30\text{ }^{\circ}\text{C}$ with a cooling rate of $30\text{ }^{\circ}\text{C}$ per min, and (b) less compact structure with fewer branched fibers formed at $T_g = 50\text{ }^{\circ}\text{C}$ with a cooling rate of $10\text{ }^{\circ}\text{C}$ per min. (c) Power-law behaviours of the plateau values of the elastic moduli with respect to the gelator concentrations from the GP-1/PG gels formed at $T_g = 30\text{ }^{\circ}\text{C}$ ($\alpha \sim 3.2$) and $T_g = 50\text{ }^{\circ}\text{C}$ ($\alpha \sim 1.6$). (d) Fractal analysis of the kinetic data acquired from dynamic rheological measurements in terms of the extended Dickinson model (eqn (4)) for the two GP-1/PG gels shown in Fig. 2a and b. The linear fits were conducted for the first stages of the kinetic processes to extract the D_f values.

were produced only for the first zone kinetic curves, to extract D_f values for the gels studied here.

IV Results and discussion

In previous studies, we have demonstrated that tunable gel microstructures of the GP-1/PG system can be achieved by regulating the formation kinetics *via* thermal treatment,^{24,25} solvent selection,^{26,27} and chemical additives.²⁸ Herein we use the above fractal analysis method to gain a further understanding on the role of kinetic controls by different methods in the microstructure engineering of fibrous gels.

4.1 GP-1/PG gels formed with different thermal treatments

The regulation of the gelation temperature (T_g) and the cooling rate in the gelation process resulted in different fractal structures of the GP-1 fibrous gels. For example, for a 3% GP-1/PG system, compact spherulitic fiber networks with highly branched fibers (Fig. 2a) were formed at $T_g = 30\text{ }^{\circ}\text{C}$ and a cooling rate of $30\text{ }^{\circ}\text{C}$ per min; while less compact spherulites with a low degree of fiber-branching (Fig. 2b) formed at $T_g = 50\text{ }^{\circ}\text{C}$ and a cooling rate of $10\text{ }^{\circ}\text{C}$ per min. The effects of thermal controls on the size and compactness of the spherulitic fiber networks have been discussed in previous studies.^{11,24,25} This study further revealed that the power-law behaviour of the plateau values of the storage moduli with respect to the gelator concentrations in these two gels are different, as is shown in Fig. 2c.

A larger value of the scaling exponent α (~ 3.2) indicates a compact network structure of the GP-1 gel, while a lower value of α (~ 1.6) is a reflection of a less compact network structure.^{23,33} From the fractal analysis of the kinetic data (Fig. 2d), the values of D_f obtained are 2.13 and 1.52 for the two gel networks, respectively. Such a difference in the extent of compactness reflected by the values of D_f is in accordance with the structural features displayed in the optical micrographs for the two gel networks (Fig. 2a and b).

4.2 GP-1 fibrous networks formed in different solvents

Fig. 3 shows a significant difference in the microstructures and the formation kinetics of the GP-1 gels induced by using different solvents. The fiber network of the GP-1/PG gel (4%, $T_g = 40\text{ }^{\circ}\text{C}$) consists of a collection of compact spherulitic networks (Fig. 3a); while the GP-1/ISA gel (6%, $T_g = 15\text{ }^{\circ}\text{C}$) is displayed as an open structure consisting of a network of interconnecting fibers (Fig. 3b). Considering the difference in the solubility of GP-1 in the two solvents (GP-1 has a lower solubility in PG due to the higher polarity of this solvent), we selected different concentrations and gelation temperatures for these two systems, in order to achieve equal levels of supersaturation σ (ref. 26) ($\sigma = 15$ for both gels) for the growth of fiber networks. The power-law behavior of the storage moduli with respect to the gelator concentrations (Fig. 3c) suggested a scaling exponent α of 2.5 for the GP-1/PG gel and α of 1.1 for the GP-1/ISA gel. The values of D_f derived from the kinetic data

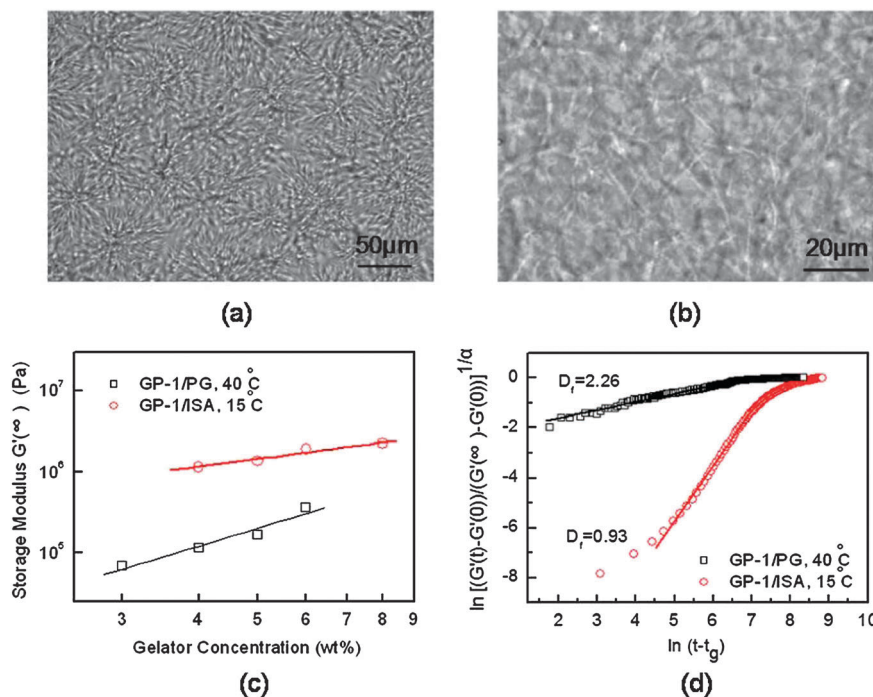


Fig. 3 Optical micrographs of (a) the spherulitic networks of 4% GP-1/PG gel formed at $T_g = 40\text{ }^{\circ}\text{C}$ with a cooling rate of $20\text{ }^{\circ}\text{C}$ per min and (b) the interconnecting fiber networks of 6% GP-1/ISA gel formed at $T_g = 15\text{ }^{\circ}\text{C}$ with a cooling rate of $30\text{ }^{\circ}\text{C}$ per min. (c) Power-law behaviors of the plateau values of the elastic moduli with respect to the gelator concentrations of the GP-1/PG gel formed at $T_g = 40\text{ }^{\circ}\text{C}$ ($\alpha \sim 2.5$) and GP-1/ISA gel formed at $T_g = 15\text{ }^{\circ}\text{C}$ ($\alpha \sim 1.1$). (d) Fractal analysis of the kinetic data acquired by dynamic rheological measurements in terms of the extended Dickinson model (eqn (4)) for the two gels shown in Fig. 3a and b. The linear fits were conducted for the first stages of the kinetic processes to extract the D_f values.

for the GP-1/PG gel and the GP-1/ISA gel are 2.26 and 0.93 (Fig. 3d), respectively. From the large difference in the kinetic derived D_f values, one can see that the growth of the fiber network under the same supersaturation conditions in these two systems followed distinct kinetic pathways. A good agreement between the kinetic derived D_f values and the fractal patterns displayed in the optical microscopy was verified: while the GP-1/ISA gel showed an open/linear structure of a fiber network and hence its fractality featured a D_f value of around 1; the GP-1/PG gel showed a compact structure of a spherulitic network and featured a much higher D_f value of 2.26. A similar open-to-compact microstructure change of a fibrous gel, accompanied by a corresponding increase in D_f has also been reported in other gelling systems.¹⁴

4.3 Effect of additives on the GP-1/PG gel

Similar fractal analysis was also performed on the GP-1/PG gels with microstructures engineered using chemical additives. A comparison between Fig. 4a and b suggests that the presence of the additive PMMMA led to a dramatic change in the spherulitic networks of GP-1 (4%, $T_g = 45\text{ }^{\circ}\text{C}$ with a cooling rate of $30\text{ }^{\circ}\text{C}$ per min): a tiny amount of PMMMA resulted in the formation of fewer but larger spherulites in a fixed volume. Such a structural change was due to the inhibition of nucleation and growth of GP-1 fibers by PMMMA molecules.^{11,28} As shown in Fig. 4c, the scaling exponents obtained for the GP-1/PG gel formed without and with additives are 3.0 and 3.8,

respectively. Correspondingly, D_f values of 2.03 and 2.46 were obtained from the kinetic data of the two gels (Fig. 4d). These results suggest that a more compact network structure was induced due to the inhibited nucleation and the growth of fibers. This can be understood based on the supersaturation dependence of the gel microstructure.^{11,24} In the presence of the additive, the primary nucleation rate at the induction stage was reduced significantly due to the inhibitory effect of the additive.¹¹ Since the gelator concentration was fixed, a reduction in the number of spherulites meant that more gelator molecules (a higher supersaturation) were available for fiber branching in each spherulite during growth. This led to the growth of more fiber arms from a nucleation center.^{11,24} The retarded nucleation caused by the additive could also promote a transverse growth and the side-branching of the fibers.^{11,28} A combination of the two effects contributed to the formation of more compact spherulitic fiber networks.

To sum up, fractal analysis based on the extended Dickinson model can be used (1) to extract the fractal features of a fibrous gel from its kinetic data acquired by rheological measurements, and (2) to evaluate the role of kinetic controls in the microstructure engineering of gel networks. It is worth emphasizing that compared to the previously reported method our method is advantageous. Table 1 shows a comparison of the D_f values derived from the original Dickinson model and the extended one for the aforementioned fibrous gels. Notably, for the fractal gels with open ($D_f \sim 1$ and $1 < D_f < 1.5$) or less compact

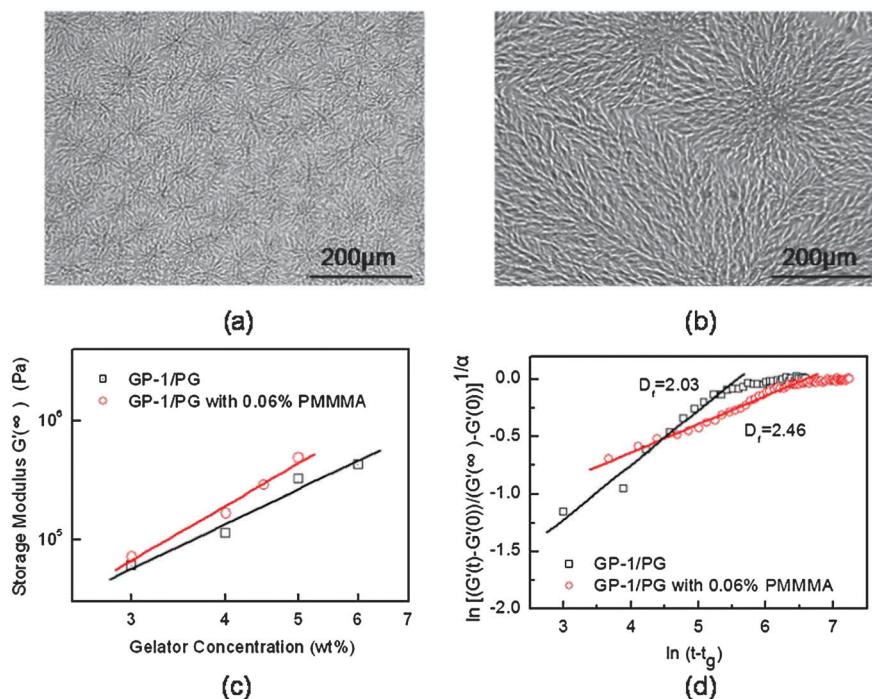


Fig. 4 Optical micrographs of the spherulitic networks of 4% GP-1/PG gel formed at $T_g = 45^\circ\text{C}$ with a cooling rate of 30°C per min (a) without additives, and (b) with 0.06% PMMMA. (c) Power-law behaviors of the plateau values of the elastic moduli with respect to the gelator concentrations from the GP-1/PG gels formed at $T_g = 45^\circ\text{C}$ without additives ($\alpha \sim 3.0$) and with 0.06% PMMMA ($\alpha \sim 3.8$). (d) Fractal analysis of the kinetic data acquired by dynamic rheological measurements in terms of the extended Dickinson model (eqn (4)) for the two gels shown in Fig. 4a and b. The linear fits were conducted for the first stages of the kinetic processes to extract the D_f values.

Table 1 Comparison of the D_f values of various fibrous gels that are obtained using different kinetic models

Samples		α	D_f^a	D_f^b
A	GP-1/PG, $T_g = 30^\circ\text{C}$, cooling rate 30°C per min	3.2	1.24	2.13
	GP-1/PG, $T_g = 50^\circ\text{C}$, cooling rate 10°C per min	1.6	1.12	1.52
B	GP-1/ISA, $T_g = 15^\circ\text{C}$, cooling rate 30°C per min	1.1	0.78	0.93
	GP-1/PG, $T_g = 40^\circ\text{C}$, cooling rate 20°C per min	2.5	1.42	2.26
C	GP-1/PG, $T_g = 45^\circ\text{C}$, without PMMMA, cooling rate 30°C per min	3.0	1.24	2.03
	GP-1/PG, $T_g = 45^\circ\text{C}$, with 0.06 wt% PMMMA, cooling rate 30°C per min	3.8	1.66	2.46

A: different thermal treatments; B: different solvents; C: effect of additives. α is the scaling factor of the plateau values of the elastic moduli for each gel. ^a From the original Dickinson model in ref. 14. ^b From the extended Dickinson model in this study.

network structures ($1.5 < D_f < 2$), the kinetic–structure relations derived using the original and the extended Dickinson models are comparable to each other.¹⁴ But for the fractal gel with highly compact networks ($2.0 < D_f < 3.0$), the extended model is more suitable for the description of the kinetic–structure relationship. In this regard, the extended model is general in its description of the gelation kinetics measured by the dynamic rheological properties of various fibrous gels.

V Summary and conclusion

We have developed a new method that can be used to do fractal analysis of the gelation kinetics occurring in both dilute and

concentrated gelling systems. The kinetic-derived structure parameter, as a measure of the extent of the compactness of the fiber networks, is in good agreement with the optical observations. Such a kinetic–structure analysis method can be used to provide a quantitative understanding of the role of various kinetic controls, such as thermal treatment, solvent regulation, and the use of additives, in the engineering of fibrous network structures. In addition, this study is helpful in understanding the kinetic–structure correlation in the gelation processes of macromolecules, since the fibrous gels formed either by small molecules or macromolecules such as polymers and proteins show very similar fractal patterns of crystalline fiber networks.

Acknowledgements

This research was supported by National Natural Science Foundation of China (10874015 and 11174033).

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