On the definition of thermoreversible gels: the case of syndiotactic polystyrene

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We consider the four criteria recently proposed by one of us (JMG) for defining a thermoreversible gel and use them with syndiotactic polystyrene/solvent systems. We show that some of these systems, considered to be gels, do not obey these criteria. In addition, a simple mechanical test is presented which allows a thermoreversible gel to be recognized.

(Keywords: thermoreversible gel; syndiotactic polystyrene; elastic response)

Introduction

Gels constitute a vast class of materials which can be subdivided into two categories: chemical gels and physical gels, the latter being also referred to as thermoreversible gels. Gels are networks of connected objects, the connectedness being achieved by covalent bonds for the former, and less energetic but co-operative bonds for the latter (the energy being of the order of $\sim kT$).

The process to obtain thermoreversible gels simply consists of cooling a mixture of miscible components, one of which (component A, say) will undergo a liquid–solid transition below a so-called gelation threshold while component B will remain liquid. Component A will therefore create a framework wherein component B will be confined[1]. In many cases, component A is a polymer or a biopolymer but it can also be a small molecule with a propensity to stack in one dimension, such as dibenzyl sorbitol, thus promoting the formation of a network[2].

Regrettably, the term thermoreversible gel is often loosely employed to designate various systems that apparently possess solid-like properties, namely systems that no longer flow. The test-tube tilting method is one of the popular tests used to claim that a gel has been formed[3,4]. If flow no longer occurs, then the system will be regarded as a gel. Although this test has been severely criticized from a rheological viewpoint[5] it is still used. Consequently, systems are often improperly regarded as gels and their mechanism of formation is added to the growing list of gelation mechanisms, which gives an unnecessarily confused picture of the phenomenon of physical gelation.

The purpose of this communication is to apply the set of criteria recently proposed by one of us[1] for defining the physical gel state to the case of syndiotactic polystyrene (sPS), for which a wide range of sPS/solvent systems are considered as gels on the only basis of the tube tilting method[6]. We shall also describe a simple mechanical test for evaluating the degree of elastic reponse of such systems.

Definition

The simplest definition of a gel which is supposed to behave as a solid is the existence of an elastic modulus at zero frequency (or infinite time). In other words, over a long period of time the system should show a constant stress at constant deformation or maintain a constant deformation at constant stress. These simple mechanical tests can be conducted without any great difficulty. Unfortunately, this definition seldom applies to thermoreversible gels since these systems often undergo a certain degree of permanent deformation[7]. One of the main reasons for this is that the physical bonds are sometimes sufficiently weak to be mobile and thus be destroyed under stress. To overcome the difficulty of defining a gel through a mechanical approach, Guenet recently proposed the use of four criteria[1]. Of the four criteria, the first two should be fulfilled unreservedly.

The first criterion deals with the gel structure. A gel is primarily a network which is defined as a large system of lines, tubes, wires, etc., that cross one another or are connected with one another (taken from ref. 8). This definition implicitly entails that the connecting objects possess cylindrical symmetry. In other words, the gel mesh size must be far larger than the cross-section of the connecting objects. Obviously, the criterion requires determining the gel structure which is often a less straightforward operation than the mechanical measurements.

The second criterion relates to the order of the phase transition taking place either on gel formation or on gel melting. The phase transition responsible for the creation of the gel junction must be first order. This ensures that co-operative bonds, and correspondingly organized junctions, are formed during the gelation process.

The third and fourth criteria are, respectively, not to disaggregate when immersed in an excess of preparation solvent and to be handled without irreversible damage being inflicted upon the gel. It is worth noting that these

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two criteria may not necessarily hold near the gelation threshold (critical gelation temperature or critical gelation concentration).

These four criteria define a class of materials which does not inevitably encompass what other authors would regard as thermoreversible gels. However, these criteria provide a clearer framework, which is a prerequisite for identifying common formation mechanisms and general properties.

In this communication, we shall review three systems that pass the test-tube tilting method: sPS/benzene, sPS/toluene and sPS/*trans*-decalin. By applying the above criteria, we shall find out whether these systems should be regarded as gels or not. We will further illustrate their differences by means of a simple mechanical test for which additional comparison will be made with isotactic polystyrene (iPS)/*cis*-decalin gels.

Experimental

The syndiotactic sample used in this study was synthesized by the method of Zambelli *et al.*[9]. Here, a deuterated sample was used on the grounds of its availability. The isotactic sample was synthesized by the method of Natta[10] and purified in the usual way[11]. Solvents were purchased from Aldrich and used without further purification.

Gels were prepared in hermetically closed test-tubes by heating near the boiling point of *trans*-decalin, and well above the boiling point of benzene and toluene. For mechanical testing, cylinder-shaped pieces of gel were cut off with a device designed to obtain samples with faces as parallel as possible (diameter = 1 cm; initial height, $h_0 = 1$ cm). These samples were submitted to mechanical testing by means of a compressive device described elsewhere[12]. For sPS/toluene systems a toluene-saturated environment was set up to prevent solvent evaporation.

The samples used for optical observation were prepared by two different methods: gels were first formed in a test-tube, then placed between glass slides, made molten again and quenched rapidly to minimize evaporation; or samples were directly prepared from a very thin piece of polymer molten between two glass slides into which solvent was allowed to diffuse at room temperature. The micrographs were then taken at the polymer–solvent interface, where the gel formed. Optical investigations were carried out with a Nikon Optiphot-2.

Electron micrographs were taken of aggregates formed in an sPS/benzene system at low concentration (0.1%). A drop of this solution was deposited onto a copper grid, subsequently dried and finally shadowed and coated as usual.

D.s.c. measurements were performed with a Mettler DSC30 apparatus on gels prepared in a test-tube beforehand, and then transferred rapidly into 'volatile' sample pans.

Results and discussion

All three systems give rise to formation exotherms as observed on rapidly cooling a homogeneous solution, and melting endotherms when heated up again (*Figure 1*). As latent heat is absorbed or released, these transitions are first order[6,13]. Therefore, all three systems fulfil the second criterion.

Conversely, only sPS/benzene and sPS/toluene systems display a network morphology while the sPS/*trans*-decalin system exhibits a spherulitic morphology over a wide range of concentration and temperature (*Figures 2a–d*). Accordingly, sPS/*trans*-decalin systems should not be regarded as gels with respect to the first criterion.

It is worth noting that gels in benzene and toluene are obtained for very low polymer concentrations [typically between 0.1% and 1% (w/w)] whereas at these concentrations sPS/*trans*-decalin systems give rise to two macroscopic phases: a polymer-poor phase and a polymer-rich phase, the latter again containing spherulites. As sPS/benzene and sPS/toluene gels are made up of a fibre-like structure, it is no wonder that they can be produced at low concentration since the overlap concentration for fibres is far lower than that for spheres. Also, sPS/benzene and sPS/toluene gels are translucent while sPS/decalin systems are turbid.

The differences between sPS/toluene gels and sPS/*trans*-decalin can be illustrated by means of a simple mechanical test. The idea is that, despite the absence of an elastic modulus at zero frequency, thermoreversible gels are liable to display some elastic behaviour unlike the sPS/*trans*-decalin system which is just a packing of spheres with minimum cohesion. The experiment consists of applying a compressive deformation λ_1 ($\lambda = h/h_0$, height after deformation over initial height), allowing the system to relax for a certain time t_1, and then quickly altering the deformation to λ_2 by raising the piston of the compression device (obviously $\lambda_2 > \lambda_1$). This immediately results in a sudden drop in stress to zero. Now, if the system still possesses elasticity, then it will tend to partially or totally regain its initial height, hence the reappearance of a stress, the magnitude of which depends upon the remaining amount of reversible deformation. Alternatively, if the system has undergone permanent, irreversible deformation, then the stress should remain at zero. Such a mechanical test is shown in *Figure 3* ($\lambda_1 = 0.85$ for $t_1 = 60$ min followed by $\lambda_2 = 0.9$). Stress gradually reappears for the sPS/toluene and iPS/*cis*-decalin gels, while stress remains at zero for the sPS/*trans*-decalin system.

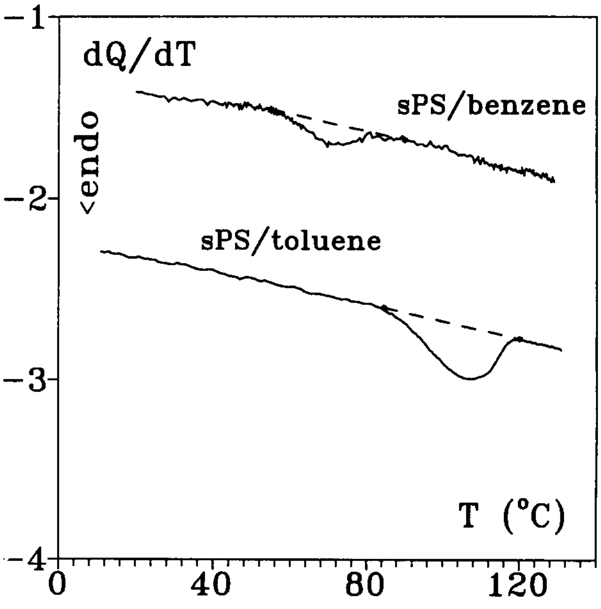

Figure 1 Melting endotherms of 10% (w/w) sPS/solvent systems (heating rate 5°C min^{-1})

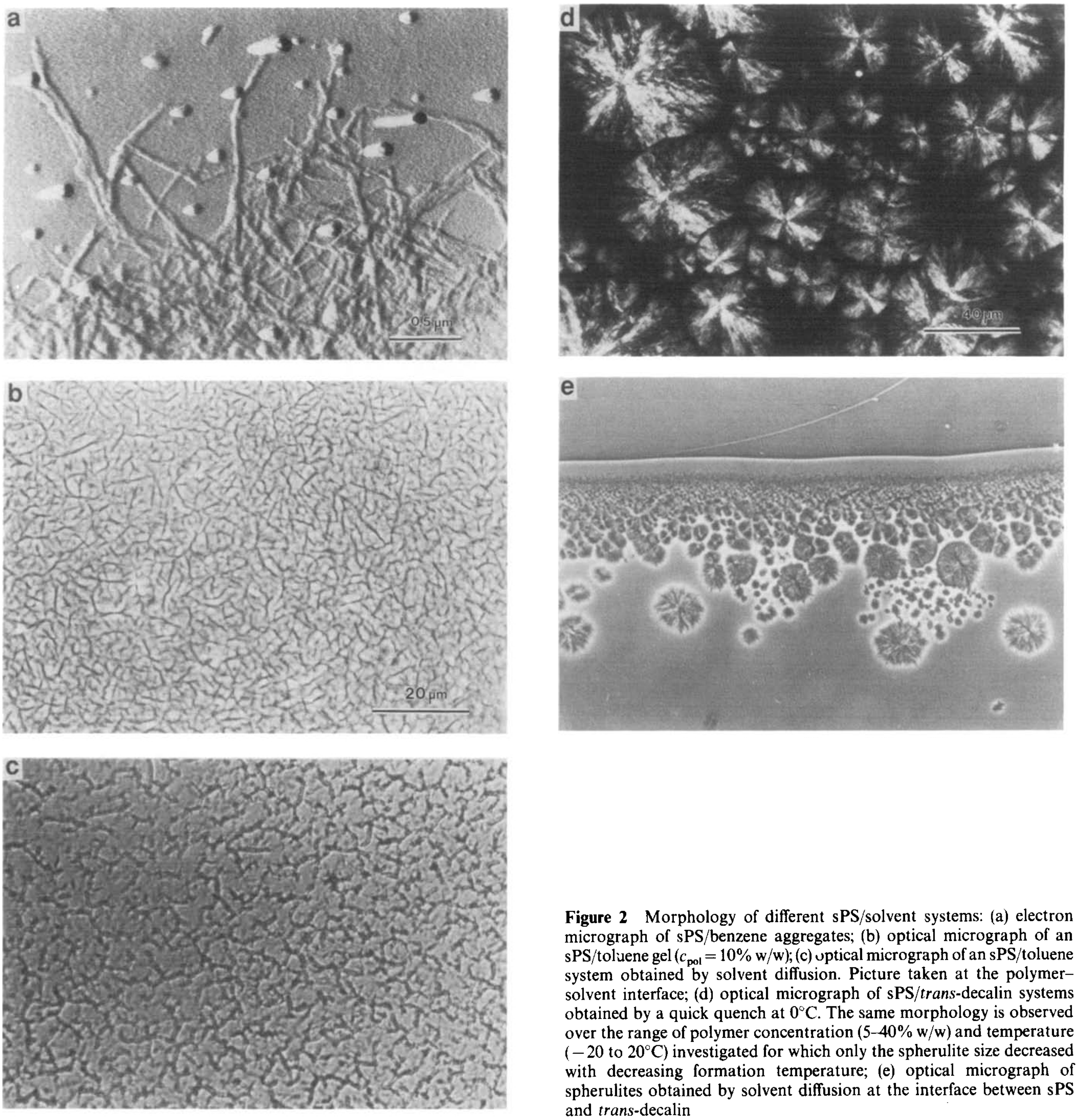

Figure 2 Morphology of different sPS/solvent systems: (a) electron micrograph of sPS/benzene aggregates; (b) optical micrograph of an sPS/toluene gel ($c_{pol} = 10\%$ w/w); (c) optical micrograph of an sPS/toluene system obtained by solvent diffusion. Picture taken at the polymer–solvent interface; (d) optical micrograph of sPS/*trans*-decalin systems obtained by a quick quench at 0°C. The same morphology is observed over the range of polymer concentration (5–40% w/w) and temperature (−20 to 20°C) investigated for which only the spherulite size decreased with decreasing formation temperature; (e) optical micrograph of spherulites obtained by solvent diffusion at the interface between sPS and *trans*-decalin

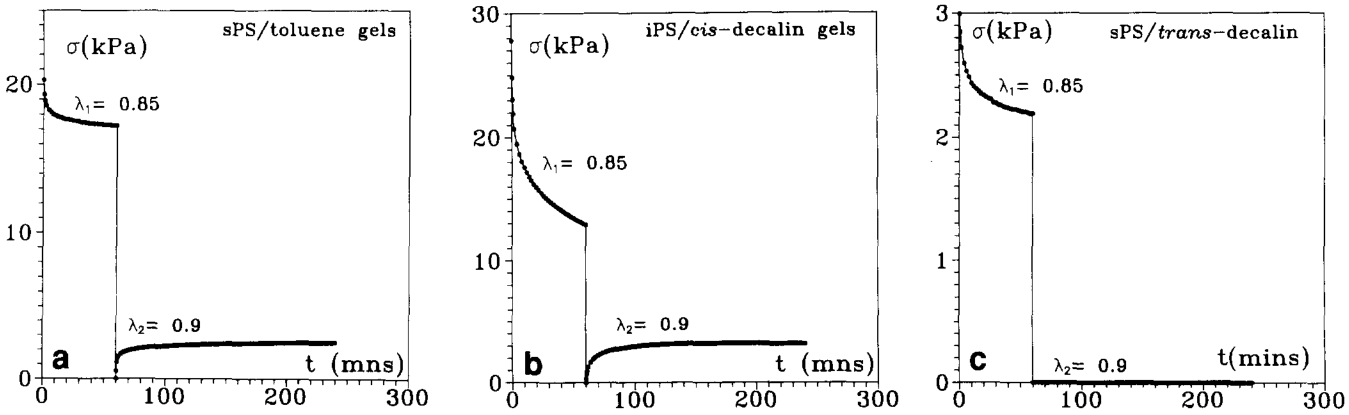

Figure 3 Relaxation curves obtained by first applying a deformation $\lambda_1 = 0.85$ for 60 min then raising the piston to $\lambda_2 = 0.9$ and allowing for a further relaxation of 180 min. The stress (in kPa) is calculated from $\sigma = F/[A_0(\lambda - \lambda^{-2})]$, where F is the measured force and A_0 is the area of the initial sample. In all cases $c_{pol} = 10\%$ (w/w). (a) sPS/toluene gels; (b) iPS/*cis*-decalin; (c) sPS/*trans*-decalin

Concluding remarks

To summarize, only sPS/benzene and sPS/toluene systems can be safely considered as thermoreversible gels while the sPS/*trans*-decalin system should not be considered as such according to Guenet's criteria. Furthermore, a simple mechanical test highlights the difference between thermoreversible gels so defined and other systems.

Manifestly, the characteristic shared by thermoreversible gels is the existence of fibre-like structures[1]. Fibre-like structures seem to imply the absence of chain folding[14]. It remains therefore to elucidate the mechanisms responsible for impeding chain folding and which, accordingly, promote gel formation.

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