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Engineering Molecular Self-Assembled Fibrillar Networks by Ultrasound

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ABSTRACT: The architecture of self-organized three-dimensionally interconnected nanocrystal fibrillar networks has been achieved by ultrasound from a solution consisting of separate spherulites. The ultrasound stimulated structural transformation is correlated to the striking ultrasonic effects on turning nongelled solutions or weak gels into strong gels instantly, with enhancement of the storage modulus up to 3 magnitudes and up to 4 times more gelling capability. The basic principle involved in the ultrasound-induced structural transformation is established on the basis of the nucleation-and-growth model of a fiber network formation, and the mechanism of seeding multiplication, aggregation suppressing, and fiber distribution and growth promotion is proposed. This novel technique enables us to produce self-supporting gel functional materials possessing significantly modified macroscopic properties, from materials previously thus far considered to be "useless", without the use of chemical stimuli. Moreover, it provides a general strategy for the engineering of self-organized fiber network architectures, and we are consequently able to achieve the supramolecular functional materials with controllable macroscopic properties.

1. Introduction

Molecular self-assembled fiber network architecture exists ubiquitously in a variety of either living or nonliving systems. Because of the diversity of functionality, the self-assembled fibrous materials find importance applications in cell bioactivity, tissue engineering, drug delivery, novel separation, etc.[1−4] Over the past decades, significant efforts have been devoted to identifying the novel gelling agents that are capable of forming a three-dimensionally (3D) interconnected fiber network structure in organic and/or aqueous solutions.[5] This includes the screening of large amounts of compounds and understanding of the intermolecular interactions involved in the molecular assembly of network formation.[5a,b] The success of these efforts is nowadays the basis of fabricating new supramolecular network materials via chemical synthesizing strategy. On the other hand, it is recognized that exploration of the effects of external stimuli or fields in the assembly process of molecular architecture is another promising strategy for creating innovative supramolecular materials and systems with dynamically controlled property/functionality.[6] The studies on stimuli-responsive assembly of small molecules in these years has inspired a research frontier in material science and technology for fabricating supramolecular materials with the dynamically control of fluidity, viscoelasticity, solvent volatility, optical transmission, ion transport, wettability, etc.[6−9]

Among a variety of external physical stimuli, light[7] and electric fields[8] have been successfully used to switch molecular aggregations involved in the formation of gel, micelles, vesicles, and membranes. However, providing a physical method of control that provides not only a reversible switching of primary molecular aggregation but also the kinetic control of the hierarchical assembly of molecules remains a challenge.

Ultrasound has long been known as a powerful stimulus in the filed of sonochemistry[10] because of its diverse physical and chemical effects, such as cavitation, agitation, acoustic streaming, diffusion, and mechanical rupture. Very recently, an intriguing double-facet of ultrasonic effects in the assembly process of gel network has attracted attention.[9] On one hand, ultrasound was reported to induce the mechanical disruption of molecular aggregates by cleaving the noncovalent bonding, leading to the suppression of a gelation process,[9a] the rupture of the gel network.[9c] On the other hand, ultrasound stimulus initiates molecular aggregation of some specific molecules like metalated peptides, promoting the gelation process.[9a,b,d,e] Although the negative effect of ultrasound in the molecular aggregation has been studied extensively and is well-understood, the principle of the positive effects of ultrasound in the molecular assembly into a gel network has not been established yet. How the ultrasound stimulus could facilitate the development of a gel network and how it affects the construction of a molecular self-assembly network remains open questions.

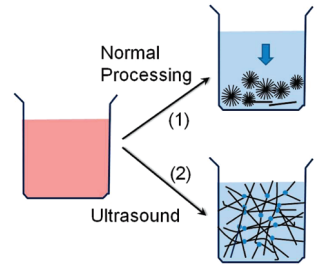

Figure 1. Illustration of micro/nanostructure engineering of soft functional materials: the control of kinetic pathway by ultrasound (route 2) with respect to normal fiber network formation (route 1).

In this work, we will study the effects of ultrasound stimulus in the hierarchical assembly of molecular gel network, particularly the control of the kinetic pathway by ultrasound that can produce macromolecular functional materials with 3D permanent interconnected nanocrystal fibrillar networks from the systems normally with separated spherulites precipitation (c.f. Figure 1). Our goal is to explore a new approach that fabricates soft functional materials with controllable macroscopic properties.

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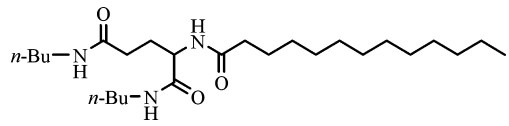
Scheme 1. Chemical Structure of *N*-Lauroyl-L-glutamic Acid Di-*n*-butylamide (GP-1)



To achieve this goal, we will also study the principle of ultrasound in manipulating the microstructure of fiber networks and consequently the structure-directing macroscopic properties of the resultant gel materials.

2. Experimental Section

The H-bonding gelator molecule, *N*-lauroyl-L-glutamic acid di-*n*-butylamide (GP-1, Scheme 1) dissolved in the solvent octanol or propylene glycol (PG) was chosen, considering that they are candidates of transdermal drug delivery carriers.[11] GP-1 (>98%) was obtained from Aijnomoto, and the solvents octanol and propylene glycol (both >99%) were obtained from Cognis. All chemicals were used as received. The clear solutions of GP-1/octanol or GP-1/PG were prepared at ~120 °C, and then quenched to room temperature. The cooling of the hot solutions at quiescent condition resulted in either an opaque viscous nongelled liquid with particulate precipitation for the samples of the gelator concentrations below the critical gelator concentration (CGC), or the weak gels for the samples of the concentrations above the CGC. The ultrasound treatment was applied to the quenched solutions (the volume of ~10 mL) at room temperature in an ultrasonic water bath (Ultrasonic LC 30H, 35 kHz, 1−4 W/cm^2) for a short period (0−2 min). For the samples with gelator concentrations above the CGCs, sonication was applied right after the hot solutions were quenched to room temperature. For the samples with the concentrations below the CGCs, sonication was applied at an early stage when some aggregation particles were visualized in the solutions. In both cases, the treated solutions after sonication were kept undisturbed under ambient condition to monitor the change in the state of liquid.

Scanning electronic microscope (SEM, JEOL JSM-5600LV), coupled with a CO_2 supercritical fluid extraction technique (Thar Design), was used to examine the nano/microstructure of samples. The purpose of implementing the latter is to remove the liquid captured in the networks, without disturbing the essential structure of networks. The GP-1 xerogels were obtained by setting the flow rate of CO_2 as 20 g min^{-1} and the extraction time as 1.5 h. For a better contrast, the GP-1 xerogels were coated with gold for 30 s. The microstructures of gel networks were then examined by SEM (at 5.0 kV).

An advanced rheological expansion system (ARES-LS, Rheometric Scientific) was used to evaluate the rheological properties of the samples. The sample was subjected to sinusoidal oscillations by moving both the upper and the lower circular plates with a diameter of 25 mm (the gap between the two plates is 1 mm). The instantaneous measurement of the applied stress and the resultant strain allows the calculation of the storage modulus G' (describing the elastic property) and the loss modulus G'' (describing the viscous property). In the time sweep experiments to examine the dynamic viscoelastic moduli, the frequency of the oscillations was set as 0.5 Hz and the amplitude was controlled to obtain a 0.05% strain to the sample. Under this strain limit, the macromolecular structure will not be destroyed by the measurements. For the gel samples, the strain sweep experiments were conducted to obtain the plateau value of the storage modulus and the critical strain at which the gel network was ruptured.

3. Results and Discussion

3.1. Ultrasound-Induced Gel Network: Microstructure and Macroscopic Properties. Normally the GP-1/octanol or GP-1/PG gels with the gelator concentration above the critical gelator concentration are turbid, and the gel networks are comprised by the spherulitic domains.[12] The CGCs are ~6 wt % for GP-1/octanol, and ~2 wt % for GP-1/PG, respectively. Ultrasound stimulus was used at the early stage of gelation, enabling not only the promotion of gelation process, but also the formation of homogeneous 3D interconnected fiber networks. Such effects are significant particularly for the gelling systems with the gelator concentrations nearby or below the CGCs.

Three wt% GP-1/octanol is a typical example, as is shown in Figure 2. The cooling of a hot solution of 3 wt % GP-1/octanol at quiescent condition resulted in a nongelled liquid as stated above. Figure 2A shows this nongelled sample stored for two more days under ambient conditions. However, after ultrasonic treatment for about 1 min, the gelation process occurred rapidly to form a stable gel within a few hours (Figure 2B). Moreover, when a heating-and-cooling treatment was applied to the ultrasound-induced gel sample, the nongelled liquid was obtained again. This implies that the gelling state and the corresponding fiber network structure are attributed to the effect of ultrasound.

In addition to the tuning of nongelled solution into gel phase, the OM and SEM micrographs from the samples demonstrate the striking effect of ultrasound stimulus in the structural transformation of gel network. The separated spherulites shown in Figure 2a were obtained from the precipitation particles of the nongelled sample of 3 wt % GP-1/octanol. One can see that each spherulite is of a porous structure formed by the fibers arrays in which the fiber arms grow radially from the center. The specific feature of the spherulitic domains can be identified by the Maltese Cross extinction pattern[13] under polarized light microscopy (Figure 2b), because of the highly ordered structure of fiber arrays. In contrast, the homogeneous 3D interconnected fiber networks were obtained from the ultrasound induced gel phase (Figure 2c). In such networks, nanometer-sized branched fibers can extend from one network to the adjacent via mutual interpenetration and entanglement. The details of the morphology of fibers and the microstructure of the interpenetrated/entangled, branched fiber networks are given in Figure 2d.

Elasticity is an important structural-directing macroscopic property of a gel network. For comparison, rheological measurements were performed for the above two samples. Figure 3 shows the modification in the storage modulus of the 3 wt % GP-1/octanol samples. The gels with 3D interconnected fiber network shows the plateau value of storage modulus $G' \approx 3600$ Pa, whereas the nongelled sample with the spherulite precipitation shows the magnitude of G' below the resolution of the instrument (<50 Pa). It suggests that the GP-1/octanol sample formed with ultrasound stimulus has the elasticity about two-orders of magnitude higher than the sample without ultrasound!

Very interesting, the ultrasound induced structural transformation from the spherulite to the interconnected fiber network can give rise to a significant enhancement of the gelation capability of the GP-1 molecules. The measure of the gelation capability of a given gelator for a gelled solvent is the critical gelator concentration, which is defined as the minimal gelator concentration capable of gelling a certain volume of liquid at room temperature.[5] Obviously, the lower the CGC is, the higher the gelation capability. By using the inverted test tube method, [5] we found that by ultrasound treatment the CGC is reduced from ~6 to ~2 wt % for GP-1/octanol system.

Apart from the above example demonstrating that the ultrasound-induced network structure transformation can lead to the switch from a nongelled to a gel state, such a structural transformation can also turn a weak gel into a strong gel. Figures 4 and 5 show the case of 2 wt % GP-1/PG samples. A weak gel was obtained in a normal processing without ultrasound stimulus. Such a gel phase is composed by the closely packed spherulitic domains (Figure 4a). The gel sample produced via

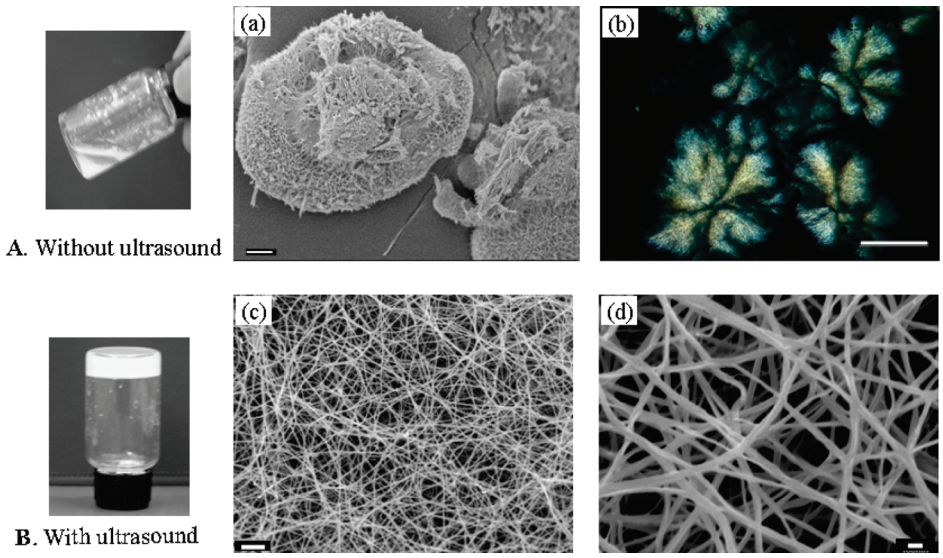


Figure 2. Three weight percent GP-1/octanol samples formed (A) without and (B) with ultrasound stimulus, respectively. The corresponding micro/nano-structures shown by SEM and OM. For the nongelled phase: (a) the precipitate particles, scale bar 10 μm; and (b) polarized light images of the spherulitic particles, scale bar 100 μm. For the ultrasound-induced gel phase: (c) the fiber network structure, scale bar 1 μm; and (d) the enlarged microstructure of the fiber network, scale bar 100 nm.

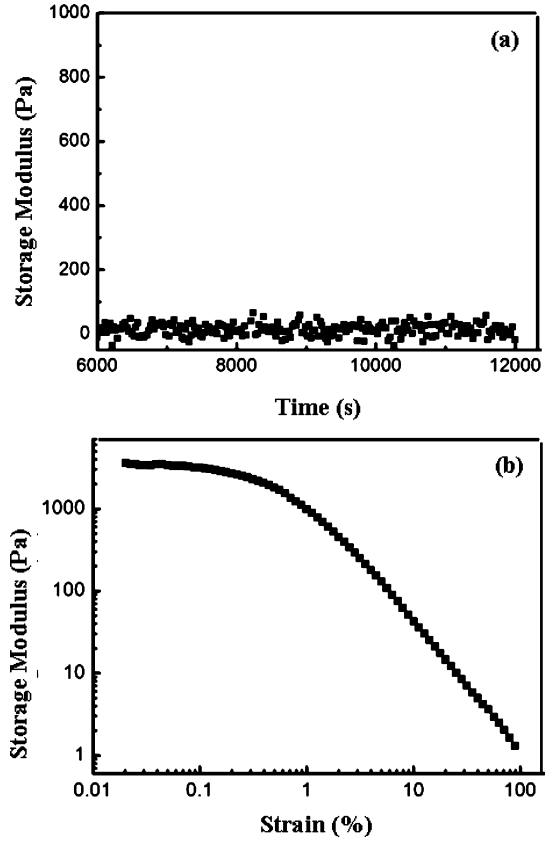


Figure 3. Storage modulus G' of the 3 wt % GP-1/octanol samples: (a) the time sweep of the dynamic elasticity measurement from the nongelled sample; (b) the strain (γ) sweep of the dynamic elasticity measurement from the ultrasound-induced gel sample.

the sonication treatment, similar to 3 wt % GP-1/octanol gel, shows a 3D homogeneous interconnected nanofiber network (Figure 4b). Again, ultrasound-induced transformation from the spherulitic structures to 3D interconnected fiber networks exerts a significant impact on the rheological properties of the gels. As shown in Figure 5, the storage modulus G' of the ultrasound-modified gel for the 2 wt % GP-1/PG is one magnitude stronger than the untreated gel.

Furthermore, each spherulite (Figure 4a) consists of very densely arranged fiber radial arms, indicating a less porosity of the spherulitic structure than the fiber network. That may be the reason for the enhanced gelation capability of the ultrasound-induced gels. Here, ultrasound makes the CGC reduced from ~2 to ~0.5 wt % for GP-1/PG system. This corresponds to the enhancement in the gelation capability of GP-1 by ~4 times.

As indicated by the aforementioned two cases, the remarkable enhancement in the rheological properties of the gels is closely correlated to the transformation of the spherulitic domains network to 3D interconnected fiber network by ultrasound, although the mechanical/rheological properties of gels depend on the thickness and density of fibers, and the nature and distribution of fiber junctions.[14] Compared with the 3D interpenetrated/entangled branched fiber networks occurring in the ultrasound induced gels, spherulitic domains in 2 wt % GP-1/PG weak gel, or 3 wt % GP-1/octanol nongelled phase show more compact or less porosity in the network structure. Probably because the fiber arms in one domain hardly interpenetrate into the adjacent spherulitic domains, spherulitic domains are spatially separated and exclusive, therefore appearing as inhomogeneous regimes in the gels. In this case, the mechanical/rheological properties of gels are determined by weak physical interactions of separated spherulitic domains, other than the fiber networks occurring within individual spherulitic domains. This is why we have poor gelation and weaker rheological property once the spherulitic domains occur in the solutions.

On the other hand, the 3D interconnected nanofiber networks occurring under ultrasound have branched fibers that interpenetrate from one network to the adjacent networks. Rheologically, such networks would behave like a single fiber network, as the interpenetrated fiber networks will be interlocked with each other via mutually entangled fibers. Under such a circumstance, the mechanical properties of gels in this case are determined by the fiber network.

We realize that the striking effect of ultrasound on the hierarchical assembly of gelator molecules into fiber networks is through the regulation of the gelation kinetic pathways, which

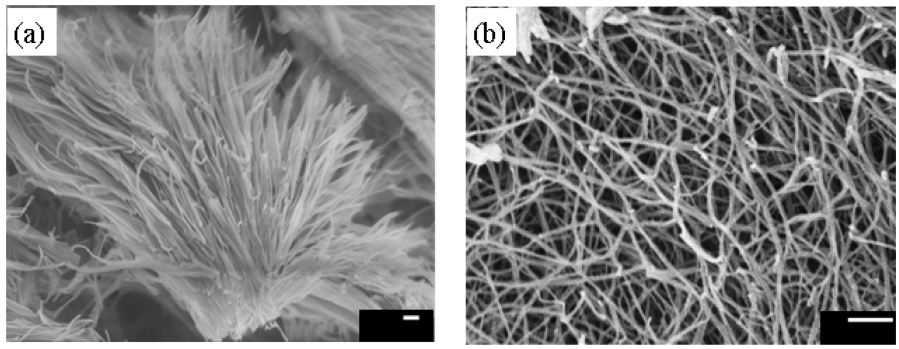


Figure 4. SEM micrographs of 2 wt % GP-1/PG gel samples. (a) spherulitic domains formed without ultrasound; (b) 3D interconnected fiber network formed with 1 min of sonication treatment. Scale bar: 500 nm.

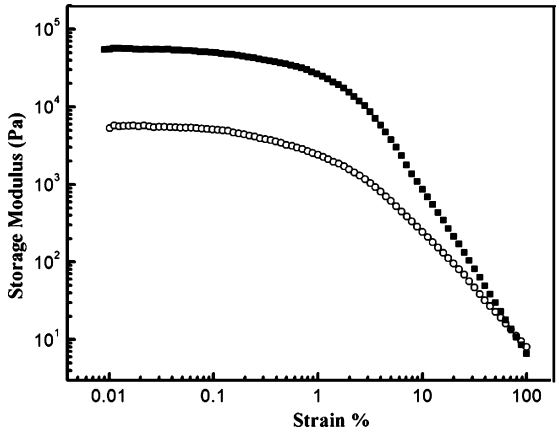


Figure 5. Storage modulus G' of the 2 wt % GP-1/PG gels formed without ultrasound (□) and with ultrasound (■), respectively.

leads to the transformation from the separated spherulitic domains to the 3D interpenetrated/entangled branched fiber networks. The key question is how the transformation occurs. Unfortunately, a thorough understanding of the influence of sonication on the gelation kinetics is still absent, although people have recognized the importance of ultrasound stimulus in the kinetic control of molecular gel formation.[9a,b,d,e] As reported in our earlier works, [15] GP-1 nano fibers have the crystalline structure, and the formation of GP-1 fibers and the fiber networks is controlled by nucleation and growth mechanism. In the following, we will attempt to elucidate, on the basis of the nucleation-and-growth model of fiber network, how ultrasound can affect the gelation kinetic pathway, leading to the above-mentioned structural transformation.

3.2. Possible Principle of Ultrasound Stimulus in the Kinetic Control of Gelation Pathways. Molecular gel is a typical example of the supramolecular network formation by the assembly of small molecules in solutions.[16] Similar to the polymer gel formation,[17] the fiber network of small gelator molecules develops through the nucleation and growth of fibers and junctions. However, in contrast to the polymer gelations where polymer chains already exist,[17c] the elemental constitutes of fibril networks of small molecule organic gelators are crystalline fibers. The first necessary step in such a gel formation is the nucleation and growth of one-dimensional fibers from small gelator molecules.[16b] In this regard, the kinetic process occurred in the small molecule organic gels formation is very different from that involved in the polymer gels formation.[18]

The start point of small molecules gelation is established on the generation and distribution of fibrous "seeds". Regulating the start point turns out to be a crucial issue in determining the kinetic pathways of a gel network development, and consequently, the final network structure and its macroscopic properties as well. As indicated by the previous studies,[12,18] the start point can be regulated through controlling the nucleation and growth behavior of fibers at the early stage. At this stage, two distinct kinetic pathways of a gel network formation, i.e., the spherulitic growth mode[12] and the fibrous growth mode,[18] can be adopted. As fiberlike GP-1 crystallites are highly anisotropic in the crystallization process, the nucleation of fibers in the liquid phase is a difficult event. Therefore, nucleation occurs only at relatively high thermodynamic supersaturations σ, in a heterogeneous manner.[15a] Because of the fiberlike growth habit, the heterogeneous nucleation will then give rise to the formation and growth of spherulites. Nevertheless, if some fiber seeds are introduced, the growth of fiberlike GP-1 crystallites can take place at very low thermodynamic supersaturations σ, as the kinetic barrier for crystallite growth is much lower than nucleation.[15a] Evidently, promoting one mode and suppressing the other will enable us to tune the fiber network of gels between the spherulite domains and the 3D interpenetrated/entangled branched fiber dominant networks, which will, consequently, modify the rheological properties of the gels. In fact, such gel fiber network tuning has been achieved before by some special treatments during the gelation process.[12,18]

The effect of ultrasound stimulus on the regulation of conventional crystallization in solution has been studied extensively.[10,19] The influence includes the promotion of primary/secondary nucleation,[10,19] the acceleration of crystal growth,[10c] the improvement of solid−liquid separation behavior, etc.[10c] According to Naota[9a] and Yi,[9e] ultrasound will promote primary/secondary nucleation in a crystallization solution. This implies that sononucleation can produce seeds for further crystallization. In our experiments, as the GP-1/PG or GP-1/octanol system normally produces spherulites at the initial stage (the spherulitic growth mode), the applied ultrasound after some spherulites occurs will break the spherulites, giving rise to a huge number of fiber seeds dispersed in the sonicated phase. In addition, sonication may also stimulate the primary nucleation of GP-1 fibers. This can be regarded as the seed multiplication effect. Ultrasound also promotes the uniform dispersal of fiber seeds in the sonicated liquid phase due to the facilitation of mass transportation,[10b] and mechanically disrupts newly formed aggregation/spherulitic domains. The two effects can be regarded as seed distribution and aggregation suppressing effects. On the basis of the nucleation-and-growth model, this will lead to the massive secondary nucleation and growth of GP-1 fibers, and cause a further development of fiber networks. The above effects of ultrasound on the early stage of gelation are schematically

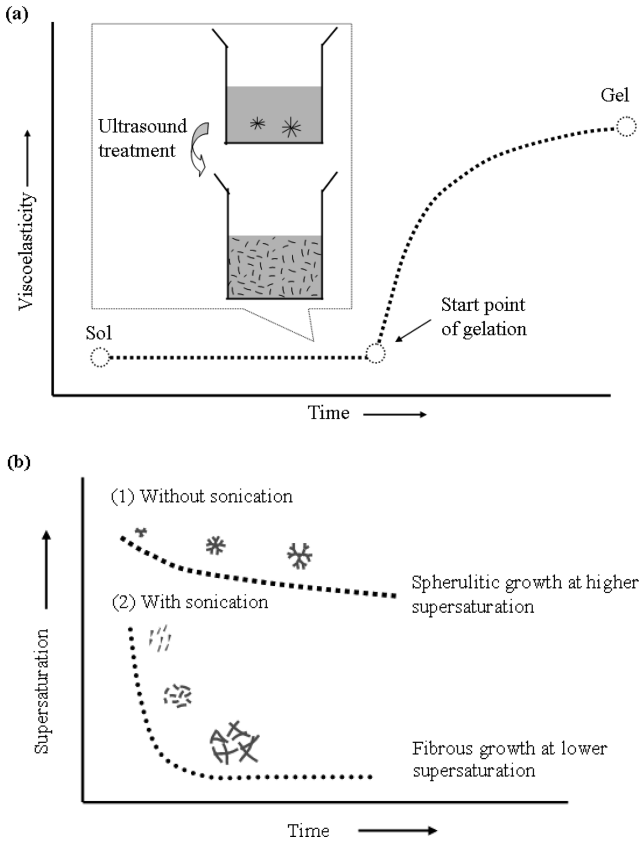


Figure 6. Schematics of the ultrasonic effects on the gelation process: (a) Ultrasound regulating the generation and distribution of fibrous seeds for the start point of gelation (illustrated in the sol−gel transition by dynamic rheological measurement). (b) Illustration of the supersaturation dependent gelation kinetic pathways with and without ultrasound stimulus for the gelling system that is normally with the spherulitic growth mode. (1) Without ultrasound stimulus, the nucleation and growth of highly branched fiber arrays (spherulitic domains) would be conducted at a certain level of supersaturation, so that the spherulitic growth proceed throughout the gradually depletion of the gelator concentration to the eventually formation of the network of domains. (2) With sonication, the generation and distribution of fibrous seeds and simultaneously the acceleration of the fiber growth from the seeds would lead to the fast decrease of supersaturation to a low level at which the one-dimensional growth of individual fibers would be favored.

shown in Figure 6a, which is used to regulate the generation and distribution of fibrous seeds for the start point of gelation. In a sol−gel transition by time-dependent rheological measurement, the starting point of gelation is defined as the onset of an abruptly rise of the viscoelastic moduli. From this point, the development of fiber network commences.

Note that due to the fact that ultrasound will facilitate mass transport, the growth of fibers will be facilitated.[10c] As the fast growth of individual fibers from all seeds in the sonicated phase will take place and numerous seeds consume the gelator molecules simultaneously, the gelator concentration decreases sharply during the gelation process (Figure 6b).[9b] This will also suppress the 3D primary nucleation of GP-1 fibers and the formation of spherulites at the later stage of gelation. It means that ultrasound stimulus would enable the fast development of a network at a relatively lower supersaturation level. In this regard, the regulation of the start point by ultrasound stimulus should facilitate the fibrous growth of a gel network, according to the supersaturation dependence of the gelation kinetics.[15a] Thereby, 3D interconnected branched fiber networks will be established through the penetration and entanglements of the growing individual fibers.

It is worth noting that the formation of 3D permanent interconnected fiber network is also strongly dependent on some other factors like gelator structure, solvent polarity, temperature, and additives.[5,15,18] For instance, in the recent work reported by different authors,[18] the minor tailor-making of molecular structure for the ALS-type (aromatic-linker-steroid) gelator was used to obtain the molecular gel with the 3D fiber network without or with fewer spherulitic domain structure. Provided that such a tailor-making of gelator molecular structure via the chemical synthesizing is a time-consuming process, ultrasound stimulus would be more efficient tool for creating homogeneous 3D interconnected fiber networks without any chemical stimuli. The advantage of providing an instant, easy-processing, and reproducible way to create 3D homogeneous gel network makes ultrasound stimulus a general and practical physical approach in the engineering of self-organized fiber network materials, much superior over other approaches.

In addition, the ultrasound-induced transformation from a lower gelation capability to a higher one, or from the liquidlike behavior to the solidlike behavior of the rheology, is reversible when a heating-and-cooling treatment is applied. These dynamically controlled properties may find important applications in pharmaceutics, for instance, in the drug-release control.

4. Conclusions

We have elucidated the significant roles of ultrasound in manipulating the kinetic pathways of a molecular gel network construction and further for promoting gelation process. For molecular solutions of hydrogen-bonded GP-1 in octanol or PG, we can obtain the stable gel phases from the normally nongelled solutions at the concentrations far below the CGC by sonication. It turns out that ultrasound can promote the transformation of the spherulitic structures to 3D interconnected branched fiber networks, resulting in the enhancement of the storage modulus up to 3 magnitudes and of the gelation capability up to 4 times. The fiber network structural transformation is mainly due to the ultrasonic seeding multiplication, fiber distribution, and aggregation suppressing effects. The ultrasound may also promote the growth of fibers, which facilitates the formation of 3D interpenetrated/entangled branched fiber networks. As an advantageous physical approach of quick and easy-controlling, reversible and reproducible, ultrasound technique may provide a general strategy for the engineering of self-organized fiber network architectures and consequently for achieving the supramolecular functional materials with controllable macroscopic properties.

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