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April 26, 2022

Dear Reviewer #2:

Thank you very much for taking the time to review our manuscript [gels-1665237](#). Our responses to your feedback is provided below in red.

Sincerely,

Darren

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I am quite prepared to accept this paper provided the authors add some elements throughout the discussion of their results.

1) There are new books on organogelation that are more physics-oriented on this phenomenon. The authors should quote them:

Guenet, J.M. Organogels: thermodynamics, structure, solvent role and properties, 2016, N.Y., Springer International Publishing

Weiss, R.G. Ed Molecular Gels, Structure and Dynamics, Monograph in Supramolecular Chemistry, 2018, Royal Society of Chemistry, London

We thank reviewer 2 for this suggestion. We are familiar with and have seen these books. These citations have been added.

2) The problem of defining a gel. As we can see from figures 7, the morphologies of the different systems are not at all the same. Guenet in the above book has discussed in details a definition of a gel. The conclusion is that a gel is a network, and a network is “a large system of lines, tubes, wires, etc. that cross one another or are connected with one another” according to the definition given by any dictionary. Again, as further discussed in the above book what is needed is a near-1D crystallization to get eventually fibrillar systems that do obey the definition.

As a result, system in figures 7a, 7b, 7h, 7i do not comply to this definition they simply are 3D crystallization.

As clearly mentioned into the caption of Fig. 7, Figures 7a and 7b are POM images of gel phases for which they cannot display any of the morphologic typical features of dried gel networks, they show instead birefringence indicating some degree of anisotropy, furthermore, Fig. 7b clearly shows highlighted strands that are SEM images on solid sample confirmed as fibers. The resolution in the SEM image in Fig 7h for a dense sample of the xerogel is not sufficient to visualize individual structures. Please note that nanofibers can be clearly visualized at the edges of the gel (see Figure S21a). Figure 7i shows an AFM image of the same sample, at higher resolution, which clearly reveals 1D structures (lines, tubes, or wires) that are connected and interwoven; isotropically ordered. Furthermore, as clearly mentioned in the maintext, “the xerogel from cyclohexane (Figure 7h and i), consisted of a dense network of ultrafine nanofibers (Figure 7i), which although are too small to be resolved in SEM images (Figure 7h), could be easily resolved by AFM. The AFM widths of the nanofibers in Figure 7i are consistent with the AFM width of the elementary nanofiber in Figure 6c (i.e., ~10 nm).”

None of the presented images therefore are referring to 3D crystallization systems. PXRD patterns are relatively broad so if 3D crystallization was the case then the peaks would be sharper and possibly greater in number, more well-dispersed etc...

Now, the authors may argue that their rheological experiments always show  $G' > G''$ . As was shown by Collin et al. (Soft Matter, 2013, 9, 2947) this can be deceiving because the explored range of frequency, especially within the low frequency range, is limited. Their experiments show that there is no modulus at infinite time, as required by a true rheological of a gel. Basically, each time they apply a new deformation, they retrieve the same value of  $G'$ , whereas this value should have increased. This should be considered and discussed.

We thank this reviewer for the insight and the reference, which we are aware of. This reference has been added along with the following text:

Although  $G'$  and  $G''$  data here were collected using a conventional rheometer and are typical of a viscoelastic material like a gel, others have shown that for low frequencies and long relaxation times this may not be the case [81]. At low frequencies only accessible with non-conventional rheological instrumentation, supramolecular gels from LMWGs may experience irreversible permanent deformations and may not be physical gels, but rather may be “solid-like networks that respond elastically for small deformations and are embedded in suspending fluids [8,81].”

3) The Hansen parameter allows one only to decide whether the solvent is not too good, thus preventing crystallization, nor not too bad, thus preventing solubilization. It cannot predict whether the system will give 1D fibrils or 3D crystallization, which is what is eventually needed. Again, see the above book by Guenet.

Note that for polymers, scientists are rather using the Flory's parameter, which is experimentally obtained, rather than the Hansen parameter.

In a recent publication by Weiss and Rogers (Langmuir 2017, 33, 10907–10916), they state “HSPs can be used as effective a priori tools for predicting the abilities of small molecules to self-assemble into SAFiNs for specific solvents.” Reviewer #2's comment seems to contradict this statement. HSPs for LMWGs are also discussed in the book by Weiss that reviewer #2 suggested citing above. Note that Weiss can be considered a pioneer and one of the biggest experts in the field of supramolecular gels. HSPs are recognized as the best current approach for predicting gelator behavior. Please see references 70-73 cited in our manuscript as well as the following references to list a few others:

1. Van Lommel et al, Gels 2021, 7, 87.
2. Nunes et al, Langmuir, 2019, 35, 7970
3. Lan et al, Soft Matter, 2019, 15, 9205--9214
4. Nunes et al, Soft Matter, 2018, 14, 4805
5. Chen et al, Materials Today Chemistry 2022, 23, 100719
6. Ge et al, Langmuir 2021, 37, 2677-2682
7. Draper and Adams, Chem 2017, 3, 390

Also, just because a compound can form 1D fibrils does not mean a gel will be formed. We did image the precipitate formed from ISA24 with hexanes by SEM, which showed the same narrow diameter nanofibers shown in Figure 6, 7 and Figures S17-S30. ISA24 formed fibers in hexanes but did not gel hexanes (unpublished results).

To the best of my understanding, Flory's parameters (Flory-Huggins interaction parameters) have not been commonly applied to LMWG systems. A few reviews have been published on the use of solubility parameters for LWMGs which do not mention Flory-Huggins interaction parameters.

4) The gel formation and melting would be better studied by DSC. The inverted tube method is not very precise. Also, about the so-called "critical gelation concentration", the authors should read the two above books above. As was also emphasized in a GELS article the T-C phase diagram by DSC is an important step in studying organogelation (R.G. Weiss, Gels, 2018, 4, 2). This concentration depends upon the temperature at which it is measured. So, it is not a critical parameter in the physical sense. Only the temperature-concentration phase diagram tells you something about the system.

We thank the reviewer for this insight, which we are aware of and agree with. We have even had samples that did not pass the vial inversion test but yet still were shown to have the typical rheological properties of gels.

We did try to measure T<sub>gel</sub> values (formation and melting) using DSC, Unfortunately, we were not able to detect any phase transitions by DSC or rheology temperature sweeps, which could be due the low gelator concentrations. This is often the case of "supergelators" indeed, since the amount of solvent is excessively high and therefore transitions are rather difficult to be observed. Alternatively, and more likely, the gel formation and melting transitions occur near or above the bp of the solvents for the gels tested. Many if not all of the gelators required heating to high temperatures (often larger than the solvent bp) in sealed vials to prevent solvent evaporation. Such high temperatures and pressures are known to affect DSC measurements using conventional DSC instruments and supplies (i.e., hermetically sealable Al pans are known to deform under high internal pressures).

Note that we clearly mentioned at the end of this section (lines 223-239) that the T<sub>g</sub> values are probably more likely decomposition temperatures rather than true melting transitions. The true melting transitions for these compounds are probably near or above the solvent bps