

Chapter 2

Gels: A Definition

Polymer thermoreversible gels and organogels are produced from solutions where the solvent is by far the major component, typically above 90 % up to 99.9 % with some biopolymers. By cooling these solutions, they turn into a solid-like material at a relatively well-defined temperature. It is customary to read in some papers that a given component *gelled a given solvent*.

Every book or review dealing with gels systematically quotes Dorothy Jordan Lloyd [1] who tackled the question of defining a gel and who eventually came to the conclusion that “*The colloidal condition, the gel, is one which is easier to recognize than to define*”. The reason lies in the fact that there is usually no clear-cut definition resting on a minimum of physical parameters while simply handling and touching a gel allows one to realize that it is neither a viscous solution nor a piece of glue nor a paste.

It is therefore worth devoting some space so as to try and provide the reader with a thorough insight into the way these systems can be, or rather may be defined. A *definition*, also called an *extensive definition* in the present case, serves to specify the *extension of a concept*. It allows one to establish a list naming every object that is a member of a specific set. In this monograph two ways of defining organogels are discussed: the *rheological aspect* and the *topological-thermodynamic aspect*. The former is the classical approach based on the rationale that a connected array of objects should possess a solid-like behavior, something testable by mechanical observations. The latter derives from the fact that organogels are thermally-reversible networks, and so relies both upon its topology, with respect to the accepted definition of a network, and upon its formation and melting properties.

These two ways of tentatively defining a gel go beyond the all too often used tube tilting or tube upside down test which may be misleading. That a solution or a suspension does not flow anymore through some jamming process does not prove at all that a gel has formed. For instance, humid sand passes the tube tilting test and yet nobody would seriously consider it a gel.

2.1 Rheological Definition

The very first rheological apparatus granted by nature to man is one's fingers. Compressing a system between one's finger and thumb allows one to decide whether one is dealing with a viscous solution or a gel. Yet, this apparatus is far from perfection, and often deceiving as it provides no information on long relaxation processes.

In the case of polymers, rheological properties are considered to differentiate a gel, whose existence arises from chemical or physical cross-linking, from a highly viscous solution. Typically, a gel is a solid-like system that can be studied by classical techniques such as oscillatory, relaxation, and creeping experiments [2]. From these experiments parameters such as G' , G'' , $\tan \delta = G'/G''$, E or J can be derived where G' and G'' are the storage modulus and the loss modulus, E the Young's modulus, and J the compliance. Relaxation experiments are carried out by application of a given deformation ε which relates the resulting stress to the Young's modulus ($\sigma(t) = E(t)\varepsilon$) while creep experiments are performed by application of a given stress σ_0 which relates the compliance to the deformation $\gamma(t)$ ($J(t) = \gamma(t)/\sigma_0$). In order to identify the typical behavior of a solid, two criteria must be strictly fulfilled:

- (1) **criterion 1:** in oscillatory experiments G' must be much larger than G'' , usually over a decade, which implies that stress-strain relaxation is chiefly governed by an elastic process [3];
- (2) **criterion 2:** in a relaxation experiment $E(t_\infty) = \text{const} = E(t_0)$, or in a creep experiment $J(t_\infty) = 1/E = 1/E(t_0)$ emphasizing the solid-like behavior as opposed to what is seen in highly viscous solutions.

For instance, vulcanized rubber used in the making of car tyres fulfills all these criteria, while native rubber displays a strong relaxation. Vulcanization is obtained through chemical cross-linking thus establishing covalent bonds between the rubber chains. Covalent bonds are of sufficient energy to prevent from disentanglements by reptation that otherwise occurs in native rubber entailing permanent deformation. As a rule, chemically cross-linked gels, namely of the same type of molecular architecture as cross-linked rubber yet highly swollen by a solvent, behave the same [4].

Strangely enough, despite the abundant literature on organogels, not so many rheological experiments have been reported so far. Terech et al. [5] and later Collin et al. [6] have studied in depth about these systems either by oscillatory experiments by means of a classical cone-plate apparatus (Terech et al.) or with a piezorheometer where opposite ceramics vibrate in the shear mode (Collin et al.). These experiments are performed in a limited range of frequency typically from 10 to 500 Hz with classical cone-plate rheometer, while a piezorheometer allows one to extend the frequency range from 0.2 to 1000 Hz. A typical variation of G' and G'' as shown in Fig. 2.1 is observed in both studies.

Although G' looks virtually constant and is much larger by approximately a decade than G'' , the behavior shown in Fig. 2.1 can be deceiving despite the large

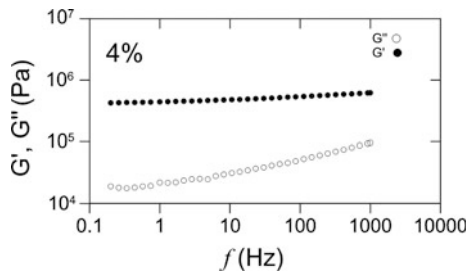


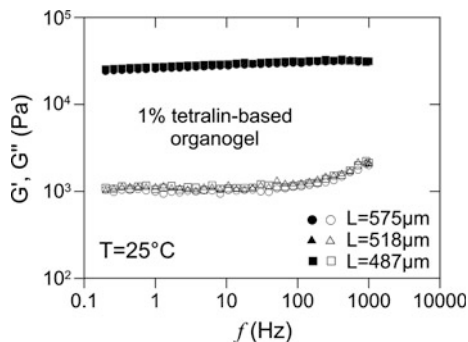
Fig. 2.1 Variation of the storage modulus G' (●) and the loss modulus G'' (○) as a function of shear frequency for experiments carried out by means of a piezorheometer at very low strain (10^{-5}). The organogel is a 4 % mixture of a modified peptide (w/v) in tetraline. From Collin et al. [6]

frequency range swept. Apparently, criterion 1 is obeyed, yet relaxation experiments over longer period of times, namely as if the frequency range were extended to much lower values, may reveal subsequent relaxation down to $E(t_{\infty}) = 0$. The organogel may therefore experience irreversible, permanent deformation which implies that the rheological approach is possibly not appropriate for a non-questionable definition of these systems.

This behavior has already been observed by Guenet and McKenna [7] with gels from isotactic polystyrene, a stereoregular polymer that display significant relaxation when submitted to a given deformation: usually the stress falls to zero after 24 h. Yet, the very primitive handling and/or touching test unquestionably shows one is dealing with a gel.

Recent results by Collin et al. [6] have observed a similar behavior. Their experiments consist in applying a given deformation, and then submitting the sample to a vibrating shear mode. This is seen in Fig. 2.1. Yet, by compressing further, the response is identical to the previous one (Fig. 2.2). Clearly, application of a compressive deformation has led to an irreversible modification of the organogel. Would the gel have not undergone irreversible deformation, then G' should have drastically increased. This behaviour is equivalent to the stress relaxation phenomenon

Fig. 2.2 Variation of G' and G'' of a 1 % tetralin-based organogel as a function of frequency for different thicknesses resulting from a gradual static compression of the sample. The measurements were performed at 25 °C. From Collin et al. [6]



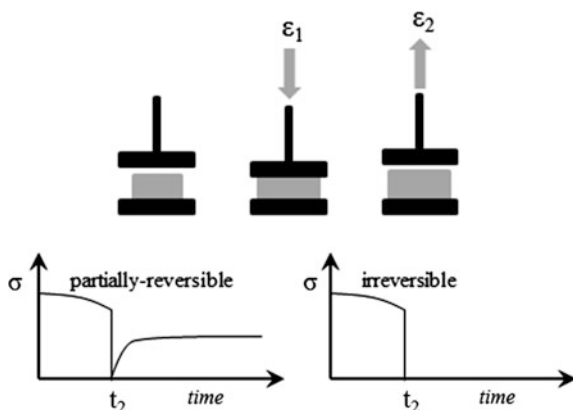


Fig. 2.3 Rheological test designed by Daniel et al. [8]. A cylinder-like piece of gel is placed between two plates. A deformation ε_1 is applied to the sample and the stress σ is measured as a function of time. At $t = t_2$ the *upper plate* is pulled up to a deformation ε_2 , which entails a sharp drop of the stress σ . For a partially reversible system, a stress will gradually reappear (*graph left*), while for an irreversible system (a paste for instance) the stress remains 0 independent of ε_2 (*graph right*). [8]

observed with iPS gels. Therefore, these organogels do not meet criterion 2 although they meet criterion 1, at least when low shear deformation are used.

Guenet and coworkers realized that failure to meet these rheological criteria was due to the degree of interaction between the object involved in the gel architecture. They accordingly proposed another test involving compression measurements for determining the degree of interaction by investigating the degree of recovery after submitting the gel to a deformation [8]. Indeed, if applying a deformation to the organogel entails destruction of connecting bonds this can be evaluated through the simple test schematized in Fig. 2.3.

This test consists in measuring the stress resulting from the compression of a cylindrical sample to a deformation ε_1 , and then at $t = t_2$ moving the piston to a deformation ε_2 with $\varepsilon_2 < \varepsilon_1$. A stress should reappear if connecting bonds are still present. Conversely, if these bonds have been destroyed or if they did not exist in the first place, then the stress remains zero. This test was successfully applied to thermoreversible gels from stereoregular polymers. It could be equally used for characterizing organogels.

This test allows one to offer a way of measuring the degree of reversibility, $r(\varepsilon_1)$ for a given deformation. It suffices to determine at which value of ε_2 set at always the same time t_2 there is no recovery at all. Then, $r(\varepsilon_1)$ is simply $r(\varepsilon_1) = \varepsilon_1/\varepsilon_2$. Admittedly, this kind of analysis is tedious and time-consuming but it provides one with tangible data of the system under study.

It is worth stressing that destruction of interfibrillar bonds is possible under mechanical constraint because these bonds are of energy lower than covalent bonds. In the literature, these systems are often said to be *thixotropic*. Actually, the same

phenomenon occurs with solid ice. It is well-known that a weight will sink down through a piece of ice through local destruction and reformation of the hydrogen bonds. This phenomenon is well-known in glaciers. The same occurs with thermoreversible polymer gels and organogels: van der Waals or hydrogen interfibrillar bonds can be disrupted, yet may reform. This is sometimes described as a yield stress phenomenon [5] although recovery may take place with time, which is reminiscent of a healing process through the reformation of interfibrillar bonds.

It is worth emphasizing that systems may show a storage modulus higher than the loss modulus in a large frequency range in oscillatory experiments [9] while they do not pass the test designed by Daniel et al. [8]. An extension to very low frequencies, which is equivalent to very long relaxation times may reveal that G'' becomes larger than G' in the end. Usual rheometers do not give access to very low frequencies so that a relaxation experiment is more informative in most cases. This will be discussed in more details in Chap. 6.

2.2 Topological-Thermodynamic Definition

Rheology and/or the test developed by Guenet and coworkers are clearly not sufficient to decide whether a system can be considered gel or not. The topology together with the thermodynamic of these systems brings probably a better way of tackling the question. This definition was already proposed by Guenet and coworkers for polymer thermoreversible gels [10].

It is customary to regard a gel as a network of connected objects. The definition of a network that is provided by any dictionary is

a large system of lines, tubes, wires, etc., that cross one another or are connected with one another (Longman dictionary [11]).

Note that this definition is basically the same in French, Spanish, and German, and possibly in many other languages, which makes it universal. In all cases, elongated objects are involved in the formation of a gel. Therefore the gel status can be inferred from structural or morphological investigations. This *is the topological criterion*. A typical example is given in Fig. 2.4 left.

In addition, polymer thermoreversible gels, and similarly organogels, are thermally-reversible systems: they can be melted and reformed at will. As a result, one has to introduce an additional criterion to differentiate these gels from those that are thermally-irreversible such as polymer chemical gels. This is the *thermodynamic criterion* which states that: *the formation and melting of these gels proceed via first order transitions,¹ and that the process is perfectly reversible* [10]. A typical example is given in Fig. 2.4 right.

¹Not to be confused with *first order reactions* that describe chemical processes.

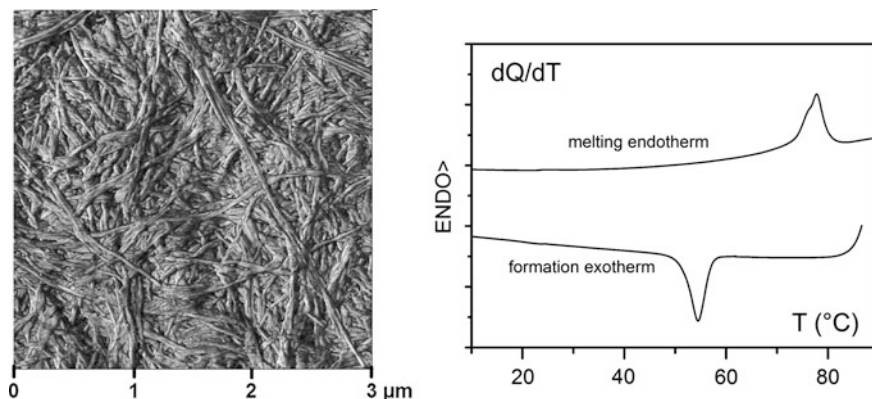


Fig. 2.4 *Left* AFM picture of a xerogel from an oligophenylenevinylene molecule in benzyl methyl ether ($C = 0.4\%$ w/v) (OPVE, synthesized by Ajayaghosh et al. [12]). Micrometric fibrils are seen with cross-sections in the nanometric range; *right* typical DSC traces obtained on cooling (formation exotherm) and heating (melting endotherm). These are typical examples of first order thermodynamic transitions. The associated enthalpies are given by the area under the peaks after proper calibration. Case presented here a tripod molecule (BHPB-10 synthesized by Mésini and coworkers [13]) in fluorotoluene (Courtesy Guenet, private communication)

This particularly means that one should be able to detect formation exotherms and melting endotherms in calorimetric investigations, yielding the formation and melting temperatures together with the associated enthalpies.

These two criteria make it possible to differentiate gels from deceiving systems such as phase-separated glasses (may show network architecture but no first-order phase transitions) and spherulitic systems (may show first-order phase transition but no network architecture). It seems therefore unfortunate that papers may describe spherulitic systems as gel which eventually throws the scientific community into confusion [14].

It is worth elaborating further concerning the latter system, namely assemblies of spherulites. Tilting test tube will show the absence of flow. In experiments with classical rheometers, this system may also exhibit apparent elastic properties, particularly at very small deformation. The reason lies simply in the imbrications of spherulites within one another, something reminiscent of the burrs of burdock that keep sticking to clothes. Yet, these assemblies eventually behave like a paste. A striking example is given by Daniel et al. for systems prepared with syndiotactic polystyrene (sPS) on the one hand, and poly phenylene oxide (PPO), on the other hand in 1,2 dichloroethane [15].

As shown in Fig. 2.5, sPS/1,2 dichloroethane solutions form fibrillar networks unlike PPO/1,2 dichloroethane solutions from which spherulites are obtained. Daniel et al. have further dried the samples by exchanging the solvent with supercritical CO_2 extraction. The advantage of this solvent extraction procedure lies in the absence of surface tension effects so that the original morphology is usually kept. As can be seen in Fig. 2.5, only sPS systems retain their initial shape while

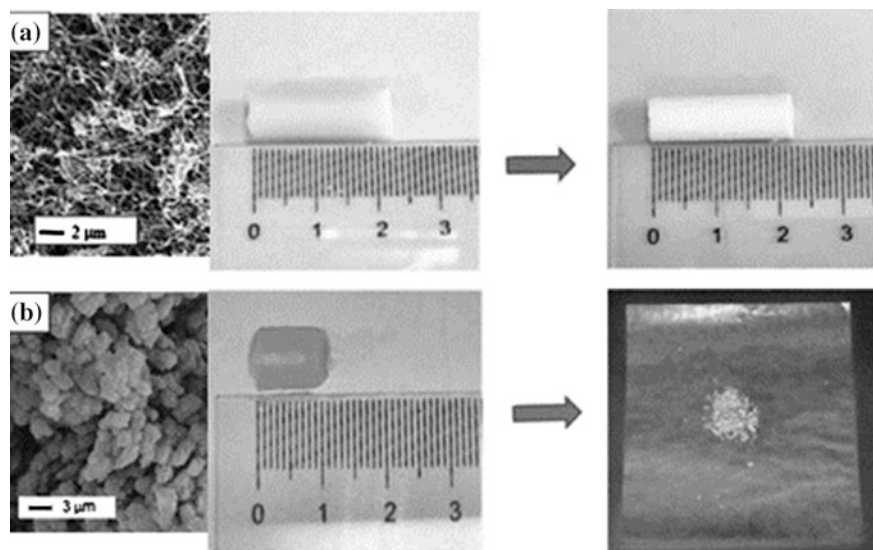


Fig. 2.5 Comparison between sPS/1,2 dichloroethane systems (*upper figures, a*) and PPO/1,2 dichloroethane systems (*lower figures, b*) after supercritical CO_2 extraction. *Left* SEM pictures showing a fibrillar morphology for the sPS systems, and a spherulitic morphology for the PPO systems. *Middle* both systems before extraction; *right* systems after extraction. Only the sPS system retains its initial shape (courtesy by Daniel from Daniel et al. [15])

PPO systems become powdery. This outcome clearly shows that spherulitic assemblies produced from solutions cannot be considered a network based on the current definition by language dictionaries.

It is worth stressing that connections between spherulites will occur in polymers solutions for very high concentrations and in the solid state because of the high level of chain entanglements. Such entanglements do not exist for oligomolecules so that increasing the organogelator concentration will not create any connections between spherulites.

2.3 Summary

If we refer back to the necessity of deriving a definition, namely to specify the *extension of a concept* and to establish a list naming every object that is a *member of a specific set*, then the topological-thermodynamic definition is probably best suited to reach this goal. To be sure, a large majority of papers published on these systems display AFM pictures that exhibit typical fibrillar morphology. Yet, it still remains of interest to find out to which extent these fibrils are interconnected, a property which is best determined by rheological experiments.

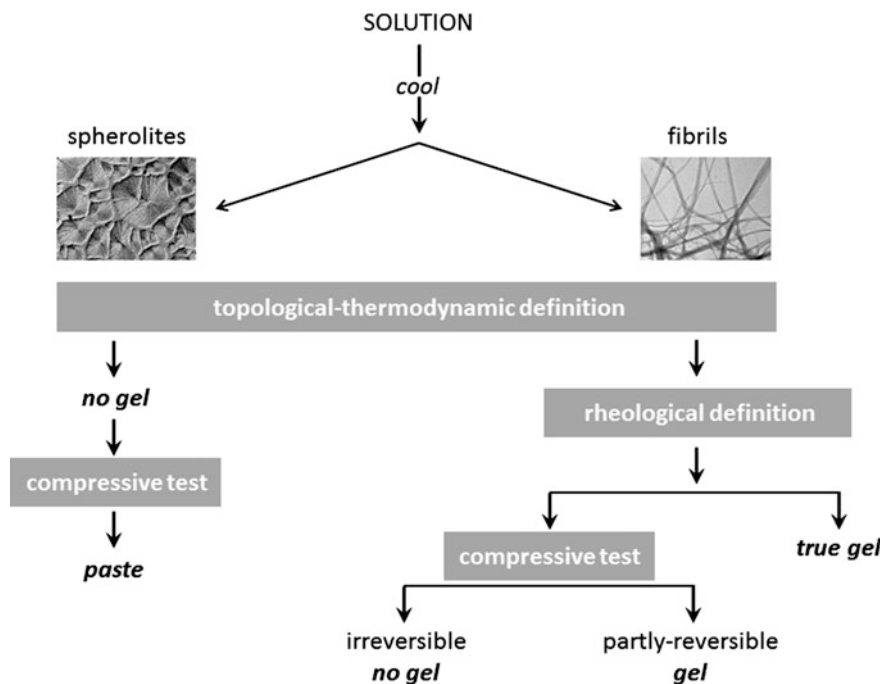


Fig. 2.6 Sketch of the cascade of definitions and test that should be used for evaluating the gel status of a crystallizing system. Irreversible and partly-reversible stand for the degree of gel shape recovery after compression. As shown, the first level of definition should be the thermodynamic-topological definition, and then followed by the rheological definition

Admittedly, a set of randomly dispersed fibrils with no interfibril connections might not be worth considered a gel either unless some “sticking” process operates. Such a case is reminiscent of the *Mikado game* where sticks are in contact but without any specific interaction otherwise. Application of a double criterion to spherulitic systems, namely topological definition and the compressive test, allows one to discard them definitely from the realm of gels [8]. The sketch in Fig. 2.6 summarizes the cascade of criteria and test that should allow one to decide about the gel status of the system under study. Systems studied by Collin et al. [6] ought to be therefore discarded on the basis of this set of criteria.

This tentative set of criteria developed above for defining a gel brings one back to the remark by Lloyd about the difficulty in designing a nice, self-containing definition. After all, we are in the realm of soft matter where defining things is ultimately a complex task.

In any case it must be clear that only interconnected fibrillar systems only ought to be regarded as gels. They do represent a specific set.

References

1. Lloyd, D.J.: In: Alexander, J. (ed.) *Colloid Chemistry: Theoretical and Applied*, vol. 1, p. 7. The Chemical Catalog Co, New York (1926)
2. Barnes H.A., Hutton J.F., Walters, K.: *An Introduction to Rheology*. Elsevier Science Publishers, Amsterdam (1989)
3. Ferry, John D.: *Viscoelastic Properties of Polymers*. Wiley, New York (1980)
4. Candau, S., Bastide, J., Delsanti, M.: Structural, elastic, and dynamic properties of swollen polymer networks. *Adv. Polym. Sci.* **44**, 27–71 (1982)
5. Terech, P., Pasquier, D., Bordas, V., Rossat, C.: Rheological properties and structural correlations in molecular organogels. *Langmuir* **16**, 4485–4494 (2000)
6. Collin, D., Covis, R., Allix, F., Jamart-Grégoire, B., Martinoty, P.: Jamming transition in solutions containing organogelator molecules of amino-acid type: rheological and calorimetry experiments. *Soft Matter* **9**, 2947 (2013)
7. Guenet, J.M., McKenna, G.B.: The concentration dependence of the compression modulus of iPS/cis-decalin gels. *J. Polym. Sci. Polym. Phys. Ed.* **24**, 2499 (1986)
8. Daniel, C., Dammer, C., Guenet, J.M.: On the definition of thermoreversible gels: case of syndiotactic polystyrene. *Polymer* **35**, 4243 (1994)
9. Guenet, J.M.L.: unpublished observations
10. Guenet, J.M. *Thermoreversible: Gelation of Polymers and Biopolymers*. Academic Press, London (1992)
11. *Dictionary of English language and culture*, Longman Group UK Ltd, Harlow (1992)
12. Dasgupta, D., Srinivasan, S., Rochas, C., Ajayaghosh, A., Guenet, J.M.: Hybrid thermoreversible gels from covalent polymers and organogels. *Langmuir* **25**, 8593 (2009)
13. Diaz, N., Simon, F.X., Schmutz, M., Rawiso, M., Decher, G., Jestin, J., Mesini, P.J.: Self-assembled diamide nanotubes in organic solvents. *Angew Chem. Int. Ed.* **44**, 3260 (2005)
14. Huang, X., Terech, P., Raghavab, S.R., Weiss, R.G.: Kinetics of 5 α -cholestan-3 β -yl N-(2-Naphthyl)carbamate/n-alkane organogel formation and its influence on the fibrillary networks. *J. Am. Chem. Soc.* **127**, 4336 (2005)
15. Daniel, C., Longo, S., Cardea, S., Vitillo, J.G., Guerra, G.: Monolithic nanoporous-crystalline aerogels based on PPO. *RSC Adv.* **2**, 12011–12018 (2012)

Organogels

Thermodynamics, Structure, Solvent Role, and
Properties

Guenet, J.-M.

2016, XII, 122 p. 90 illus., 17 illus. in color., Softcover

ISBN: 978-3-319-33176-8