# Microfibrillar Networks: Polymer Thermoreversible Gels vs Organogels

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**Summary:** This paper is intended to review some aspects of fibrillar networks by comparing polymer thermoreversible gels and organogels, the latter being obtained through the self-assembling of small organic molecules. The morphology, the rheological properties and the gelation mechanisms are particularly examined. The possibility of preparing hybrid materials is discussed.

**Keywords:** fibrils; polymer-solvent compounds; thermoreversible networks

## Introduction

Microfibrillar networks, materials belonging to the realm of *finely-divided matter*, are of special interest both for basic and applied research. The understanding of the *formation mechanisms* and the *thermodynamic properties* together with the determination of the *molecular structure* of such networks represent major challenges to basic research, while their special microfibrillar morphology offers applications such as filtering membranes, encapsulating media, food thickeners, nucleating agent, substrates for living tissue reconstruction, and the like. Microfibrillar networks can be particularly obtained with two different systems: from *polymers solutions*, which once cooled to below the gelation threshold, produce fibrillar ***physical gels*** [1] and from *organic moleculessolutions*, that self-assemble and give birth to ***organogels*** [2]. Both systems are *thermoreversible* as they can be melted and reformed at will through heating and cooling cycles without significantly altering the chemical structure of their constituents.

In this paper, *polymer thermoreversible gels* and *organogels* will be compared in order to highlight their similarities. First, a short paragraph will be dedicated to the way these networks can be defined. In this aim a simple rheological experiment will be described, that should allow one to recognize them. Their gelation mechanisms, their molecular structure and their morphology will be then examined.

### On the Definition of Thermoreversible Gels

Thermoreversible gels are often referred to as physical gels because the interactions involved in the connecting domains are of the order of *kT*, and can therefore be destroyed and reformed *reversibly* by heating and cooling the system. As to chemical gels cross-links involve covalent bonds so that they are *heat-irreversible*. Destroying the cross-links ultimately implies chemical degradation of all the system.

The widely accepted definition of a gel is usually based on a rheological approach and reads: a *network which possesses an elastic modulus at zero frequency* (oscillatory experiments) *or at infinite time* (relaxation experiments). While this behaviour pertains to chemical gels, it is seldom observed for physical gels. In oscillatory experiments $G''$ becomes larger than $G'$ for low frequency while in relaxation experiments, relaxation rates $d\log\sigma/d\log t$ are often larger than 0.1 [1]. This behaviour is rather ''liquid-like'' although these systems are certainly different from viscous solutions.

Clearly, defining a thermoreversible gel in a very simple, elegant way is therefore doomed to failure. In view of the difficulties

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in putting forward such a definition, Guenet has proposed to consider two main criteria instead [1]:

1) **Criterion 1**: the gel topology is primarily that of a ***network***. Contemplating the definition of a network given in dictionaries [3]: "*a large system of lines, tubes, wires,.. that cross one another or are connected with one another*" implies that the framework of the gel is made up with objects of very high aspect ratio, such as threads, ribbons,...that will be quoted as *fibrils* in what follows. Assemblies of spherulites are therefore disqualified.
2) **Criterion 2**: the formation and melting of a thermoreversible gel should occur through a first order transition as some type of order is created out of a totally disordered solution.

Most of the fibrillar polymer gels comply to these two criteria, but organogels also do as we shall discuss it below.

These criteria require the use of sophisticated techniques, particularly criterion 1, to decide whether the system under study can be considered a thermoreversible gel. Usually mechanical testing are easier to bring about, and so Daniel et al. devised a simple mechanical process in this aim [4]. Daniel et al. argue that the relaxation observed with this system is due to the lability of the polymer chains within the physical junction. This lability depends on the degree of order within the junction. If this junction is highly crystalline, then chain lability is highly impeded and correspondingly the relaxation rate is quite low. Conversely, if the order within the junction is rather poor, then chain lability is increased and the relaxation rate is quite high. They further consider that if the relaxation experiment is stopped before the stress becomes zero, there is still some reversibility which arises from the elasticity of the objects joining at the junction (as will be discovered below these objects are fibrils).

Clearly, if an initial compressive deformation $\lambda_1$ is applied to the sample and then after some time another deformation $\lambda_2$ is applied with $\lambda_2 > \lambda_1$ (the piston is pulled up, see Figure 1), then at the change of deformation the stress should drop to zero

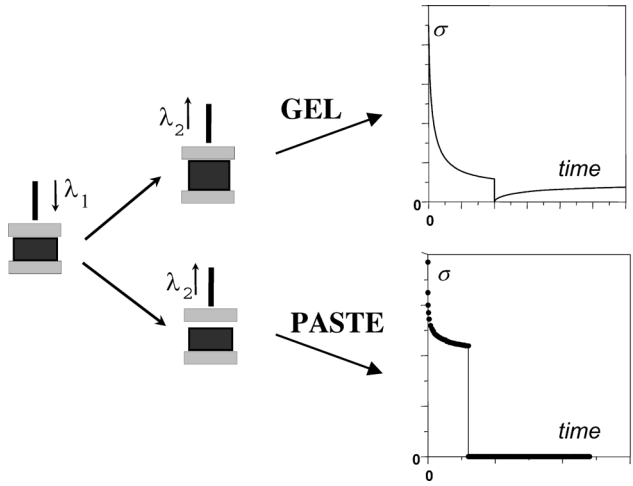


***Figure 1.***
Schematic representation of a relaxation experiment intended for discriminating between a paste and a thermoreversible gel. Both display relaxation when a deformation noted $\lambda_1$ is applied ($\lambda_1 = l_o - l_1/l_o$ where $l_o$ is the original height and $l_1$ the height after deformation, with $l_o > l_1$). Conversely, when the piston is pulled up to a deformation $\lambda_2$ (where $\lambda_2 > \lambda_1$) the stress in both cases drops to zero, yet it reappears in the case of a gel while it remains zero in the case of a paste. Here the paste is an assembly of spherulites (sPS/*trans*-decalin system). The gel has been obtained from an iPS/*trans*-decalin solution.

 

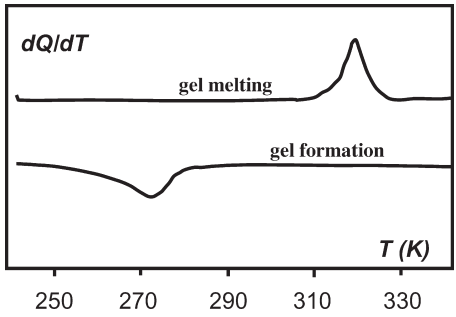


***Figure 2.***
Typical DSC thermogrammes produced by thermoreversible gels from polymer solutions. Here case of iPS/*trans*-decalin gels ($C_{iPS} = 0.1$ g/cm$^3$). Upper curve shows the melting endotherm and lower curve the formation exotherm.

but gradually reappears thanks to the reversible part of the deformation process. Conversely, if one is dealing with a paste, the deformation is totally irreversible , so that the stress remains zero. This mechanical process is illustrated in Figure 1.

Note that this approach is better than the ball drop method, which cannot distinguish between a paste and a gel. As a result, assemblies of spherulites, that do not comply to the above criterion, have all too often, in the author's opinion, be termed thermoreversible gels.

The systems tested in Figure 1, namely a gel prepared from isotactic polystyrene/*trans*-decalin solutions [5], and a paste obtained from the crystallization of a syndiotactic polystyrene/*trans*-decalin solution [6] obey both criterion 2, namely formation

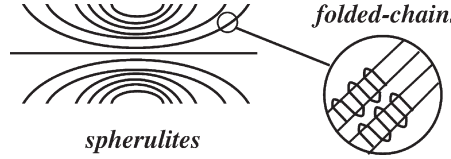


***Figure 4.***
Schematic representation of spherulites made up from the piling of lamella. The blow-up shows the detail of a lamella and the folded conformation of the polymer chains.

and melting occur through first order transitions as shown in Figure 2, yet syndiotactic polystyrene/*trans*-decalin system fails to comply to criterion 1. Indeed, as illustrated in Figure 3 the spherulitic morphology observed for the sPS/*trans*-decalin system cannot be regarded as a network in the sense taken from the dictionary. The simple mechanical test proposed by Daniel et al. is therefore relevant for deciding whether a system can be considered a gel or not.

As is shown throughout this Macromolecular Symposia volume, *organogels* display also a microfibrillar morphology [7], and the investigations performed by by Ajayaghosh et al. [8] clearly show that gelation occurs through first order transitions. Although the type of rheological investigations described in Figure 1 are still missing at the moment, one can guess that these *organogels* are likely to behave the same as the polymer thermoreversible gels.

At this point, it is worth dwelling upon the fact that DSC experiments may reveal the

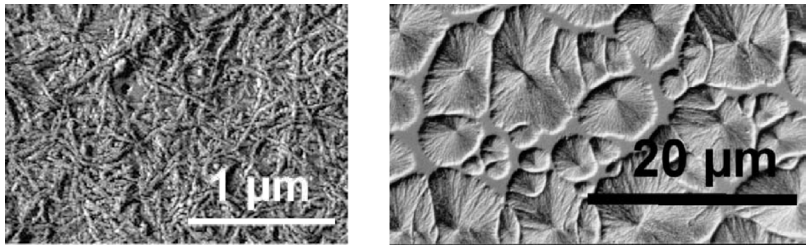


***Figure 3.***
***left***: AFM image of an iPS/*trans*-decalin gel highlighting the presence of an array of fibrils of cross-sections of about 10 nm ($C_{iPS} = 0.04$ g/cm$^3$), ***right***: optical micrograph (nomarsky phase contrast) of a sPS/*trans*-decalin mixture showing spherulites of about 10 µm diameter ($C_{sPS} = 0.1$ g/cm$^3$).

 

occurrence of aggregation through first order transitions, although no infinite three-dimensional network is formed. Finite-sized microgels may be obtained instead, particularly if the systems are prepared below the critical gel concentration. Hence, the gel point as determined by rheological method cannot be exactly the same as that determined by DSC.

It is also worth emphasizing that thermoreversible gelation is not necessarily a percolation process as has been recently discussed [9].

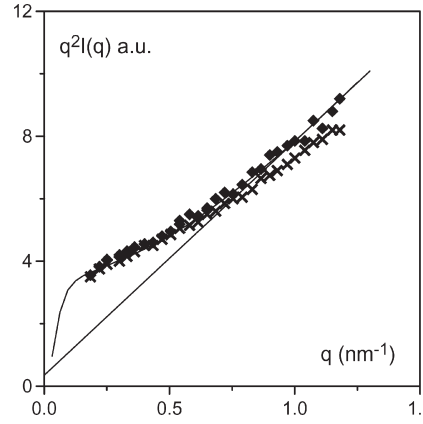


***Figure 5.***
Neutron scattering curves obtained on iPS/*cis*-decalin gels $C_{pol} = 0.15$ g/cm$^3$ [11]. The fraction of deuterated chains is $X_D = 0.06$. × = gel state; ◆ = solution at T = 66 °C after gel melting. The full line is a fit with a worm-like chain of persistence length $l_p = 4$ nm. The straight line shows the 1/q asymptotic behaviour [14,15].

**On the Gelation Mechanism**

Flexible, semi-crystallizable polymers usually produce spherulitic morphology (see Figure 3 right) which arises from the piling of lamellae. Lamellae are formed because of chain-folding. As a matter of fact, the chains take on a rod-like structure only on a few nanometers (10–20 nm) and then fold (see Figure 4).

Clearly, if fibrils are to be obtained instead of lamellae, chain-folding must be impeded to a large extent, or even totally. There may be several ways of preventing chains of flexible, semi-crystallizable polymers from folding. One way is the stabilization of the helical structure of the polymer as has been reported for stereoregular polystyrene. The stabilization process occurs through the formation of a polymer-solvent compound. This compound consists of solvated chains, where the solvent is housed within the cavities created by the protruding phenyl groups [10]. As has been observed from neutron scattering experiments on iPS/*cis*-decalin gels [11] (see Figure 5) but also on sPS/benzene and sPS/toluene gels [12,13], the originally flexible chains become more rigid. In the case of iPS/*cis*-decalin gels it has been shown that their persistence length increases from $l_p = 1$ nm to $l_p = 4$ nm. Interestingly, after gel melting the chain conformation remains the same, namely the persistence length is still of about $l_p = 4$ nm, which shows the efficiency of the stabilization process. Under normal conditions the persistence length should retrieve a value of about 1 nm after melting.

To be sure, gelation occurs in solvent wherein the chain persistence length can be enhanced to such an extent as to impede

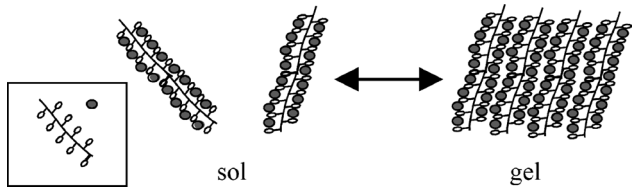


***Figure 6.***
Schematic representation on how chains, whose persistence length turns out to be enhanced through compound formation, aggregate on cooling without folding and so form fibrils instead of chain-folded crystals. Inset: schematic representation of solvent molecules (ball) and the chain with protruding phenyl groups while in the 31 helical form.

 

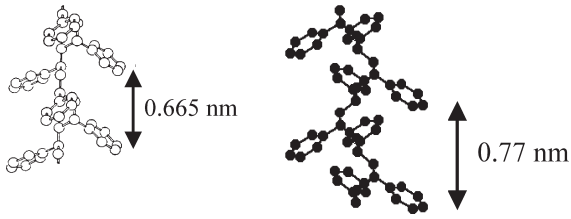


***Figure 7.***
The $3_1$ *helix* of iPS (left) and the $2_1$ *helix* of sPS (right). Figures indicate the value of the helix pitch.

chain-folding. Fibrils are then obtained by sideways aggregation of the solvated chains (Figure 5).

Interestingly, there exist systems, such as agarose solutions, that only produced fibrillar gels, and therefore that support the above mechanism. A careful study of the agarose chains conformation has revealed that the intrinsic persistence length of this polymer is quite large, [16] typically larger than 9 nm, and so chain-folding is definitely impeded and chain-folded crystals can never be formed with this natural polymer. This shows that a *large persistence* length is required for obtaining fibrillar gels. The polymer can therefore be intrinsically rigid, as is the case of agarose, or flexible but placed in a solvent that will form a compound and thereafter will stabilize the helical structure.

The chain microstructure, namely the external shape arising from the combination of the helical form and the chemical structure, plays a major role in the helix stabilization by a given solvent. As has been already highlighted above, iPS forms gels with *trans*-decalin while sPS does not. This arise from the differing helical forms: a $3_1$ *helix* for iPS [17] a $2_1$ *helix* for sPS [18,19] (Figure 7). The pitch of the $2_1$ helix of sPS is larger than that of the $3_1$ helix of iPS (0.77 nm against 0.66 nm). As a result, *trans*-decalin molecules are less fitted for stabilizing the $2_1$ helix of sPS, in the sense that their size is slightly smaller that the cavity created by the protruding phenyl groups, hence failure to form a gel.

So far the gelation mechanism of *organogels* is not fully elucidated. What is clearly needed is promoting a one-dimensional growth process so as to obtain fibrils instead of three-dimensional crystals. As with polymers, the question is why are spherulites formed in some cases, and fibrils in other cases? Does this arise from constraints on the lateral crystal growth which then favors 1-D organization? Also, are the fibrils growing at their tips, or do 1-D filaments form first and then aggregate sideways? The second situation would be reminiscent of polymer

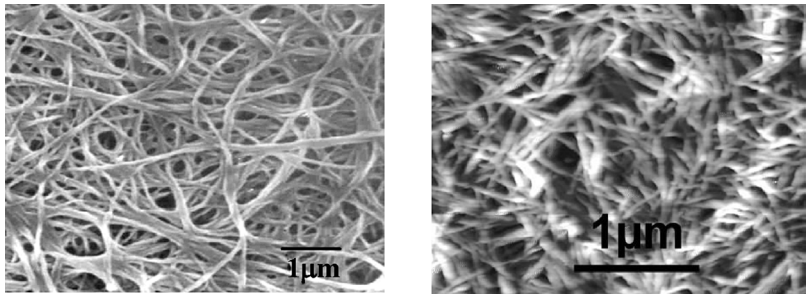


***Figure 8.***
Electron micrograph of an oligo(*p*-phenylenevinylene) organogel [Courtesy of Pr. Ajayaghosh, see ref. 8] (*left*) and AFM picture of a syndiotactic poly[styrene] gel [21] (*right*). The sPS gel has been prepared with a solid solvent at room temperature, namely naphthalene.

 

gelation as described above. The occurrence of 1-D filaments has already been reported for self-assembling molecules [20], although the growth of fibrils was not observed.

### The Morphology

As can be seen throughout the present *Macromolecular Symposia* volume the morphologies revealed by various type of experiments (transmission electron microscopy on freeze-fractured systems, scanning electron microscopy, AFM..) are all of the microfibrillar type. As is highlighted in Figure 8, morphologies are undistinguishable although the starting materials are very different.

Note that gel morphology can also be obtained from solvents that are solid at room temperature. As is purposefully shown in Figure 8, this is the case with sPS/naphthalene systems, but also with sPS/biphenyl and the like. This has some advantages, one being the possibility of extracting the solvent out of the network at room temperature by sublimation. The latter process is often more efficient than evaporation of liquid solvents, and has less effect on the original gel morphology.

### Concluding Remarks

Polymer thermoreversible gels and organogels, although made up with differing building bricks, turn out to be very similar as far as morphology and rheological properties are concerned. This suggests that hybrid materials can certainly be prepared such as interpenetrated networks of *polymer thermoreversible gels* and *organogels*. One could then play with the different melting points of either gel. For instance, in the case of $\pi$-conjugated systems, described by Ajayaghosh and coworkers in this volume, the colour of which depends on whether they are gelled or not, one should be able to control the colour while still having a solid gel by simply choosing a polymer thermoreversible gel of higher melting temperature. Making these hybrid materials is feasible because at high temperature, the polymer and the organomolecules are compatible has as been shown recently [22,23]. This allows one to make a homogeneous solution of the two components at high temperature, and then by toying with temperature and cooling procedures to control the growth of either component.

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