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Critical behavior of confined supramolecular soft materials on a microscopic scale†

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The formation of fiber networks and the resulting rheological properties of supramolecular soft materials are dramatically influenced when the volume of the system is reduced to a threshold. Unlike un-confined systems, the formation of fiber networks under volume confinement is independent of temperature and solute concentration.

Supramolecular soft materials formed by the self-assembly of molecules have attracted significant attention in recent years.1 The macroscopic properties and in-use functions of such a material are mainly determined by its network structures.2 Small molecule organogels, as one class of supramolecular soft materials, have important applications in drug delivery, tissue engineering, synthesis of nanomaterials, to name but a few.3 Recently, in order to achieve a better control over the fabrication of soft materials, much attention has been focused on the formation mechanism of fiber networks in these materials and the correlation to the performance of them.4 The engineering of the microstructure of the materials and consequently the macroscopic properties have been implemented via different techniques, including controlling supercoiling,5 adding additives,6 and ultrasound.7 However, the existing studies are mainly concentrated on the materials formed in an unlimited space with respect to the size of fiber networks. In fact, soft materials occurred on a micro- or nanometre scale (microgels and nanogels) are more important in various areas, such as tissue engineering, nanofabrication and drug delivery.8 Under such circumstances, whether a soft material will behave the same as it does in a confined space remains as an open question. Therefore, to acquire a good understanding of the characteristics of the fiber network formation in a confined space and its impact on the performance of a material is particularly important for the design and fabrication of soft materials with desired performance and the understanding of biomechanics of living organisms comprising of self-assembled supramolecular materials of intracellular and intercellular structures.9

It is known that a condensed material system in a confined space behaves differently than it does in an unconfined space. Specifically, the surface tension and viscosity become more dominant than the gravity and inertia forces in determining its performance.10 There are plenty of processes in nature occurring on the micrometre scale and much work has been carried out to acquire the understanding and control of the microfluidic effect10 and the behavior of colloidal particles in a confined space.11 However, the implication of the impact from a confined space particularly on the formation and properties of supramolecular soft materials remains to be explored.12 In this work, we will examine the volume confinement effect on the formation of (spherulitic) fiber networks in supramolecular soft materials and its impact on the performance of the materials. Small molecule organogels formed by the gelation of N-lauroyl-L-glutamic acid di-n-butylamide (GP-1) in ethylene glycol (EG) and propylene glycol (PG) are selected as two model systems. We will show that the impact of a confined volume can give rise to some abnormal behaviors of these materials. This will on one hand advance the understanding of the performance of confined soft materials, and on the other hand open a new area in the design of soft functional materials on a micro-/nanometre scale.

It has been generally accepted that one of the governing mechanisms for the formation of the fiber network in a physical gel is the nucleation mediated network formation mechanism.12 On the basis of this mechanism, the formation of fiber networks takes place via the primary nucleation of the gelators, followed by the subsequent growth of the fibers. In this regard, the nucleation behavior is of great importance because of its strong influence on the topological structure and fiber size of the network, and consequently the macroscopic properties of the material.10,11 Those materials consisting of only one set of fiber networks within the material are regarded as single-fibre network dominated systems, while those consisting of several mutually exclusive fiber networks are considered as multi-domain network systems, in which the domains correspond to the individual and mutually exclusive fiber networks. A multi-domain network structure can be commonly found in...
polymers, protein crystallites and other supramolecular soft materials.\textsuperscript{1,10} For such a system, the weak and transient physical contact between adjacent domains is predominant in determining the macroscopic rheological properties of the material, and a parameter $\zeta$ (defined as the average distance between the centers of adjacent fiber networks, i.e. the size of a single fiber network domain) is normally taken to characterize it.\textsuperscript{1,10,13} In a multi-domain network, the number of the primarily formed nuclei in a unit volume will determine the number and eventually the size of the fiber networks per unit volume.\textsuperscript{12}

The primary nucleation rate $J$, defined as the number of nuclei successfully generated per unit time unit volume, is determined by the free-energy barrier $\Delta G^*$ as:\textsuperscript{12}

$$J \propto \exp(-\Delta G^*/kT)$$  \hspace{1cm} (1)

where

$$\Delta G^* \approx 1/[(T_{eq} - T)/T_{eq}^2]$$  \hspace{1cm} (2)

where $k$ is the Boltzman constant; $T_{eq}$ and $T$ denote, respectively, the equilibrium and actual temperature at which nucleation occurs (cf. ESI†). The above equations indicate that at a fixed solute concentration, the degree of supercooling (defined as $(T_{eq} - T)/T_{eq}$, a parameter describing how far a system goes beyond an equilibrium state) is a key factor influencing the primary nucleation rate within the system. For a gelling system, the solute is the gelator and the temperature $T$ at which a new phase (fiber) forms is the gelling temperature $T_g$. With a given solute concentration, the nucleation rate $J$ can be controlled by changing $T_g$.

Fig. 1 shows the micrographs of the evolution of the fiber networks of GP-1 formed in EG at a given gelator concentration in an unconfined space. A notable supercooling dependence of $\zeta$ can be observed and is plotted in Fig. 3. $\zeta$ increases from about 45 $\mu$m to more than 1.3 mm with increase in $T_g$ (supercooling from $\sim$0.78 to $\sim$0.29), which can be described by a power law equation as $\zeta = 64.5((T_{eq} - T)/T_{eq})^{-2.26}$. The supercooling dependence of the fiber network shows similar behavior at different spacing values (from 0.5 to 0.1 mm) (cf. Fig. S1†).

It is interesting to observe that when the spacing is reduced to a certain value of 0.05 mm, the supercooling dependence of the size of the fiber networks does not exist. Fig. 2 shows the microstructure of the gels formed within a 0.05 mm space at different $T_g$ (supercooling from $\sim$0.74 to $\sim$0.26). The spherulitic networks maintain similar appearances at different $T_g$ and no obvious supercooling dependence of the spherulite size can be observed. For all the temperatures, $\zeta$ remains about 115 $\mu$m (cf. Fig. 3), which is about 2.3 times that of the spacing value $L$.

The quantitative relationship between $\zeta$ and the rheological properties such as the storage modulus $G'$ of a material formed in an unconfined space has been obtained as $G' \propto \zeta^{0.13}$. This implies that the elasticity of a gel can be adjusted by controlling the size of the fiber networks under this situation. The interesting volume confinement effects on the microstructures of fiber networks observed in this work prompt us to investigate whether the volume confinement can bring dramatic changes to the macroscopic properties of the material. To achieve this, the rheological properties of the gels were monitored in situ.

Typical curves for the evolution of $G'$ of the gel formed at two gelling temperatures of 40 and 85 $^\circ$C are presented in Fig. 4. Within an unconfined space of 0.50 mm, a great difference between the curves at the two temperatures can be observed. At 40 $^\circ$C (supercooling $\sim$0.65), $G'$ increases quickly and reaches a constant value within 500 s. An elevated $T_g$ (decreased supercooling) corresponds to an increase of $G'$ (cf. Fig. S2†) as a result of the decreased boundary effect within the material. As a consequence, an abrupt rise in $G'$ can be obtained at a higher temperature once the size of spherulitic networks matches the value of the spacing. For the curve at 85 $^\circ$C (supercooling $\sim$0.26), $G'$ keeps increasing even after a long time (9000 s) to a much larger value ($G' \sim 1.5 \times 10^3$ Pa). Under this condition, only one spherulite can be accommodated in the direction of lowest dimension within the system ($L/\zeta = 1$, Fig. 3 inset), leading to a structural transition from a multi-domain network to a single network.\textsuperscript{13} Compared with the unconfined cases, within a severely confined volume of 0.05 mm (hollow spots in Fig. 4, the measurements come with a large scattering in the later space due to the equipment limit), $G'$ keeps increasing at both 40 $^\circ$C and 85 $^\circ$C to a large value. This indicates that the structural transition between a multi-domain network and a single network occurs under both conditions. The number of spherulitic networks in the respective direction should be one as well, which is consistent with our optical observation.

Similar volume confinement effects on fiber networks of GP-1 formed in another solvent (PG) were also observed (cf. Fig. S3†). Within a confined system, the size of the spherulitic network has been regulated to a value of $\sim$2.1 times that of the spacing, being independent of the solute concentration.
This journal is significant than in an unconfined system. As a result, the size of the spherulitic network turns out to be

Compared to the supercooling effects, the influence from the dynamic heterogeneities are regarded as the only cause. A

A spacing of 0.50 mm was taken here for the un-confined system

It has been suggested that in a nucleating system, the creation of new active domains (nucleating centers) are influenced by both static (i.e. dust particles or bubbles) and dynamic (demonstrating a phenomenon that some molecules move differently from the others) heterogeneities. In a clean system without impurities, dynamic heterogeneity occurs especially in a highly supercooled liquid, in which the difference of the movement might be orders of magnitude for molecules situated only nanometres away. The heterogeneity phenomenon significantly influences the molecular translation and rotation, which directly control the manner by which molecules attach and align with the growing crystal in a crystallization progress. Within a confined system, the effect of viscosity on the behavior of the fluid is more significant than in an unconfined system. The reorientation of the molecules can be greatly disturbed by the high viscosity. Compared to the supercooling effects, the influence from the high viscosity in a confined volume becomes predominant in determining the formation of new active nucleation centers. As a result, the size of the spherulitic network turns out to be volume-dependent instead of supercooling dependent.

In summary, the 1D volume confinement effect on the network structure of supramolecular soft materials is evidenced from optical observation and rheological measurements. Within a confined volume, the size of the spherulitic fiber networks formed in the model supramolecular materials are independent of the gelling conditions such as the gelling temperature or solute concentration. This effect might result from the dynamic heterogeneous nucleation, which is mainly determined by the promoted viscosity of the fluid within a confined space. More in-depth studies are needed to get a clear understanding of the mechanism. Such a network adjustment effect is of special significance for the design of materials with tailored microstructure and macroscopic properties.

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