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Jamming transition in solutions containing organogelator molecules of amino-acid type: rheological and calorimetry experiments†

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The liquid to organogel transition of solutions containing new organogelator molecules of the amino-acid type is studied using rheological and differential scanning calorimetry (DSC) techniques. This paper describes the formation of the organogel as a function of the temperature for various concentrations of the organogelator molecules, and the mechanical properties of the organogel as a function of concentration, frequency, thermal history and aging. We show that the organogel is not a physical gel, but a jammed suspension. The viscoelastic behavior at different extents of the jamming can be scaled onto a single master curve describing the growth of a solid network in a background fluid. The formation of the solid network exhibits a critical-like behavior that is reminiscent of elasticity percolation. Four characteristic temperatures have been identified: the temperature at which the clusters begin to form, the transition temperature between the liquid and the organogel, the onset temperature of the percolation-like behavior of the solid component of the system and the temperature at which the solid component has a pure elastic response. The comparison between the rheological measurements and the DSC measurements shows that the rheological measurements detect the fluid-to-organogel transition, whereas DSC detects the molecular associations in the material, which are at the origin of the formation of the clusters. The two temperatures differ significantly from each other and their difference gives the temperature range where the clusters are crowding. This study demonstrates for the first time that an organogel is not a physical gel, as it is currently believed, but a jammed suspension.

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1 Introduction and motivation

Some systems of soft matter exhibit a transition from a liquid-like state to a solid-like state, commonly called gelation, which results from the formation and growth of clusters. Three main groups of gelation phenomena have been distinguished: chemical¹ and physical^{2,3} gelation, and jamming-induced gelation.^{4,5}

Chemical gelation is a percolation transition characterized by covalent and therefore permanent cross-links, which connect molecules into a three-dimensional network. The gel point is reached when the connectivity correlation length diverges to infinity. At the gel point, the system, named critical gel, is characterized by a power law of the real G' and the imaginary G'' part of the shear modulus as a function of frequency, which is given by $G' \sim G'' \sim \omega^n$, where ω is the angular frequency and n

the relaxation exponent. As a result, G' and G'' are parallel in a log-log plot and the tangent of the loss angle δ , given by $\tan \delta = G''/G'$, becomes frequency independent. The observation of this particular behavior of G' and G'' determines the gel point.^{1,6} Since the cross-links have an infinite lifetime, the chemical gels are irreversible. In the hydrodynamic regime, they are characterized by a frequency-independent behavior of G' and a behavior of $G'' \sim \text{frequency}$.

In physical gels, the bonds are reversible. Physical gelation results from the growth of clusters that are connected if the lifetime of the bonds is sufficiently long.^{2,3} As for chemical gelation, the gel point is reached when the correlation length diverges to infinity. Thus, similar behavior should be observed at the gel point with physical and chemical gels. Power law behaviors were indeed observed for physical gels,^{7,8} as for chemical gels.^{1,6} As a result of the transient nature of the bonds, physical gels are thermo-reversible, *i.e.* they transform themselves into a liquid phase when the temperature is high enough. In contrast to chemical gels, where the branching point is well defined by the functionality of the molecules, the size and the number of the cross-linking domains of physical gels can vary throughout the sample. The gels do not form necessarily instantly, and their properties, when formed, can evolve over

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time. They do not have a generic rheological signature within the frequency range commonly used. For example, G' and G'' can be approximately frequency-independent or show a relaxation process at low frequencies illustrating the transient nature of the gel.³ Physical gels are often obtained with systems exhibiting, for example, hydrogen bonds, crystalline regions, or electrostatic forces, which give rise to the physical junctions at the origin of the network.

The third type of liquid-to-solid transitions is not related to percolation. These transitions are non-equilibrium transitions that are observed in some systems exhibiting attractive or repulsive interparticle interactions, such as colloidal suspensions^{9–11} or multi-arm star polymers.^{12–14} They are driven by the crowding of the clusters resulting from these interacting particles, which causes a progressive arrest of their dynamics leading to an elastic solid formed by their jamming. In contrast to percolation, the clusters have a finite size and touch together without cross-linking. Concomitantly with this liquid-to-solid change, the system becomes non-ergodic because the constituent particles are becoming unable to explore the phase space on the experimental time scale. Review articles focusing on the dynamical arrest in colloidal gels¹⁵ and on the elasticity aspects of these systems¹⁶ have been reported. A marked difference with the physical gelation concerns the rheological behavior at the transition point since the physical gelation is characterized by a critical gel, contrary to the jamming-induced gelation for which the solid-like and the liquid-like components behave independent of one another. As a consequence, the frequency dependence of the shear moduli at the transition point is different for both types of transition. The measurement of the frequency dependence of G' and G'' is therefore an essential experiment to determine whether the liquid-to-solid transition is a physical gelation or a jamming-induced gelation. A simplified generic model known as “the soft glassy rheology model” has been developed to describe the dynamics of such jammed systems in terms of the dynamics of their mesoscopic elements.¹⁷

The organogels are composed of low-molecular-weight organic molecules called organogelators in a suitable solvent and are currently described as thermoreversible physical gels,¹⁸ and their formation as a physical gelation. The gelation process depends not only on the organogelator molecules but also on the solvent, which makes the organogels difficult to obtain. Although these systems have been an object of a great number of studies because of their technological significance,^{18,19} to our knowledge there are no measurements of G' and G'' as a function of frequency in the vicinity of the transition point allowing us to determine whether these systems are physical gels or jammed suspensions.

Recently, a family of new organogelator molecules of the amino-acid type was synthesized, allowing the preparation of low molecular weight organogels in solvents such as toluene, tetrachloroethylene and tetralin.^{20,21} The present study aims to characterize the formation and the melting of these new organogels as well as their mechanical shear properties, in order to decide whether the gelation transition is a jamming transition or a physical transition. Three different experimental devices were used: (a) a conventional rheometer to perform

measurements related to the formation and melting of the organogels, (b) a piezoelectric rheometer to determine the shear modulus of the organogels on a wide frequency range and by applying very low strains and (c) differential scanning calorimetry (DSC) techniques to determine whether the gelation temperature is the same or not as that given by the mechanical measurements. The studied systems were toluene-based and tetralin-based solutions.

This paper is organized as follows: after a section on the Materials and methods, the experimental results dealing respectively with the formation and the dynamical properties of the organogels are presented. Then, the whole results are discussed in the context of physical gelation and jamming-induced gelation.

II Materials and methods

2.1 Compounds

The organogelator molecule used to form the toluene-based and the tetralin-based organogel was synthesized at the Laboratoire de Chimie Physique Macromoléculaire de Nancy. This is a peptide protected by a benzyloxycarbonyl (Z) group at its N-terminal end and by a hydrazine-naphthalimide (NH-Napht) group at its C-terminal end (Fig. 1). Different spectroscopy techniques such as Nuclear Magnetic Resonance (NMR), Infra Red (IR) spectroscopy, fluorescence and circular dichroism were used to elucidate the formation and structure of the organogel.^{20,21} From these experiments, it turns out that the process of gelation is driven by the formation of columns due to hydrogen bonds between the organogelator molecules followed by the association of these columns by π - π stacking interactions, leading to a fibrillar structure. Fig. 2 shows a schematic drawing of these molecular associations. A detailed account of the procedures used to prepare the samples for the shear and DSC experiments will be described in the sections dealing with these measurements.

2.2 Mechanical devices

Measurements of the complex shear modulus G^* were performed using the piezoelectric rheometer we developed over more than a decade and applied to the study of the dynamic properties of liquid crystal elastomers,^{22–31} conventional flexible and liquid crystal polymers,^{32–35} uniaxial magnetic gels,³⁶ suspension of magnetic particles,³⁷ hydrogels³⁸ and

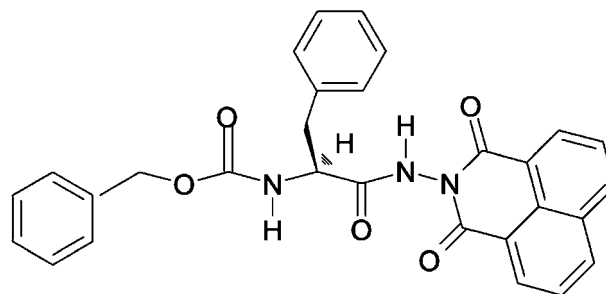


Fig. 1 Chemical composition of the organogelator molecule.

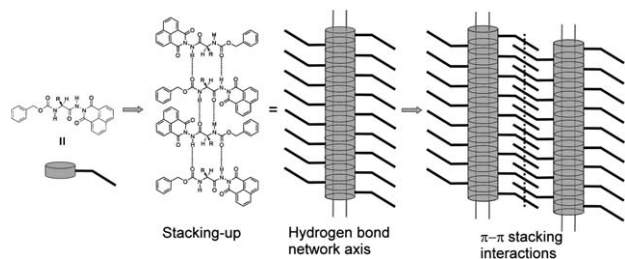


Fig. 2 Schematic picture showing the associations between the organogelator molecules.

polyelectrolyte films.³⁹ This device is a plate-plate rheometer operating with piezoelectric ceramics vibrating in the shear mode. The principle of measurement of the device is shown in Fig. 3. It consists in applying a very small strain ε on the sample through the glass slide attached to the emitting ceramics and measuring the stress σ received by the glass slide attached to the receiving ceramics. The complex shear modulus G^* is given by the relationship $G^* = \sigma/\varepsilon$.

The measurements were taken on organogel samples prepared in a mold. The procedure used was the following: the solution containing the organogelator molecules was first heated in a vessel at a temperature located well above the gelling temperature. At this temperature, the solution was vigorously stirred on a vortex for 2 minutes in order to achieve a complete homogenization of the sample. Then the solution was introduced into the mold and heated at the same temperature. The mold was sealed and placed on a steel plate at room temperature for 40 min. This time is the time required to move from the high temperature where the mold was filled to room temperature at which the experiments were performed. The concentrations of the organogelator molecules were between 0.5% and 6%. The samples studied had thicknesses around 600 microns. The measurements were performed at frequencies ranging from 0.2 Hz to 1000 Hz, with very low strains of $\approx 10^{-5}$. To reduce the fast drying of the studied samples during the shear measurements, a special oven was built, which can be saturated with vapors of the solvent used. The temperature of the measuring cell was controlled to within a few tenths of a degree Celsius.

As the piezorheometer is not sensitive enough to measure very small shear moduli, typically below a few tens of Pascal, a conventional rheometer (Haake MARS-III) was used for taking

the data associated with the formation of the organogels. This formation being associated with a transition of the liquid-to-solid type, we used a geometry allowing taking measurements at constant sample thickness. The Couette geometry was preferred to the plane-plane geometry because of its greater sensitivity that makes easier acquiring reliable data in the liquid phase. The procedure chosen for these studies was the following: the solution containing the organogelator molecules was first heated at 110 °C and stirred at this temperature for ≈ 30 minutes using a magnetic stirrer. The solution was then placed in the rheometer cell at 80 °C (toluene-based solution) or at 90 °C (tetralin-based solution) and pre-sheared for ≈ 3 minutes to obtain a homogeneous solution. The rheometer cell was cooled from 80 °C to 25 °C for the highest concentrations of organogelator molecules and from 70 °C to 2 °C for the lowest concentration (0.2%). For the data taken at 1 Hz, the cooling rates were ranging between 0.5 K min⁻¹ and 0.2 K min⁻¹. As these experiments were performed to follow the formation of the organogels, we have checked the values of G' and G'' in the high temperature range where these values are very small. The G'' measurements were checked by additional experiments measuring the stress as a function of the rate of deformation. The value of the viscosity deduced from this experiment was found to be identical to the value deduced from the G'' measurements, thus demonstrating the validity of the oscillatory measurements. For G' , it turns out that the response of the empty cell plays a crucial role when the shear modulus of the material becomes small. The value of G' is therefore given by the difference between the measured value of G' and the value of the empty cell. We have also detected some non-linearity in the response of the samples within the temperature range (± 1.5 °C) located near the liquid-to-solid transition temperature and observed that the location of this temperature is not affected by these non-linear effects. We have also performed experiments as a function of frequency around the transition temperature. For these experiments, the time required to take a frequency-spectrum was typically slightly below 5 min, and the cooling rate between two consecutive temperatures, for which a frequency-spectrum was taken, was ~ 0.2 K min⁻¹.

2.3 Differential scanning calorimetry (DSC)

The thermal behavior of the various samples was characterized by using the Diamond DSC from Perkin-Elmer and the Setaram micro DSC-III calorimeter.

The Perkin-Elmer device was used to take measurements on solutions prepared with concentrations of organogelator molecules ranging from 1% to 5%. The measurements were performed at different heating or cooling rates, ranging from 5 K min⁻¹ to 25 K min⁻¹ over a temperature range from 25 °C to 130 °C. For each experiment, about 50 mg of the solution containing the solvent and the organogelator molecules was placed in the capsule of the calorimeter that was heated up to 130 °C and maintained at this temperature for ≈ 1 minute, in order to obtain a homogeneous solution. The measurements were taken first by decreasing the temperature down to 25 °C and then by increasing it up to 130 °C.

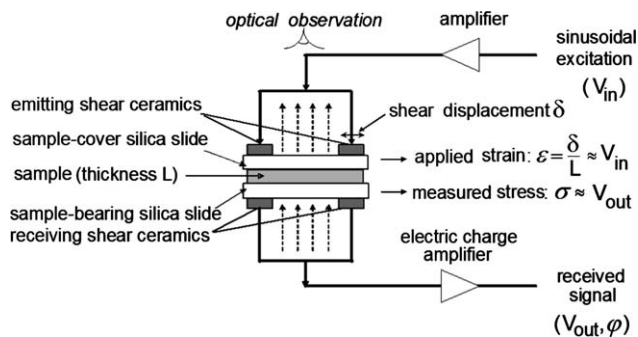


Fig. 3 Block diagram of the piezorheometer.

The Setaram micro-calorimeter was used for studying solutions containing small concentrations of organogelator molecules (between 0.2% and 1%) with slow cooling and heating rates (0.2 K min^{-1} and 0.5 K min^{-1}). These cooling and heating rates were chosen similar to those used for the rheological measurements in order to make significant comparisons between the two experiments. In these experiments, one of the two capsules of the calorimeter was filled with $\approx 700 \text{ mg}$ of the solution containing the solvent and the organogelator molecules, and the other capsule with $\approx 700 \text{ mg}$ of the solvent. The difference in weight between the two filled capsules was chosen to be as small as possible ($\approx 50 \text{ ng}$) in order to increase the accuracy of the measurements. After filling, the cells were heated up to 80°C for 20 minutes and measurements were performed by decreasing the temperature down to $\approx 2^\circ\text{C}$, and then by increasing it up to 80°C .

III Results

3.1 Liquid-to-solid transition

3.1.1 Experiments performed at 1 Hz as a function of temperature. These experiments were aimed to characterize the formation and melting processes of the organogels. As explained in Section 2.2, they were performed with the Haake rheometer, working in the Couette geometry with the oscillatory mode.

Formation of the organogel. A typical example illustrating the influence of temperature in inducing the liquid-to-solid transition is shown in Fig. 4 for a tetralin-based solution with a concentration of 0.2% of the organogelator molecules. The cooling rate is 0.2 K min^{-1} and the measurement frequency is 1 Hz. At higher temperatures, G'' is higher than G' showing that the system is liquid-like. By decreasing the temperature, a strong increase in G' and G'' is observed below $T \approx 30^\circ\text{C}$.

However, the response of the system is still liquid-like, because G'' remains above G' . This shows that the increase in G' and G'' comes from the presence of the clusters that are at the origin of the organogel formation. In the low temperature range, G' predominates over G'' showing that the response of the system is solid-like. The liquid-to-solid transition temperature named $T_{\text{ORGANOGE}}L$ is defined as the temperature given by the cross-over of G' and G'' . We will come back to this determination later in the section dealing with the experiments performed as a function of frequency around the transition point. $T_{\text{ORGANOGE}}L$ is $\approx 17.5^\circ\text{C}$ and is therefore located $\approx 12.5^\circ\text{C}$ below the temperature at which the increase of G' and G'' is observed. This difference between the two temperatures therefore gives the temperature range where the clusters are forming and crowding. These observations therefore show the existence of three different regions in the mechanical response of the solution, which occur by decreasing the temperature: a liquid-like region associated with the 'free' organogelator molecules, a liquid-like region associated with the clusters formed by the association of organogelator molecules, and a solid-like region.

Similar results were observed with the toluene-based systems, as illustrated by the data in Fig. 5 obtained with a concentration of 0.5% of the organogelator molecules and a cooling rate of 0.5 K min^{-1} . However, reliable shear measurements turned out to be difficult with these toluene-based systems because of the evaporation of the solvent. In particular, measurements at concentrations higher than 0.5% were not possible, because the formation and melting temperatures of the organogels are becoming too close to the boiling temperature of toluene ($\approx 110^\circ\text{C}$). Therefore, most of our experiments dealing with the formation and melting of the organogels were performed by using tetralin as solvent, whose boiling temperature is $\approx 210^\circ\text{C}$.

We have also studied the influence of the cooling rate and of the concentration of the organogelator molecules on the

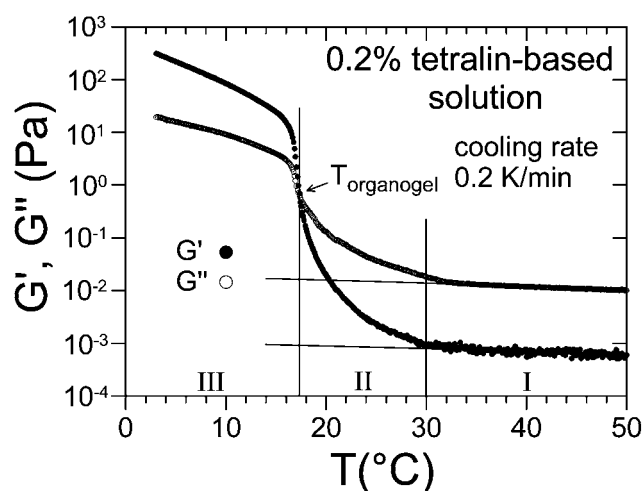


Fig. 4 Temperature dependence of the real part G' and imaginary part G'' of the shear modulus at a frequency of 1 Hz, for a tetralin-based solution. The concentration of the organogelator molecules was 0.2%, and the cooling rate was 0.2 K min^{-1} . The gelation temperature $T_{\text{ORGANOGE}}L$ is defined as the temperature for which $G' = G''$. $T_{\text{ORGANOGE}}L$ is $\approx 17.5^\circ\text{C}$. The straight lines are drawn to show the deviation from the classical liquid-like behavior (i.e. without clusters).

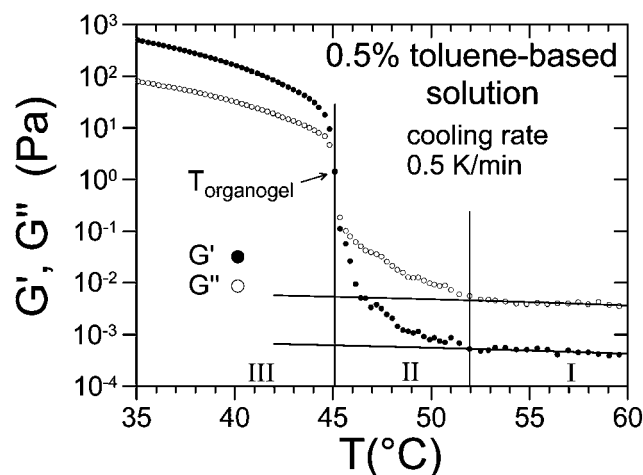


Fig. 5 Temperature dependence of the real part G' and imaginary part G'' of the shear modulus at a frequency of 1 Hz, for a toluene-based solution. The concentration of the organogelator molecules was 0.5%, and the cooling rate was 0.5 K min^{-1} . The gelation temperature $T_{\text{ORGANOGE}}L$ is $\approx 45^\circ\text{C}$, and the straight lines show the deviation from the classical liquid-like behavior (i.e. without clusters).

formation of the organogels. The measurements performed on solutions with the same concentration in organogelator molecules show that the cooling rate plays an important role in the formation of the organogel. This is illustrated by the data in Fig. 6 obtained for a 0.2% tetralin-based solution, which shows that $T_{\text{ORGANOGE}}L$ is $\approx 10^\circ\text{C}$ for a cooling rate of 0.5 K min^{-1} , whereas $T_{\text{ORGANOGE}}L$ is $\approx 17.5^\circ\text{C}$ for a cooling rate of 0.2 K min^{-1} (Fig. 4). The influence of the concentration of organogelator molecules on the formation of the organogel can be seen by comparing the results of Fig. 7 obtained on a 1% tetralin-based solution to those of Fig. 6 obtained on a 0.2% tetralin-based solution, the cooling rate being the same in both cases. It can be seen that $T_{\text{ORGANOGE}}L$ is $\approx 55.5^\circ\text{C}$ for the 1% solution, whereas $T_{\text{ORGANOGE}}L$ is $\approx 10^\circ\text{C}$ for the 0.2% solution. Similarly, the temperature where G' and G'' start to increase is $\approx 60^\circ\text{C}$ for the 1% solution, so that the temperature range associated with the formation of clusters is $\approx 4.5^\circ\text{C}$ for the 1% solution, whereas it is $\approx 15^\circ\text{C}$ for the 0.2% solution. As a result, the increase in the concentration of organogelator molecules has two effects: it shifts the temperature of formation of the organogel towards the high temperatures, and reduces the temperature range (region II) where the clusters are forming and crowding.

Melting of the organogel. Once the thermally induced organogel is formed, heating to the initial temperature yields melting of the organogel and leads to the initial liquid. A typical example of the behavior observed is given in Fig. 8, which shows the results obtained on a 0.2% tetralin-based organogel with a heating rate of 0.2 K min^{-1} , identical to the cooling rate. It can be seen that the solid-like behavior, defined as $G' > G''$, persists up to $T \approx 42^\circ\text{C}$, where $G' = G''$. We define this temperature as the melting temperature of the organogel. Above this temperature, the system returns to its liquid-like state ($G'' > G'$). This melting temperature is much higher than the temperature $T_{\text{ORGANOGE}}L$ of the organogel formation. It is located $\approx 24.5^\circ\text{C}$ above $T_{\text{ORGANOGE}}L$, showing a marked thermal hysteresis between the cooling and heating processes.

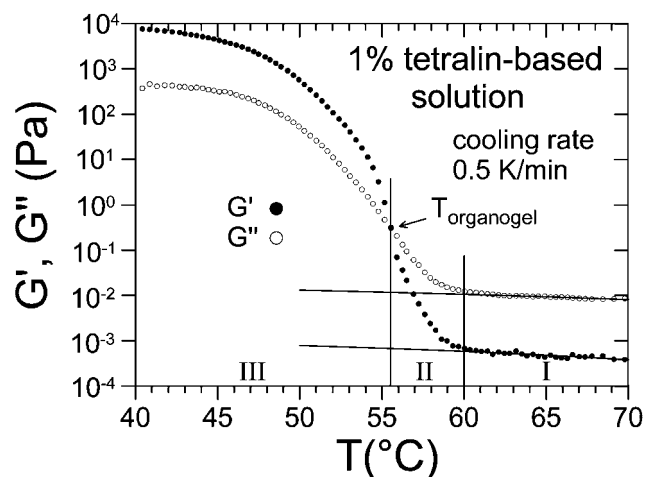


Fig. 7 Same as Fig. 4, but with a concentration of 1% and a cooling rate of 0.5 K min^{-1} . $T_{\text{ORGANOGE}}L$ is $\approx 55.5^\circ\text{C}$.

3.1.2 Experiments performed as a function of frequency around the transition temperature. As noted previously, the frequency dependence of G' and G'' at the transition temperature constitutes a crucial test for determining whether the solution undergoes a physical gelation or a jamming transition. Fig. 9 shows the behaviors of G' and G'' as a function of frequency at some selected temperatures around the transition temperature $T_{\text{ORGANOGE}}L$ which is defined as the temperature where G' and G'' measured at 1 Hz are equal, in the measurements performed by decreasing the temperature. It can be seen that the transition temperature is 15.8°C , and that G' is frequency independent, whereas G'' increases with frequency for all the temperatures located between 14.8°C and 18.2°C . The behavior expected for the physical gelation ($G' \sim G'' \sim \omega^n$) is therefore not observed, showing that the transition is not a percolation transition with the consequence that the organogel is not a physical gel. It should be noted that the behavior of G' and G'' cannot be associated with aging since G' remains

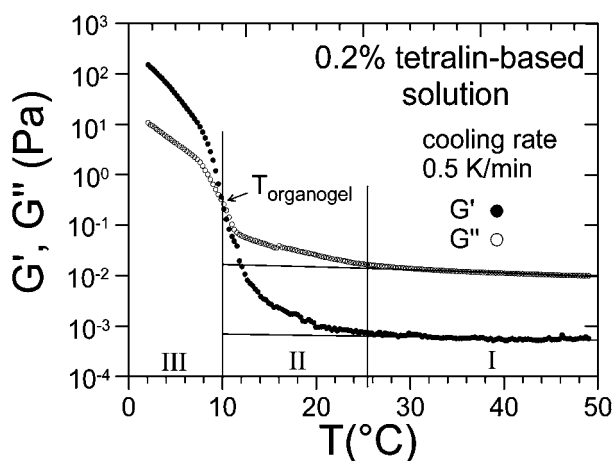


Fig. 6 Same as Fig. 4, but with a cooling rate of 0.5 K min^{-1} . $T_{\text{ORGANOGE}}L$ is $\approx 10^\circ\text{C}$.

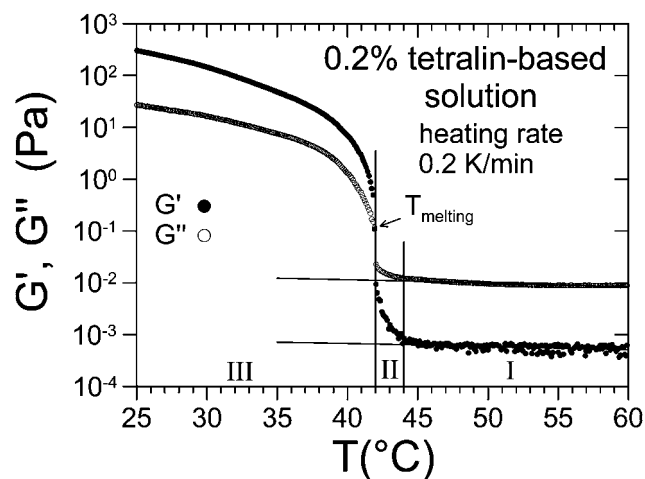


Fig. 8 Same as Fig. 4 but with a heating rate of 0.2 K min^{-1} . The melting temperature T_{melting} of the organogel is defined as the temperature for which $G' = G''$. T_{melting} is $\approx 42^\circ\text{C}$.

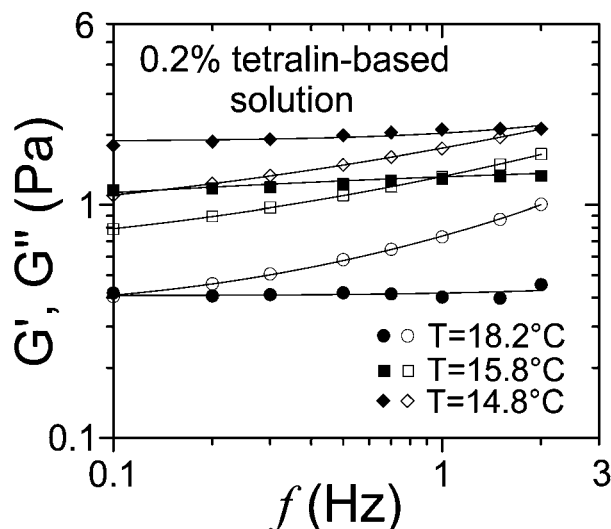


Fig. 9 Behavior of G' and G'' as a function of frequency for some temperatures located around the transition temperature determined by the cross-over of G' and G'' .

frequency-independent during the time required to take a frequency-spectrum (~ 5 min, see Section II, 2.2). On the other hand, the transition temperature $T_{\text{ORGANOGELE}}$ is close but slightly different from that ($T = 17.5^\circ\text{C}$) of Fig. 4, determined at 1 Hz with a similar cooling rate of 0.2 K min^{-1} . This shows that the system ages very slowly during the time required to move from the high temperature range to $T_{\text{ORGANOGELE}}$. The unusual and simultaneous behavior of G' and G'' around the transition temperature suggests that the solution is a system composed of two independent components, a solid and a liquid. Let us note that the elastic response is observed at temperatures well above the transition temperature, up to $\approx 19^\circ\text{C}$. Above this temperature the elastic behavior progressively changes to a viscoelastic behavior. As we will see in Section IV (Discussion), the rheological response of the system can be represented by a master curve summarizing the behaviors of the two independent components of the system.

3.1.3 DSC measurements. As noted in Section 2.3, the DSC measurements on the solutions prepared with concentrations of the organogelator molecules ranging from 1% to 5% were taken with a Perkin-Elmer device, and those with a concentration from 1% to 0.2% with a Setaram micro-calorimeter. For all the solutions, the DSC scans show an exothermic peak on cooling and an endothermic peak on heating. The variation of the position of the DSC peaks obtained with a cooling rate and a heating rate of 0.5 K min^{-1} for the various concentrations of organogelator molecules used is shown in Fig. 10 for tetralin-based solutions. The straight lines show that the concentration dependence is well described by the following van't Hoff-type equation,⁴⁰ in which the equilibrium constant associated with the association-dissociation process of the organogelator molecules is assumed to be nearly proportional to the concentration

$$\frac{d\ln(C)}{d(1/T_{\text{peak}})} = -\alpha \frac{\Delta H}{R} \quad (1)$$

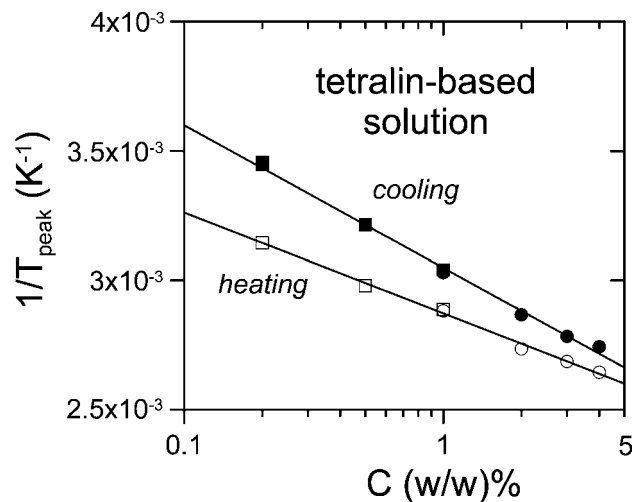


Fig. 10 Effect of the concentration on the position of the DSC peak. The circles correspond to the values extrapolated from the variation of T_{peak} as a function of the cooling or heating rates (Perkin-Elmer device) and the squares to direct measurements (Setaram calorimeter). The cooling and heating rates were 0.5 K min^{-1} .

where ΔH is the enthalpy change of the process, R the gas constant and α a constant. As α is not known, the value of the enthalpy change ΔH cannot be deduced from the slope of the straight line. However, this ΔH value can be deduced from the analysis of the surface area of the peaks obtained for the various concentrations and is $\approx 10\text{ kJ mol}^{-1}$. As IR and NMR experiments have shown that the formation of the network is governed by the formation of columns due to H-bond between the organogelator molecules and by π - π stacking interactions between these columns, the observation of a single DSC peak suggests either that the H-bond and π - π stacking interactions operate simultaneously or that the π - π stacking interactions are too weak to be detected for the small concentrations of organogelator molecules used. This is supported by our enthalpy value of $\approx 10\text{ kJ mol}^{-1}$, which is higher than the value ($< 3\text{ kJ mol}^{-1}$) of the π - π stacking enthalpy.^{41,42} For the toluene-based solutions, a similar van't Hoff-type curve and a similar value of the enthalpy change ($\Delta H \approx 12\text{ kJ mol}^{-1}$) were also obtained, leading to the same conclusion.

The comparison between the DSC and the rheological measurements both performed with the same cooling rate shows that the DSC peak does not appear at the transition point ($T_{\text{ORGANOGELE}}$). This is illustrated by comparing the data obtained for a cooling rate of 0.5 K min^{-1} which show that the DSC peak appears at $\approx 17^\circ\text{C}$ (Fig. 10) whereas the transition point appears at $\approx 10^\circ\text{C}$ (Fig. 6). This shows that the temperature of formation of the organogel is given by the rheological measurements and not by the DSC measurements. On the other hand, the onset of the DSC peak occurs at the temperature where G' and G'' start to increase. This shows that the temperature at which the molecular associations appear in the system is directly connected to the temperature of formation of the clusters. This is clearly seen in Fig. 11 which compares the temperature dependence of the DSC thermogram with that of G'

and G'' for a 1% tetralin-based solution and a cooling rate of 0.5 K min^{-1} . The same result is obtained with the 0.5% toluene-based system.

3.2 Mechanical properties of the organogels

For the experiments described below, the organogels were prepared in a mold at high temperature and then rapidly cooled ($\approx 40 \text{ min}$) to $T = 25^\circ\text{C}$, as explained in Section 2.2. Our measurements were in the linear response regime, as a result of the very weak strains used in the experiments (between 10^{-6} and 10^{-4}). A typical example showing the absence of variation of the complex shear modulus as a function of the amplitude of the sinusoidal strain applied to the sample is shown in Fig. 12 for a 4% tetralin-based organogel.

3.2.1 Variation of G' and G'' as a function of frequency for various concentrations of organogelator molecules. Fig. 13 shows the variation of G' and G'' as a function of frequency for two different concentrations of the organogelator molecules. The comparison between the results obtained for these two organogels shows that G' remains (almost) frequency-independent when the concentration of the organogelator molecules increases and exhibits therefore a plateau-like behavior, in contrast to the behavior of G'' . This difference in behavior is reminiscent to the one observed in the measurements taken as a function of temperature. It shows again that the clusters do not contribute to G' and G'' in the same way and suggests that G' is associated with the network and G'' with the fluid. A similar behavior of G' and G'' was also observed for the toluene-based organogels.

3.2.2 Power-law behavior of G' as a function of concentration of organogelator molecules. Fig. 14 shows the variation of the elastic plateau G'_p as a function of the concentration of the organogelator molecules for a tetralin-based organogel. It can be seen that G'_p follows a power law behavior, as shown by the fit performed with the equation $G'_p = G_0(C - C^*)^{\nu_C}$, where G_0 is a constant, C^* the critical concentration from which the

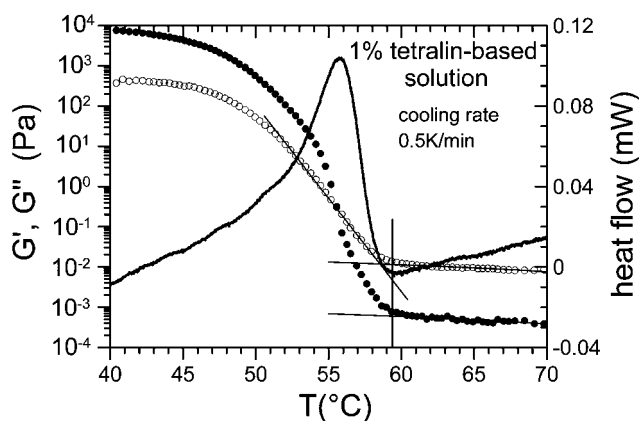


Fig. 11 Comparison between the behavior observed by DSC and the behaviors of G' and G'' . In the two experiments, the cooling rate and the concentration of the organogelator molecules were the same. The vertical line shows that the onset of the DSC peak appears at the temperature where G' and G'' are beginning to rise.

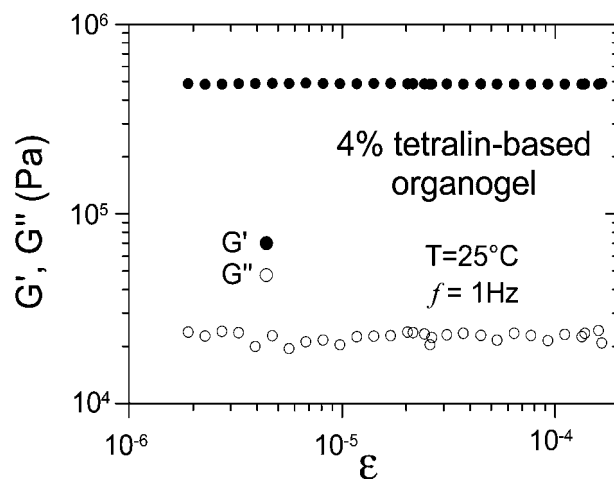


Fig. 12 Variation of the real G' and imaginary G'' part of the shear modulus as a function of the applied strain. The sample was a 4% tetralin-based organogel. The measurement frequency was 1 Hz, and the temperature was 25°C .

organogel is forming, and ν_C the critical exponent. The resulting parameters are $G_0 = (3.3 \pm 0.8) \times 10^4 \text{ Pa}$, $\nu_C = 1.95 \pm 0.15$, and $C^* = (0.10 \pm 0.12)\%$. For the toluene-based organogel, the variation of G'_p as a function of concentration also follows a power law behavior with the following fitting parameters: $G_0 = (2.4 \pm 0.4) \times 10^4 \text{ Pa}$, $\nu_C = 1.91 \pm 0.10$ and $C^* = (0.09 \pm 0.07)\%$. These parameters are very similar to those obtained for the tetralin-based organogels. They show that the solvent does not play a crucial role in the formation of the network (same value of

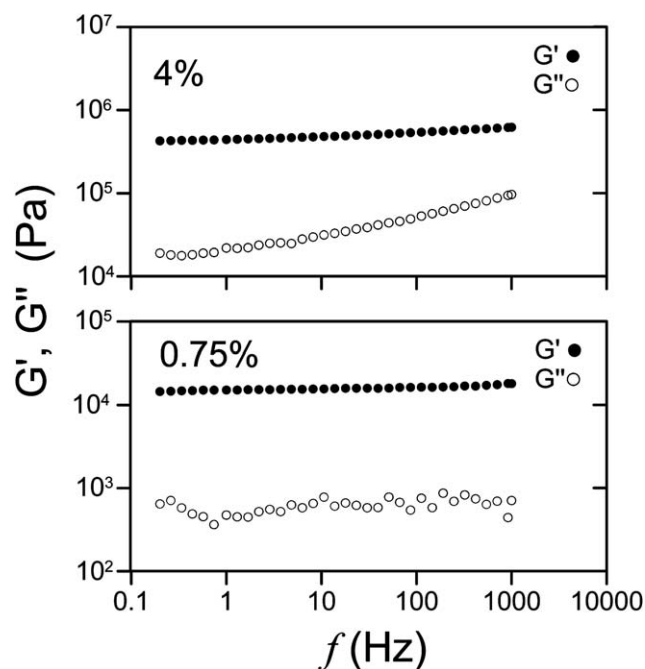


Fig. 13 Variation of G' and G'' as a function of frequency for two tetralin-based organogels differing in the concentration of organogelator molecules. The measurements were performed at $T = 25^\circ\text{C}$, and the strains imposed to the samples were $\sim 10^{-5}$.

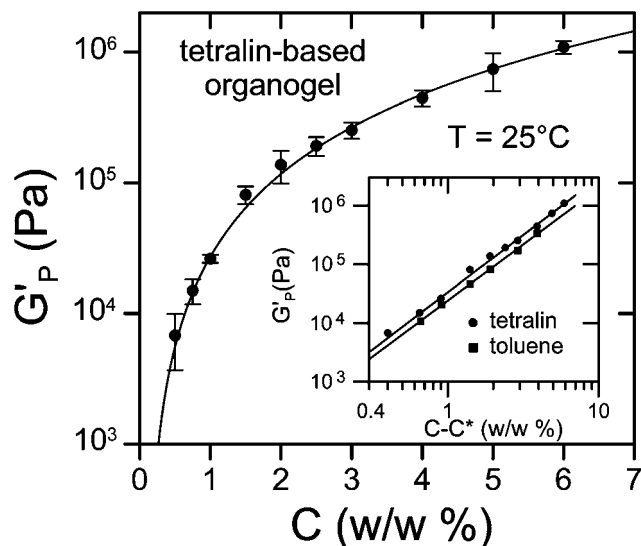


Fig. 14 Variation of the elastic plateau G'_p of a tetralin-based organogel as a function of the concentration of organogelator molecules. The line is the fit with the power law equation $G'_p = G_0(C - C^*)^{\nu_c}$ (see text). The inset shows that a similar power-law behavior is obtained with the toluene-based organogel. For clarity, the error bars have not been shown in the inset. The temperature was 25 °C.

the exponent) but that it modifies the value of G_0 which is slightly smaller for toluene than for tetraline. This effect could reflect the influence of the nature of the solvent, since this one modifies the chirality of the fibrillar structure of the clusters.²⁰

3.2.3 Influence of a static compression applied to the organogel. In this experiment we have followed the change in the response of the sample when it was submitted to a static compression that was induced by bringing together the sample-bearing glass slides. Fig. 15 shows the results obtained on a 1% tetralin-based organogel by progressively bringing closer the sample-bearing glass slides from 575 μm to 487 μm . It can be seen that the behaviors of G' and G'' remain unchanged. This

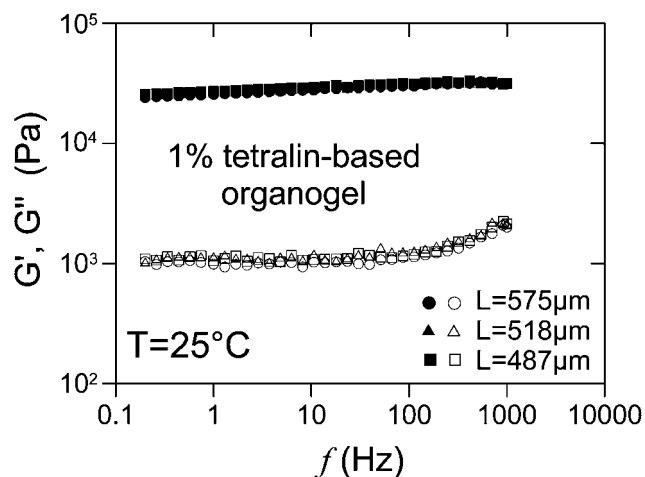


Fig. 15 Variation of G' and G'' of a 1% tetralin-based organogel as a function of frequency for different thicknesses of the sample resulting from a progressive static compression of the sample induced by bringing closer the sample-bearing glass slides. The measurements were performed at 25 °C.

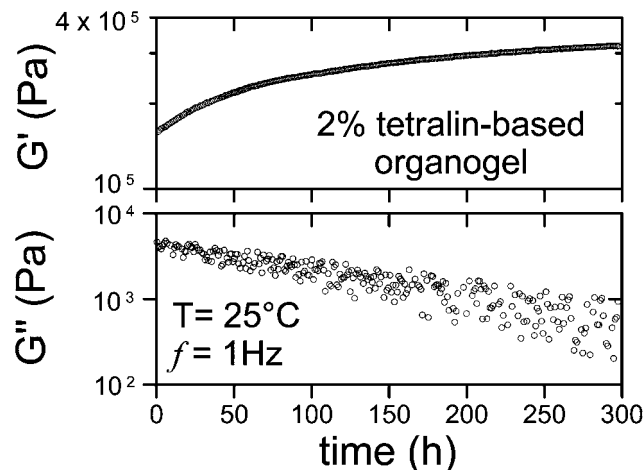


Fig. 16 Behavior of G' and G'' as a function of time for a 2% tetralin-based organogel. The frequency and the temperature were 1 Hz and 25 °C, respectively.

shows that the organogels do not present elasticity but a thixotropic behavior indicating that the overall structure of the organogel is liquid-like.

3.2.4 Evolution of G' and G'' as a function of time. The experiments performed as a function of time show that G' and G'' evolve with time showing again that the organogel is a system out of equilibrium. The age dependence of G' and G'' measured at 1 Hz is shown in Fig. 16. It can be seen that G' increases with time whereas G'' is decreasing. These concomitant behaviors are consistent with those predicted by the rheological model of soft glassy materials.¹⁷

IV Discussion

Our rheological results show that the organogelator solutions exhibit three distinct regions characterized by three different rheological behaviors: Region I is a liquid state that corresponds to the high temperature range where the organogelator molecules are “free”. Region II is also a liquid-like state. It occurs on cooling when the organogelator molecules form clusters resulting from the formation of columns *via* hydrogen bonds and from their association by π -stacking interactions. These clusters are the origin of the increase in G' and G'' when the temperature decreases. Region III is a solid-like state—the organogel—that occurs when the crowding of the clusters exceeds a critical value. The transition temperature, T_{ORGANOGE} , between the liquid and the organogel corresponds to the cross-over of G' and G'' and the width of Region II is given by the difference between T_{ORGANOGE} and the temperature where G' and G'' are starting to increase. The value of T_{ORGANOGE} is a function of the cooling rate and also of the concentration of organogelator molecules. This latter effect arises because the number of clusters depends on the concentration of organogelator molecules, leading consequently to a decrease (respectively an increase) of the transition temperature T_{ORGANOGE} when the concentration is decreasing (respectively increasing). A similar state sequence is also observed by increasing the temperature, but it is shifted to higher temperatures showing

the presence of thermal hysteresis in the cooling and heating processes.

The DSC peak does not correspond to the gelation temperature $T_{\text{ORGANOGE}}L$ but to the temperature where G' and G'' are starting to increase. This is due to the fact that DSC measurements detect the thermal effects associated with molecular associations, such as hydrogen bonds, in a material and not the connectivity phenomena that are linked to the formation of a network. The difference between $T_{\text{ORGANOGE}}L$ and T_{DSC} decreases with increasing the concentration of organogelator molecules, as we have seen previously for the difference between $T_{\text{ORGANOGE}}L$ and the temperature where G' and G'' start to increase. For the higher concentration, $T_{\text{ORGANOGE}}L$ and T_{DSC} occur practically at the same time, which indicates that the number of clusters becomes so large that they immediately fill the whole space to form the network. The difference between T_{DSC} and the liquid-to-solid transition temperature and the absence of discontinuities in the behaviors of G' and G'' have also been observed for solutions exhibiting a physical gelation, such as the gellan gum solutions.⁴³ This result is in contrast to the statement that the sol-gel transition should be a first order transition with an enthalpy of transition given by the DSC results.² The large thermal hysteresis observed in both the rheological and the DSC measurements comes from the fact that the hydrogen-bond formation and the π -stacking associations are more difficult to achieve than their breaking. Indeed, upon cooling, the organogelator molecules must find the other ones to form the columns, then the associations between columns and finally the clusters at the origin of the network. This effect does not exist in the heating process, which leads to the large hysteresis between the cooling and the heating process.

The rheological measurements also show that the critical gel, characterized by the relationship $G' \sim G'' \sim \omega^n$, is not observed, which indicates that percolation is not the mechanism for the formation of the organogel. As a result, the liquid-to-solid transition is not a sol-gel transition and consequently the organogel is not a physical gel. Additional supports showing that the organogel is not a physical gel come from the thixotropic behavior resulting from the static compression applied to the organogel (Fig. 15), and from the variation of G' and G'' as a function of time (Fig. 16). Since the system is not a physical gel, the transition temperature can be defined as the temperature at which $G' = G''$. This transition temperature depends on several factors such as the frequency, cooling rate and concentration of organogelator molecules.

The data around the transition temperature show that there are two independent contributions to the rheological response: a frequency-independent elastic contribution whose magnitude depends on the temperature and a viscous contribution associated with the response of the suspending fluid. As a result, the system can be considered as a solid-like network that responds elastically for small deformations and that is embedded in a suspending fluid.

As shown in Section 3.2.2, the results obtained as a function of concentration at $T = 25^\circ\text{C}$ show a critical-like behavior of the elastic plateau G'_p with a critical exponent $\nu_c \approx 1.95 \pm 0.15$, and

a critical concentration $C^* \approx (0.10 \pm 0.12)\%$ for the tetralin-based organogel, and with $\nu_c \approx 1.91 \pm 0.10$, and $C^* \approx (0.09 \pm 0.07)\%$ for the toluene-based organogel. This power law behavior is reminiscent of equilibrium critical phenomena, but it must be considered only as a convenient description of the formation of the network, because the jamming transition is a non-equilibrium transition. Values of 2.1 and 3.3 of the critical exponent ν_c have been reported for colloidal systems⁴⁰ and interpreted in the context of elasticity percolation that predicts a value of 2.1 for bonds resistant to stretching, which occurs when the bonds are formed by long-range attractive interactions between the clusters,⁴⁴ and a value of 3.75 for bonds resistant to both stretching and bending, which occurs for short range interactions.⁴⁵ Our value of ≈ 2 suggests that the organogel has bonds that resist stretching but not bending.

The power law behavior is not restricted to changes in concentration for a fixed temperature. It also occurs as a function of temperature for a fixed concentration. This can be shown by analyzing the G' data taken around and below the cross-over temperature $T_{\text{ORGANOGE}}L$ with the following power law $G' = G_0(T^* - T)^{\nu_r}$, where T^* is the temperature for which the elastic clusters make the bridge between the inner and the outer cylinders of the Couette cell. Let us note that T^* and $T_{\text{ORGANOGE}}L$ are not the same because they do not reflect the same physics. T^* concerns the physics of the solid alone and is associated with some 'type of percolation', whereas $T_{\text{ORGANOGE}}L$ concerns the physics of the whole system, since it is the temperature for which the elastic response of the solid component becomes equal to the viscous response of the liquid component.

A typical example of the fits obtained is shown in Fig. 17 for the 0.2% tetralin-based organogel prepared with the cooling rate of 0.5 K min^{-1} , for which Fig. 6 shows that $T_{\text{ORGANOGE}}L$ is $\approx 10^\circ\text{C}$ at the frequency of 1 Hz. The fit has been performed

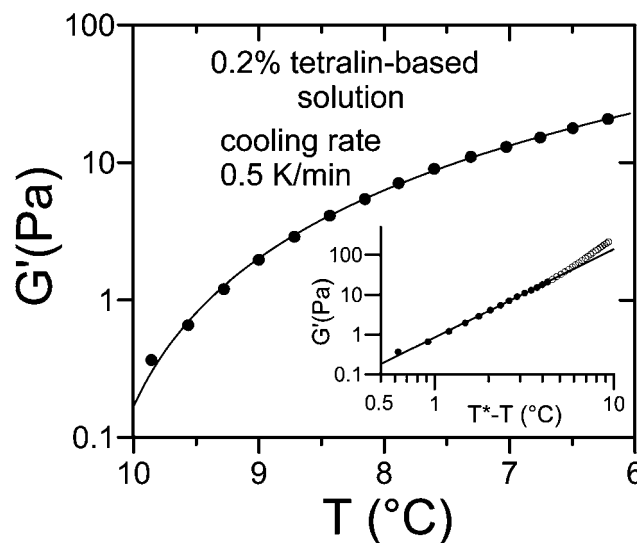


Fig. 17 Variation of G' as a function of temperature for a 0.2% tetralin-based solution. The line is the fit with the power law equation (see text) $G' = G_0(T^* - T)^{\nu_r}$ (see text). The inset shows that the power law is not obeyed for the data taken deep in the solid state, illustrating the evolution of the solid during the time required to take the measurements. The frequency measurement was 1 Hz.

within a temperature range of about 3.6 °C, extending from 9.85 °C to 6.22 °C. It can be seen that the variation of G' follows a power law with $G_0 = (0.84 \pm 0.33)$ Pa, $T^* = (10.48 \pm 0.21)$ °C and $\nu_T = 2.21 \pm 0.21$. The quality of the fit shows that the data located around $T_{\text{ORGANOGELE}}$ are not affected by the time required to take the data. The organogel is therefore in a pseudo-equilibrium state during these measurements, which confirms the conclusion of the analysis done in Section 3.1.2. In contrast, aging plays a role for the data taken at temperatures distant from $T_{\text{ORGANOGELE}}$, as revealed by the deviation from the power law shown in the inset of the figure. This conclusion is in agreement with the experiments performed as a function of time on a formed organogel, which are reported in Fig. 16 and which show a slow aging over a period of ~ 300 hours. However, the value of the critical exponent ν_T depends on the temperature range of the analysis. As shown in Fig. 18, the value of the exponent increases (a) when the temperature range of the analysis increases, which reflects the progressive change in the structure of the network due to the aging associated with the time required to take the measurements, and (b) when the temperature range of the analysis decreases because there are not enough data to perform a significant fit. We believe that the fit of Fig. 17 represents the best compromise between these two effects. This is supported by the fact that the value of the exponent is consistent, within the error bars, with the value of the exponent ν_C being deduced from the experiments performed at a fixed temperature as a function of concentration. Finally it should be noted that the value of T^* is found slightly higher (≈ 0.5 °C) than the value of $T_{\text{ORGANOGELE}}$.

The analysis of the data taken for the other organogels shows a temperature-variation of G' that is qualitatively similar to the one in Fig. 17 corresponding to the organogel formed with the concentration of 0.2% and the cooling rate of 0.5 K min⁻¹. This confirms that aging plays a role only for the data taken far below $T_{\text{ORGANOGELE}}$. We have also observed that gelation depends on

the strength of the applied strain, which, for example, induces the non-linear effects occurring near the transition point.

We close this section by showing that a master curve can describe the mechanical behavior of the solution, although the solid and the liquid components are two independent components. This master curve, shown in Fig. 19, was built by taking, as a reference, the data taken at $T = 15.8$ °C for which the cross-over between G' and G'' occurs at 1 Hz (see Fig. 9), the other curves being displaced along the frequency axis (scaling factor a) and the modulus axis (scaling factor b). The result therefore represents the viscoelastic response of the system for this temperature and this frequency of reference. Above the cross-over temperature, the elastic contribution of the solid is weaker than the viscous contribution of the liquid, so that the system behaves as a liquid. Below the cross-over temperature, the elastic contribution of the solid is larger than the viscous contribution of the liquid, with the consequence that the system behaves as a solid. Strictly speaking, the cross-over temperature is not a transition temperature between two states, but a temperature that is associated with a change in the response of the system, the elastic contribution of the solid component becoming larger than the viscous contribution of the fluid component. The dashed line in Fig. 19 shows that the purely elastic response of the solid extends over about a decade ($af \approx 10$ Hz) above the cross-over temperature ($af \approx 1$ Hz). For the data belonging to the region $af > 10$ Hz, the master curve shows that the response of the solid is no longer purely elastic. The solid exhibits therefore a loss modulus that contributes to the apparent viscous modulus, which explains the departure from the flow behavior ($G'' \sim f$) observed for the region $af > 10^4$ Hz. Of course, the data for the high-temperature range, *i.e.* those of Region I, which corresponds to the liquid phase without the

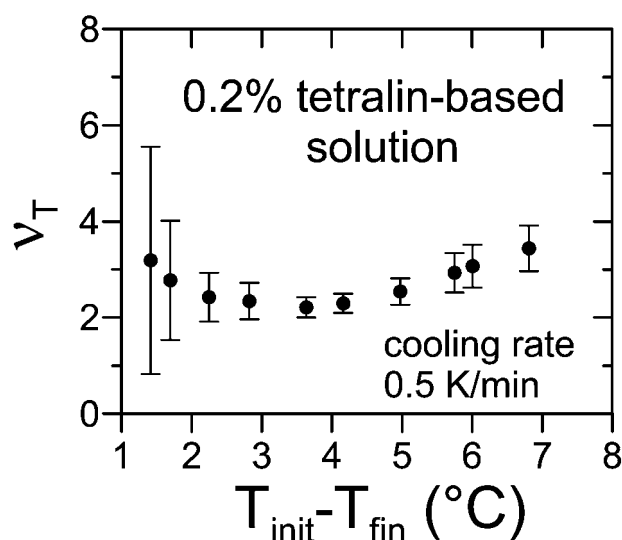


Fig. 18 Variation of the critical exponent ν_T as a function of the temperature range used for the analysis. The initial temperature was 9.85 °C.

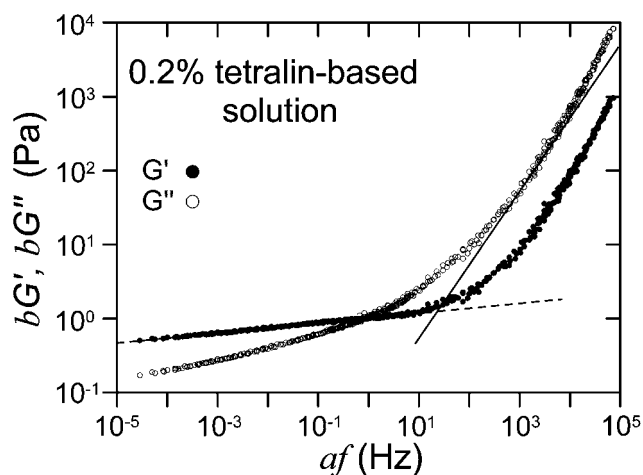


Fig. 19 Master curve resulting from shifts of the data along the G -axis (scaling factor b) and along the frequency-axis (scaling factor a). The data have been normalized at the transition temperature ($T = 15.8$ °C) determined by the cross-over between G' and G'' , observed at 1 Hz in the measurements performed as a function of temperature. The dashed line indicates the elastic behavior, and the solid line the flow behavior expected for the liquid component of the system. The deviation from this behavior, which is observed at high frequency, comes from the contribution to G'' of the viscoelastic response of the solid component of the system (see text).

clusters, cannot be scaled on the master curve. Similar master curves were obtained for carbon black solutions⁴⁶ and solutions of colloidal particles with an attractive depletion interaction.¹⁰ The variation of the shift factor b as a function of the shift factor a is plotted in Fig. 20, and it shows the presence of two regimes. Given that the previous analyses have shown that structural arrest and aging control the viscoelastic properties of the system, we attribute the behavior of b versus a to the presence of these two processes. These two processes are also observed for aqueous suspensions of Laponite particles, in experiments performed as a function of time for a fixed temperature.⁴⁷

All our results converge to show that the organogelator solutions undergo a reversible liquid-to-solid transition induced by a progressive crowding of the clusters when the temperature is decreasing, leading to a dynamical arrest of these clusters. The liquid-to-organogel transition is therefore a jamming transition that occurs when the clusters become jammed to form the network. Concomitantly with the crowding of the clusters, the system becomes non-ergodic, because the clusters, as a result of their dynamical arrest, are no longer able to explore the phase space on the experimental time scale. The fact that the master curve is built with the data belonging to Regions II and III suggests that the ergodic to non-ergodic transition occurs within Region II. Consequently, this temperature differs significantly, especially at low concentration, from the temperature of the liquid-to-solid transition that appears at $T_{\text{ORGANOGE}}L$. Finally, as was already pointed out in the manuscript, some types of materials such as colloidal suspensions^{9–11} and star polymers^{12–14} exhibit a jamming transition. The liquid to solid transition observed in flexible³³ and liquid crystal³⁵ polymer melts when the glass transition is approached by decreasing the temperature can also be described as a jamming transition, the solid network being formed by pre-glassy elastic clusters (frozen long range density fluctuations) emerging in the polymer melt. These jamming-type transitions seem therefore to be generic to systems exhibiting interparticle interactions⁴

and the present paper illustrates the case of an organogel formed by small organogelator molecules.

V Conclusion

In summary, we have studied the liquid to organogel transition of a solution containing new organogelator molecules of the amino-acid type using rheological and DSC techniques. We show that this transition is not a sol-gel transition but a jamming transition. The organogel is therefore not a gel, but a jammed suspension that can be described as a system combining the elasticity of a solid network formed by the clusters of organogelator molecules, and the viscosity of the suspending fluid. Above the cross-over temperature between G' and G'' , the apparent response of the system is similar to that of a liquid, because the elastic contribution is weak. Below the transition, the apparent response of the system is similar to that of a solid, because the elastic contribution is predominant. The transition temperature between the two regimes is given by the temperature where the real part of the shear modulus becomes identical to the imaginary part. Although the system is a two-component system, a master curve can nevertheless be constructed by shifting the data measured at the different extents of the jamming phenomenon along both the G axis and the frequency axis. Our results also show that several characteristic temperatures are involved in the jamming phenomenon observed by decreasing the temperature. First, there are temperatures associated with the behavior of the solution: (a) the temperature at which the clusters arise in the solution and (b) the temperature named $T_{\text{ORGANOGE}}L$, at which the mechanical response of the solution changes from a liquid-like response to a solid-like response. Second, there are temperatures concerning only the solid component of the system: (a) the temperature named T^* , at which the solid clusters make the bridge between the inner and the outer cylinders of the Couette cell, and (b) the temperature at which the response of the solid becomes purely elastic. All these temperatures are different from each other. Finally, our results also demonstrate that the temperature of formation of the organogel is given by the rheological measurements and not by the DSC measurements. This arises because the rheological measurements detect connectivity, whereas DSC measurements detect the thermal effects associated with the molecular associations in the system which are at the origin of the gelation. This remark on the respective contribution of the DSC and rheological measurements also applies to physical gels. This study demonstrates for the first time that an organogel is not a physical gel, as it is currently believed, but a jammed suspension. We expect this jamming behavior to be general for low-molecular-weight organogelators. However, this remains to be checked.

Acknowledgements

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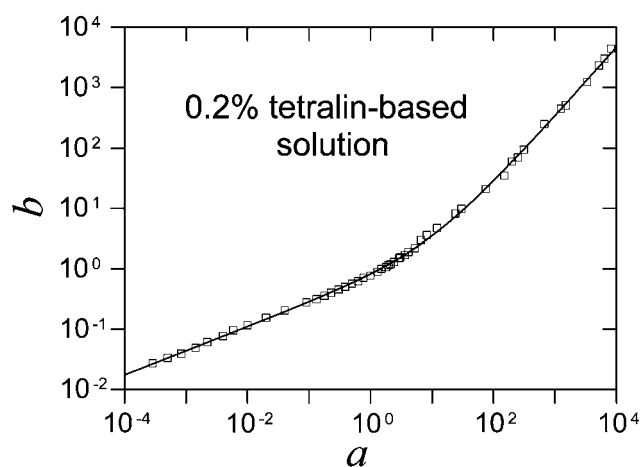


Fig. 20 Shift factor b as a function of the shift factor a showing the presence of two distinct processes, structural arrest and aging. The line is a fit to $b = pa^s + qa^t$ with $s = 1.14 \pm 0.05$, $t = 0.40 \pm 0.02$, $p = 0.13 \pm 0.04$, $q = 0.70 \pm 0.07$. The first and the second terms correspond to structural arrest and aging, respectively.

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