Nanostructured polymers with embedded self-assembled reactive gel networks†

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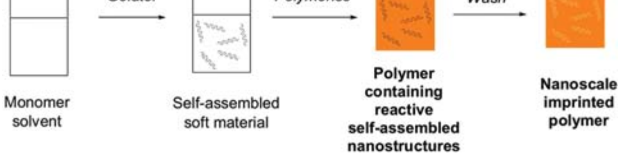
Generating polymers in the presence of a self-assembling gelator with terminal double bonds yields polymeric materials with embedded reactive nano-skeletons—subsequent washing gives nanoscale imprinted materials with fibrillar architectures.

It seems increasingly likely that nanochemistry will underpin manufacturing methods of the 21st century, with the self-assembly of molecular-scale building blocks providing a simple method of generating nanoscale objects.[1] Gel-phase soft materials assembled from low molecular weight building blocks provide an excellent example of the bottom-up assembly of nanomaterials.[2] However, these materials are generally relatively weak in terms of their macroscopic rheological properties, being held together by non-covalent interactions. A number of attempts have been made to 'capture' self-assembled nanostructures. Gel-phase organic nanostructures have been transcribed into inorganic materials such as silica,[3] cadmium sulfide[4] and zinc oxide.[5] Polymerisable groups have been incorporated into gelators, and the gel fibres polymerised.[6] Alternatively monomeric solvents which can subsequently be polymerised (*e.g.* styrene or methyl methacrylate) have also been gelated, with polymerisation capturing an embedded nanoscale gel-phase network (Scheme 1).[7] Stupp and co-workers reported changes in the materials properties of nanostructured polymers.[8] An alternative approach to gelator-modified polymers assembles gel fibres within a pre-formed polymer.[9] Embedded self-assembled structures can subsequently be 'washed out' to yield nano-imprints,[7] a general approach with great untapped potential.

In this communication, we introduce the concept of incorporating reactive nanoscale self-assemblies within polymeric materials. Gelator **1**, assembles nanoscale morphologies with reactive peripheral alkene groups. Preliminary mechanical testing proves the embedded nano-scaffold has a profound effect on materials' behaviour. The embedded network can be washed out to yield 'nano-imprinted' materials.



Scheme 1 Use of self-assembling low molecular weight gelators to nanofabricate polymers.

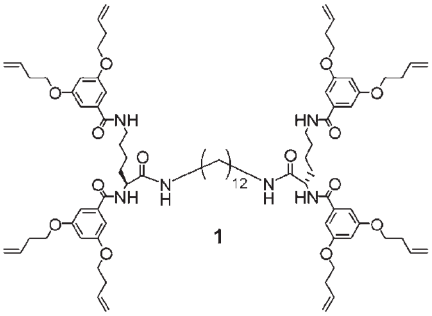


Fig. 1 Gelator **1**.

Gelator **1** (Fig. 1) was synthesised using a combination of our lysine based methodology[10] and chemistry developed by Wendland and Zimmerman[11] (see ESI†). This gelator should give rise to reactive alkene-functionalised gel fibres within the nanostructured polymer. Compound **1** was demonstrated to form effective gels in styrene–divinylbenzene (DVB) (9 : 1) using a simple tube inversion methodology.[12] Using this approach, it was possible to assess the thermal stability of the gel. Fig. 2 illustrates the effect of concentration on the gel–sol phase boundary. At low concentrations, relatively poor gels were formed, but above 20 mM gelation was more effective.

In order to assess the nanostructure of the self-assembled gel, a sample was allowed to dry, and was imaged using field emission gun scanning electron microscopy (FEGSEM). As

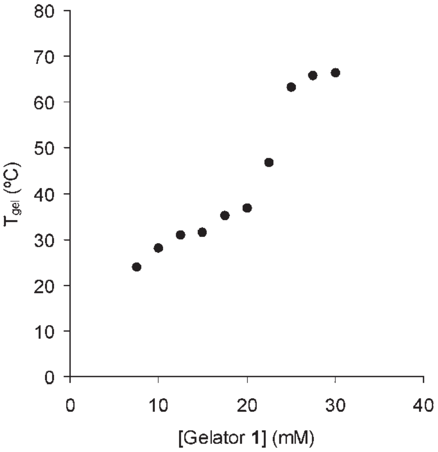


Fig. 2 Thermal stability of gelator **1** in styrene–divinylbenzene (9 : 1).

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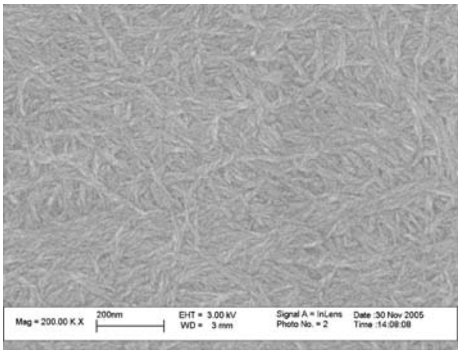

Fig. 3 FEGSEM image of gelator **1** (scale bar = 200 nm). Gel formed in styrene–DVB (9 : 1) at a concentration of 20 mM, and then allowed to dry under ambient conditions.

Fig. 4 TEM image of cross section of the poly(styrene–DVB) wafer created in the presence of gelator **1** (20 mM). Reactive staining agent: OsO_4. Scale bar: 200 nm.

expected, the gel had a fibrillar morphology (Fig. 3)—indeed fibres with very small diameters (< 10 nm) were observed.

Polymerisation of the styrene–DVB solvent in this gel was then achieved using UV initiation, at wavelengths > 300 nm, with 4,4′-bis (dimethylamino)benzophenone as sensitizer. It should be noted that it was possible that the double bonds in gelator **1** could also have reacted/polymerised under these conditions, however, this was not the case (evidence below). The polymerisation was performed in a flat glass mould under nitrogen to produce polymer wafers with dimensions of *ca.* 5 cm × 5 cm × 200 μm. The mould was water-cooled in order to prevent UV-induced heating effects from destroying the self-assembled gel-phase network during polymerisation. In the absence of gelator, the polymerisation of styrene–DVB (9 : 1) yielded a polymer standard—a homogeneous material which gave featureless electron microscopy images.

Variable depth infrared spectroscopy studies on the polymer wafer formed in the presence of gelator **1** indicated that the gelator was distributed evenly through the polymer, with bands associated with the gelator (*e.g.* N–H, C=O *etc.*) being observed throughout the material (data not shown). By FEGSEM imaging, however, the polymer wafer appeared to be relatively featureless and homogeneous—fibrillar assemblies were not observed. We therefore used transmission electron microscopy (TEM) in an attempt to image the nanoscale fibres. We employed a reactive stain (OsO_4), which should selectively react with the alkene groups on the self-assembled gelator (assuming that the double bonds in gelator **1** remained unreacted). Fig. 4 shows the imaging of the nanoscale fibres embedded within the polystyrene–DVB sample. Extended fibres can be observed, whilst the dark spots probably represent fibres viewed in cross-section after fracturing the polymer. This image is perhaps the clearest visualisation of self-assembled nanofibres embedded within a polymer and demonstrates that many of the alkene groups on gelator **1** maintain their reactivity.

We then performed preliminary dynamic mechanical thermal analysis (DMTA) on the standard polymer (Fig. 5 left), and the polymer formed in the presence of gelator **1** (Fig. 5 right). In the presence of the fibrillar network, the T_g value (glass transition temperature) of the polymer increased from *ca.* 80 °C to 100 °C. Furthermore, the degree of damping at the T_g value, as given by tan δ, decreased from 0.285 to 0.235. The storage modulus (G') of the standard polymer at 20 °C was 4.0×10^9 Pa, whilst in the presence of embedded gelator **1**, G' increased by almost an order of magnitude to 1.95×10^{10} Pa. Therefore, only 3% wt/vol of gelator induced significant modification of the materials behaviour. We propose this is a consequence of the presence of the embedded nanostructured network, which can dissipate the stress exerted on the polymer. This is in analogy with the effects of other polymer additives used for toughening, such as rubber particles used in

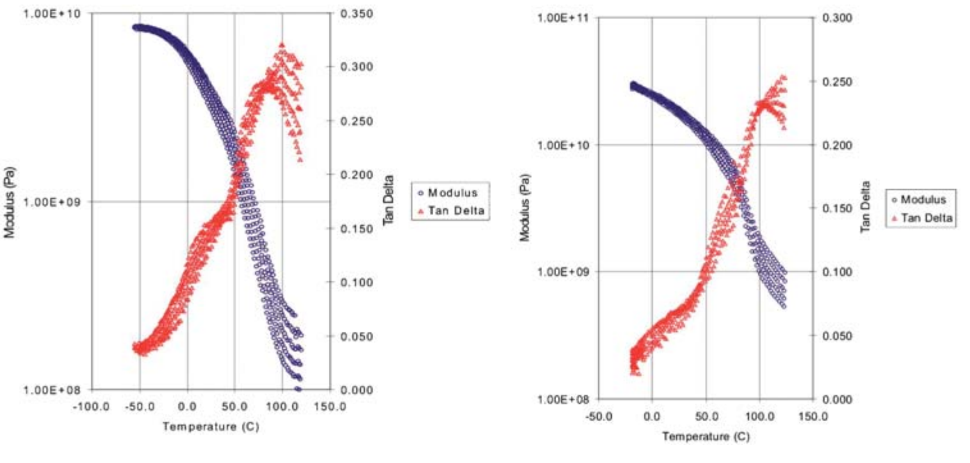

Fig. 5 DMTA data for (left) standard polymer, (right) polymer formed in the presence of gelator **1** (20 mM). Modulus is the storage modulus, G'.

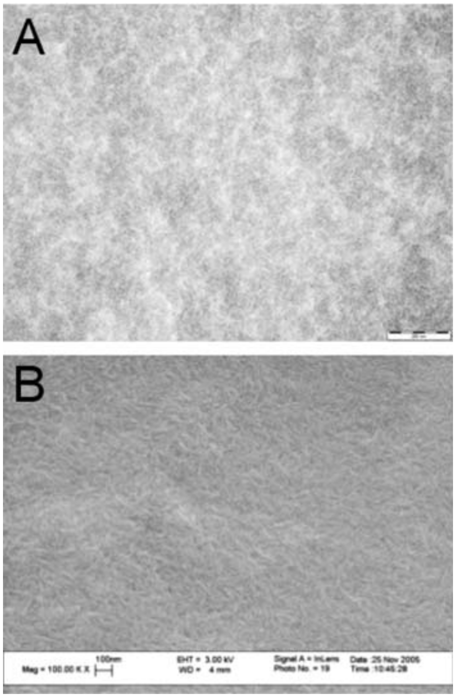

Fig. 6 (A) TEM image of cross section of the poly(styrene–DVB) wafer created in the presence of gelator **1** (20 mM) after washing with MeOH–THF. Reactive staining agent: OsO_4. Scale bar: 200 nm. (B) FEGSEM image of cross section of the same wafer—showing fibrillar nano-imprinting (scale bar = 20 nm).

high impact polystyrene (HIPS).[13] It is noteworthy that only a small amount of additive causes significant changes in the materials behaviour. Furthermore, the nanoscale nature of the additive means that it does not modify the optical properties of the material (*i.e.*, our polymer wafers with embedded nanostructures are transparent).

Finally, we washed the nanostructured polymer with MeOH–THF. This mixture was chosen because gelator **1** has a high solubility in MeOH, whilst THF provides good compatibility with the polymer film. Washing removed the majority of the gelator from the polymer, as shown by the loss of nitrogen in the elemental analysis data (see ESI†). Once again, the fact the gelator can be washed from the polymer wafer proves that the majority of double bonds on the periphery of gelator **1** had not reacted during the polymerisation of styrene–DVB. TEM imaging of the washed polymer using reactive OsO_4 stain supported this proposal, as fibrillar staining was no longer observed (Fig. 6A). Furthermore, mass spectrometric data (not shown) indicated that the gelator was washed out in monomeric form. This lack of double bond reactivity under polymerisation conditions can be rationalised, as the double bonds on gelator **1** provide much less stable sites for radical propagation than those in styrene–DVB. Interestingly, the washed material maintains its nanoscale ordering which after washing could be imaged by FEGSEM (Fig. 6B), with the polymer containing 'washed out' (imprinted) nano-fibrillar architectures.

In summary, this communication reports a gelator incorporated into nanostructured polymers, with the resultant materials having significantly modified materials behaviour. Simple solvent treatment yields 'washed-out' nanoimprints. Importantly, the gelator has been endowed with reactive double bonds, the reactivity of the assembled nanostructures has been demonstrated using OsO_4 as reagent and TEM for imaging. This approach holds out the prospect of using self-assembly to fabricate functional materials with embedded reactive nano-scaffolding, an approach which could give rise to a new generation of advanced functional materials.

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