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Rheological assessment of the sol–gel transition for self-assembling low molecular weight gelators

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ABSTRACT

The complexity of the transition from solution to gel for low molecular weight gelators in apolar solvents makes it incredibly difficult to assess the gel point. Since both nucleation and crystal growth occurs prior to the formation of a continuous three dimensional network numerous techniques, such as calorimetry and inflection point of the complex modulus, are invalid when probing the gel point. However, monitoring the frequency dependence of G′ and G″ illustrates the transition from a dilute solution to a weak gel which may be differentiated from the gel point observed by the decreasing value of the complex viscosity as a function of frequency. For 3% 12-hydroxystearic acid in mineral oil once the gelator nucleates the material behaves as a dilute solution, upon crystal growth (67 °C) we observe the true cross over point which is independent of frequency and finally a strong gel is formed at 64 °C where G′ and G″ are independent of frequency.

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1. Introduction

The significance of gels, in our everyday lives, is of utmost importance; they influence the structure and functionality of foods, functionality of cosmetics, the performance of sports equipment and are now being used for biological scaffolding in medicine. As the list of ever expanding applications increases there is a need to carefully and accurately determine the transition from liquid or solution state to the gel state. Traditionally, gels were formed utilizing long chain polymers, having a large hydrodynamic radius, which upon cooling or the addition of divalent ions interact/entangle with each other and form a continuous network with solid-like properties (Clark, 1996). In the past decade a new form of gel has been extensively studied where, instead of polymers being responsible for the gel state; the soft materials are now comprised of low molecular weight monomers, which must first self-assemble before entanglement and eventually gelling the solvent. Molecular gels have found interesting applications in art preservation (Baglioni, Dei, Carretti, & Giorgi, 2009); foods (Rogers, Wright, & Maranoni, 2009); medicine (Xu, 2009); and most recently as a "molecular condom" which is capable of entrapping the HIV virus in the gel matrix (Jay et al., 2009).

The definition of a "gel" has been evolving for more than 100 years since Thomas Graham attempted a loose definition. 65 years later, Dr. Dorothy Jordan Lloyd, stated, that "the colloid condition, the "gel", is one which is easier to recognize than to define" (Jordon, 1926). It was noted that all gels must be comprised of at least two components, a liquid and a gelling substance (i.e. a solid), and that the entire system must have the mechanical properties of a solid (Jordon, 1926). However, the exclusivity of this definition did not recognize that not all colloids are gels nor are all gels colloids. Hermans later proposed that gels are: coherent colloid dispersed systems of at least two components which exhibit mechanical properties that are consistent of the solid state; and both the dispersed (gelator) phase and dispersion medium must extend continuously throughout the system (Hermans, 1949). Because of the exclusivity of this definition, Ferry offered a more descriptive definition of a gel; "a gel is a substantially diluted system which exhibits no steady state flow" (Ferry, 1961). From this point, a gel must contain two features: 1) a continuous microscopic structure with macroscopic dimensions that is permanent on the time scale of an analytical experiment and 2) a solid-like rheological behaviour, despite being comprised mostly of liquid (Weiss, 2006). Utilizing these two points we can probe the gel point of these novel soft materials to gain a better insight into their assembling mechanisms.

Molecular gels, at elevated temperatures, exist as solution or sol and exhibit liquid properties. In many instances, molecular self-assembly occurs via a supersaturated state whereby the gelator–solvent melt is cooled below the melting point of the gelator triggering the gelator molecules to microscopically phase separate and self-assemble via stochastic nucleation events driven by enthalpic forces (Weiss, 2006). As the sol is cooled below the gelation temperature the solution becomes supersaturated and upon sufficient undercooling microscopic phase separation of the gelator molecules occurs (Weiss, 2006). The low molecular weight gelators self-assemble via non-covalent interactions while undergoing stochastic nucleation. Upon nucleation, further cooling causes the accretion of monomers onto the surface of the growing nuclei, which in the case of molecular gels, typically occurs

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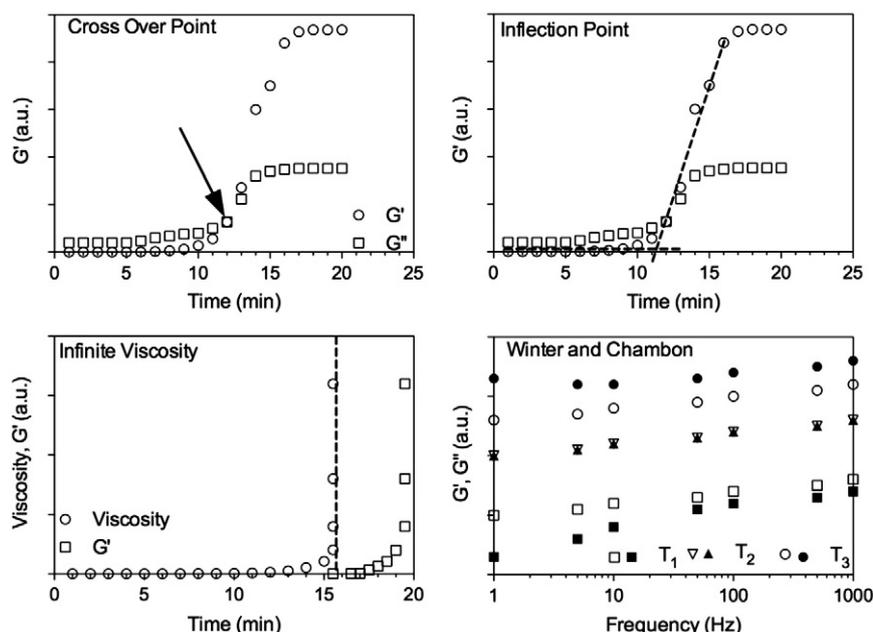E-mail address: michael.rogers@usask.ca (M.A. Rogers).

Fig. 1. Current rheological methods to determine the gel point of aggregating polymers.

along one or two aspect ratios of the crystal, giving rise to fibrillar or platelet aggregates (Weiss, 2006). Low molecular weight gelators are unlike polymer gelators because they must first self-assemble prior to viscosity enhancement of the solution. The process of one-dimensional growth requires a meticulous balance between the contrasting parameters of solubility and those which control epitaxial growth, leading to an elongated axis (Lam, Pederson, Quaroni, & Rogers, 2010; Rogers & Marangoni, 2009; Suzuki et al., 2003). In specific cases, the supramolecular assemblies may form organogels which aggregate to form three-dimensional networks entrapping the solvent phase.

Numerous rheological methods have been adapted from the field of polymer physics and applied to determine the gel point of molecular gels (Fig. 1). Commonly, the cross over point and/or the inflection point have been utilized to determine the gel point, in part, due to the ease of measurement. The cross over point was initially thought to correspond to the percolation threshold because at this instant the elastic component of the network exceeds the viscous component. However, it has been well established that the cross over point does not concur with the gel point, but occurs earlier (Chambon & Winter, 1987). Conversely, depending on the system, the inflection point may correspond to numerous physical changes during the undercooling of the melt. As organic solvents are cooled the viscosity and adhesion

forces increase which corresponds to an inflection of the loss (G″) and storage (G′) modulus. Further, upon self assembly, the hydrodymic radius of the growing aggregate increases, again leading to the inflection of G′ well before the percolation threshold. The use of the infinite viscosity is far less common and corresponds to the loss of solution behaviour. Finally, the most widely accepted method in polymer physics is the application of the method developed by Chambon and Winter which is independent of the experimental frequency (Chambon & Winter, 1987). Using the Winter and Chambon method relies on the fact that G′ and G″ are not only parallel at the gel point but also congruent across a wide range of frequencies. The purpose of this manuscript is to determine if the gel point for self-assembling fibrillar networks in an apolar solvent may be determined utilizing the aforementioned methods developed for polymer physics.

2. Methods

12 hydroxystearic acid and light mineral oil were purchased from sigma Aldrich (Oakville, ON, CAN) and were used as received. A 3 wt.% solution was heated to 90 °C for 30 min to ensure the crystal history was erased and the sample was cooled to 30 °C at 2 °C/min.
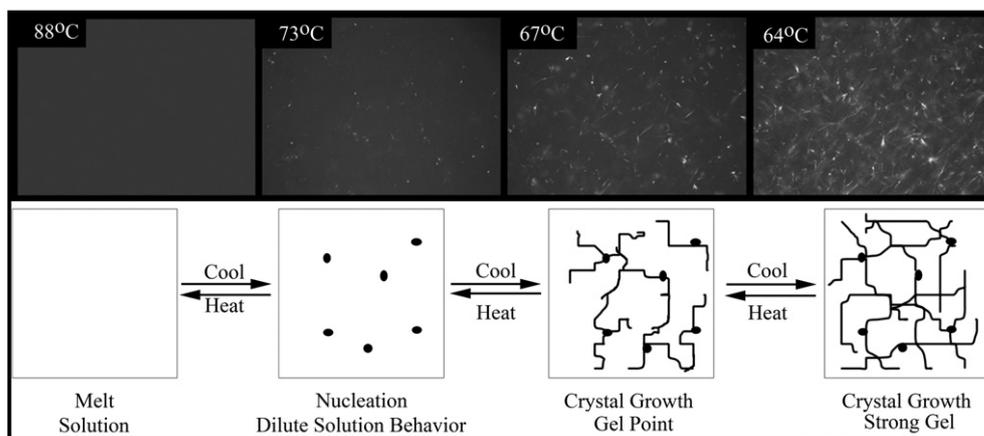

Fig. 2. Polarized light micrographs of 3% 12 hydroxystearic acid/mineral oil crystallized from 90 °C to 30 °C cooled at 2 °C/min.
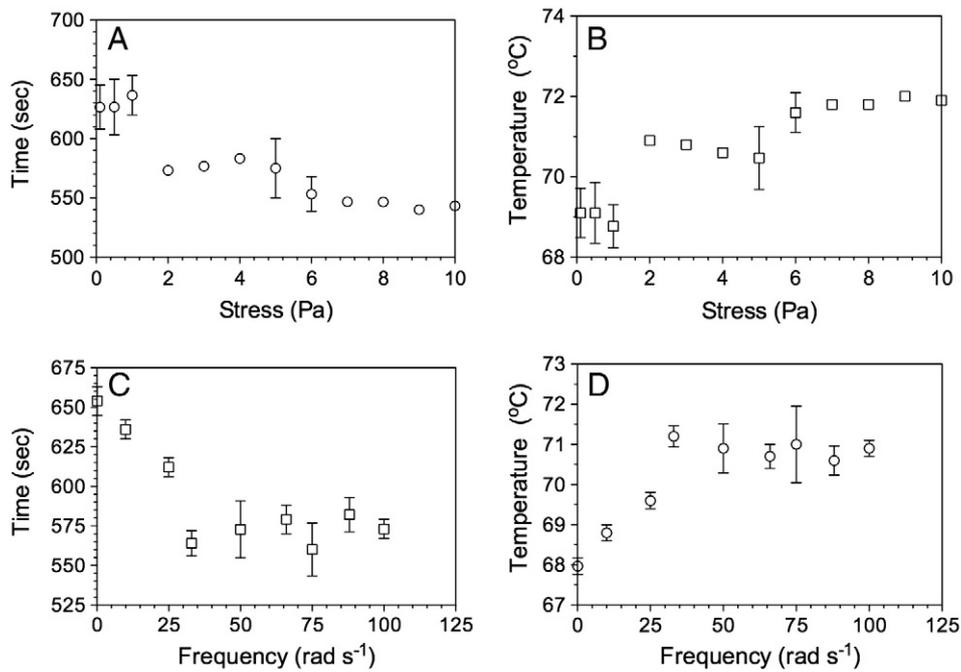
Fig. 3. Onset of gelation determined by the maximum viscosity (A,B) using a flow procedure. Frequency dependence of the onset of gelation (C,D) determined from the inflection of the storage modulus using an oscillatory stress of 10 Pa.

Polarized light micrographs were acquired using a Nikon Eclipse E400 light microscope equipped with a Nikon DS-FiL color camera and a long working distance 10× lens and condenser with a resolution of 2560×1920. Samples were cooled at 2 °C/min to 30 °C using a temperature controlled stage (LTS 120 and PE94 temperature controller (Linkam, Surrey, United Kingdom).

Rheological analysis was carried out using an AR-G2 rheometer (TA Instruments, New Castle, DE) and a cross-hatched 4 cm flat plate and a cross-hatched parallel plate apparatus. Samples were cooled at 2 °C/min from 90 °C to 30 °C using the cross-hatched parallel plate apparatus, an oscillatory stress of 10 Pa and different frequencies ranging from 0.01 rad s^{-1} to 500 rad s^{-1} were utilized. 10 Pa was selected because

it was at the low end of the linear viscoelastic region (LVR) of the gel and at the high end of the LVR for the solution. Six replicates were carried out for each sample. The sample thickness was controlled by the rheometer and held at 1000 μm.

3. Results

Self-assembly is a complex multi-step process involving numerous contrasting parameters of solubility and those which control epitaxial growth. Upon cooling below the melting point of the gelator, microscopic phase separation occurs and further supercooling results in nucleation (Fig. 2A). Depending on the degree of undercooling, the
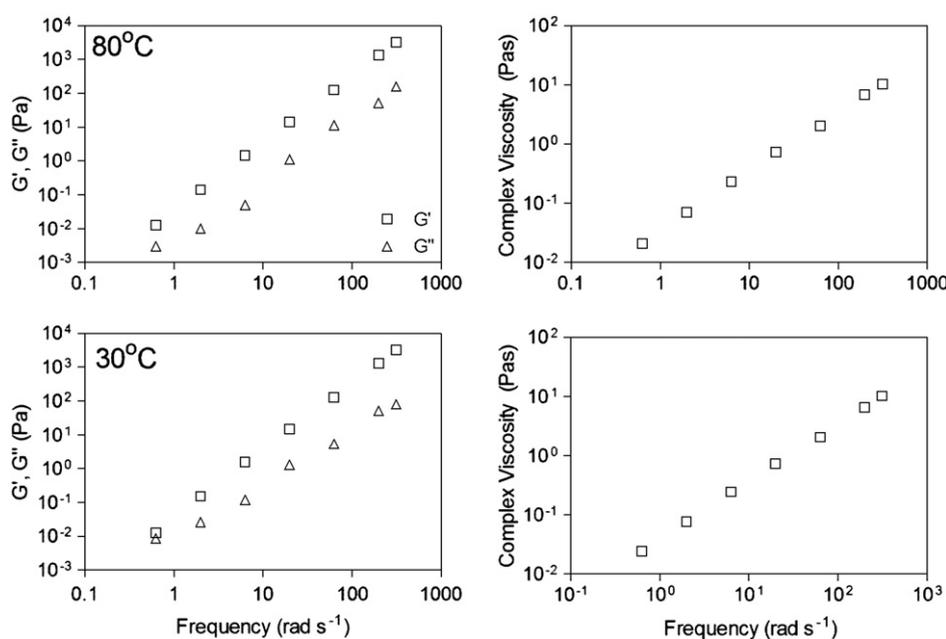

Fig. 4. Rheological characterization of mineral oil cooled non-isothermally from 90 °C to 30 °C at 2 °C/min.

number of nuclei will differ (Chambon & Winter, 1987; Lam et al., 2010). Once nucleation occurs, gelator molecules continue to diffuse to the crystal surface and accrete onto the growing crystal surface (Fig. 2B–D). This process of diffusion and accretion continues until the self-assembled one dimensional fibres entangle and form a continuous three dimensional network capable of immobilizing the liquid oil (Fig. 2C–D). It is important to note that the gel point corresponds to the development of the continuous network and solid-like network and not the initial development of nuclei. Due to the fact that nucleation and subsequent crystal growth occurs prior to the formation of a gel, the enthalpy released during these events make it impossible to determine gel point using calorimetry as is often done (Rogers, Pederson, & Quaroni, 2009).

The complex sol–gel transition for self-assembled low molecular weight organogelators may be monitored using small deformation rheology. The rheological method should limit the systematic errors associated with the operating parameters. For example, the gel point should be independent of the oscillatory stress or strain and the frequency. However, random errors associated with the stochastic nature of self assembly cannot be avoided. Typically, in the literature the gel point is determined using the cross over point between G′ and G″ or tan δ = 1 (Markovic, Dutta, Williams, & Matisons, 2003; Matejka, 1991; Mezger, 2006). Similarly, in other instances the gel point has been monitored with the inflection point of either the G′ curve using oscillatory rheology or the "infinite viscosity" using flow rheology (Liang, Cook, Sautereau, & Tcharkhtchi, 2009). Confusion over the gel point often arises because in some polymer networks these values coincidentally correspond to the gel point (Winter, 1987). Conceptually, the gel point is extremely important when shaping a material because prior to the gel state it will flow while the stress can relax to zero. We can illustrate the effect of experimental design of the gel point values using the infinite of the viscosity (Fig. 3A–B) and the inflection of the storage modulus (G′) (Fig. 3C–D). It is observed that the gel point changes as a function of stress in flow measurements and as a function of frequency in oscillatory measurements (Fig. 3). In flow measurements, the relaxation time is very long and steady state flow is not complete in the experimental time frame. As well, near the gel point the network structure is weak and disrupted causing a delay in the gel point. Further, an infinite viscosity is an unambiguous indicator of gel point which may
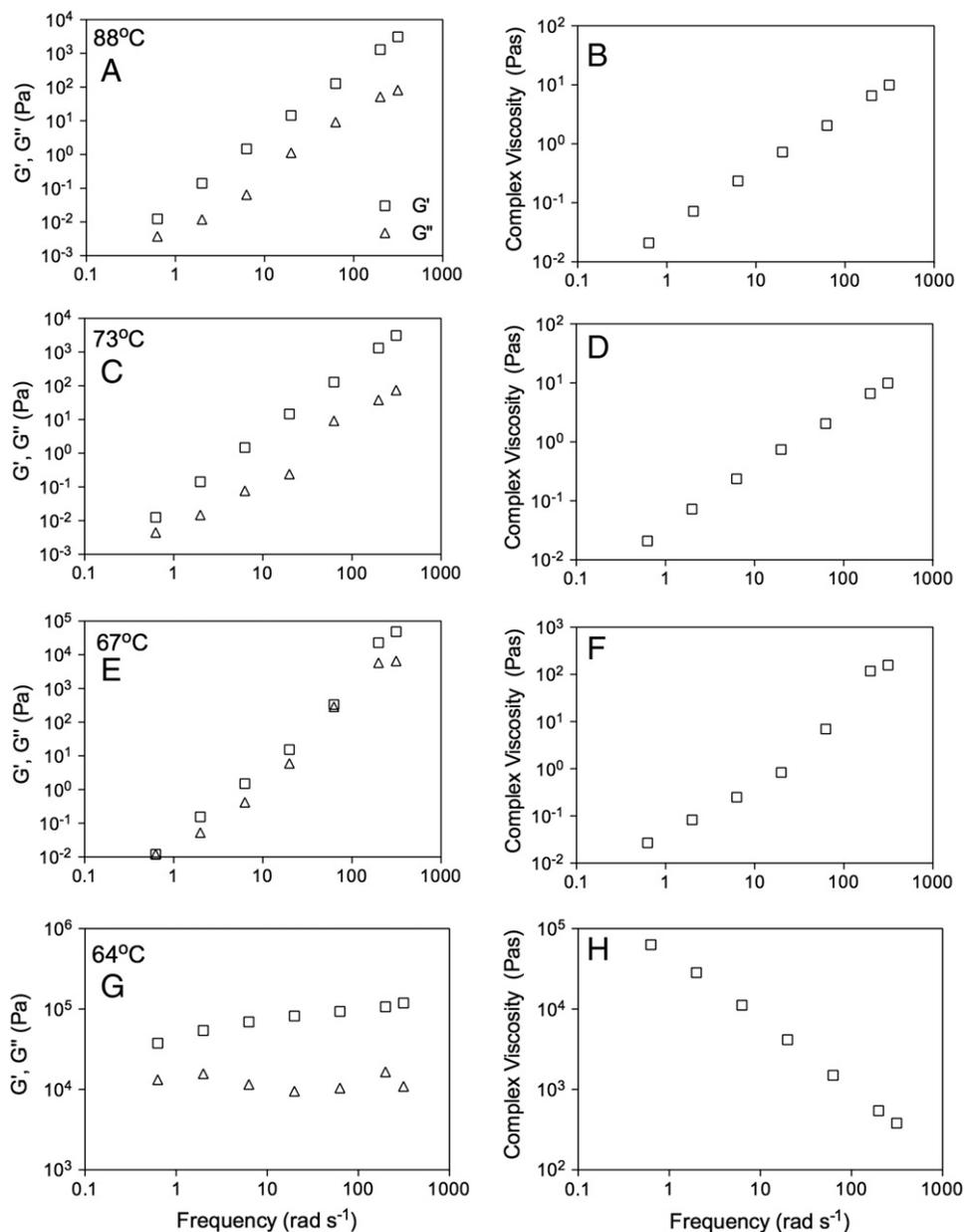

Fig. 5. Frequency dependence and complex viscosity of a 3% 12 hydroxystearic acid/mineral oil sample as it is cooled from 90 °C to 30 °C at 2 °C/min.

be related to other phenomena occurring during the process (Winter, 1987). Hence, the ideal rheological method to determine the gel point is by utilizing frequency sweeps at an oscillatory stress below the yield value and within the linear viscoelastic region.

The advantage of frequency sweeps is that dilute solutions, concentrated solutions and gels have very distinctive behaviours (Steffe, 1996). In dilute solutions G′ and G″ scale as a function of frequency. Typically in aqueous systems G″ is above G′ however, in the case of mineral oils and other apolar solvents this may not always be the case (Fig. 4). Fig. 4A and C illustrates that mineral oil when cooled typically behaves in a similar fashion to a dilute solution which is expected. Further, the complex viscosity ($n^* = G^*/\omega$) where G^* is the complex modulus and ω is the frequency, may be used to examine the relaxation time of the material. The complex viscosity is the "frequency dependent" viscosity which is related to the complex shear modulus and is the angle between the viscous stress and shear stress. Hence, if the material has a long relation time (i.e., a liquid, dilute solution, or concentrated solution) compared to the experimental time frame (i.e., the frequency) then as the frequency increases so does the G^* and hence the complex viscosity increases as function of frequency (Fig. 5B,D). The frequency dependence during non-isothermal cooling may be monitored for organogels (Fig. 5). It is apparent that in the sol state the frequency dependence suggests a dilute solution (Fig. 5A,B). Upon nucleation the frequency dependence of G′ and G″ suggests that the behaviour is a dilute solution (Fig. 5C,D). Hence, for the gel point determined using the "infinite viscosity" (gel point between 69 – 72 °C)(Fig. 5A,B) or inflection point of G′ (gel point between 68 and 82 °C) (Fig. 5C,D) the gel would occur at around the nucleation temperature as observed using brightfield microscopy. However, the solution behaviour and microscopy indicate that it still behaves as a dilute solution. After subsequent crystal growth the fiber length increases (Fig. 2C) we observe that the G′ and G″ values are equal and hence the cross-over point is independent of frequency which is the criteria for a gel and occurs at 67 °C (Fig. 5E) (Winter & Chambon, 1986). The frequency dependence illustrates a different type of solution behaviour which is slightly different from a dilute solution. It appears that the behaviour is more similar to a concentrated solution or a weak gel where the G′ and G′ scale evenly with frequency. However, as is evident with the complex viscosity, the material still has a long relaxation and still has some liquid-like properties. It is not until 64 °C that strong gel-like properties are observed (Fig. 5G,H). This is well below the gel point determined using the other rheological techniques.

4. Conclusion

Typical gel-like frequency behaviour is observed when G′ and G″ are unaffected by the frequency due to the short relaxation time of the material compared to the frequency. Further, the complex viscosity now decreases as a function of frequency which again confirms the short solid-like response of the material. For complex state transitions for self-assembled low molecular weight gelators it is insufficient to simply monitor the G′ or viscosity of the material. To get an accurate gel point the frequency dependence must be probed for the systems. Using these techniques, we cannot only observe the gel point but we can see the transition from dilute solution to concentrated solution and finally to gel.

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