Abstract: A method of forming a polymeric composition comprising the steps of: contacting a monomeric mixture with a gelator to form a mixture; allowing the gelator to self-assemble within the monomeric mixture to realise the gelating properties of the gelator; and initiating polymerisation of the mixture to form a polymeric composition having a network of gelators embedded therein; wherein the gelator comprises gelator components comprising two head groups linked by a spacer molecule, wherein the head groups compromise a multiplicity of hydrogen-bondable species to provide a multiplicity of hydrogen bonding interactions, and/or the head groups are selected so as to provide stabilising interactions such as pi-stacking. A polymeric composition comprising a network of gelator embedded therein is also provided.
The present invention relates to new polymeric compositions having a network of supramolecular fibres or structures embedded therein. There is also provided a method of forming said polymeric compositions.

It seems increasingly likely that nanochemistry will underpin the dominant manufacturing methods of the 21st century. As defined by the National nanotechnology Initiative in the USA, this area of technology focuses on:

(a) length scales of 1-100 nm,
(b) novel properties and functions of such materials,
(c) the ability to control and manipulate matter on the atomic scale.

The self-assembly of molecular-scale building blocks provides a simples method of generating nanoscale object, with synthetic methods being used to programme the molecules with the necessary information on the atomic scale so they can self-assemble in a controlled manner.

Gel-phase soft materials assembled from low-molecular-weight building blocks have been of particular recent interest [4]. However, these materials are inherently, relatively weak in terms of their macroscopic rheological properties, as they are only held together by non-covalent interactions. A number of attempts have therefore been made to 'capture' the self-assembled nanostructures. For example, gel-phase organic nanostructures have been transcribed into the growth of inorganic materials such as silica, [5] cadmium sulfide [6] or zinc oxide [7]. Alternatively, the groups of Weiss, [8] Kim [9] and Smith [10] have incorporated polymerisable groups into the organic gelators themselves,
and consequently enabled the subsequent polymerisation of gel fibres and their effective covalent capture to yield robust materials.

In several key studies, Stupp and co-workers have used their dendron-rod-coil (DRC) molecules to gelate solvents capable of being polymerised (e.g. styrene) [11]. Subsequent polymerisation of the bulk solvent medium gave rise to polymeric materials in which it was proposed that the nanoscale gel-phase network was embedded. Some modifications in the materials properties of polystyrene formed in this manner were reported.

According to a first aspect of the present invention there is provided a method of forming a polymeric composition comprising the steps of:

- contacting a monomeric mixture with a gelator to form a mixture;
- allowing the gelator to self-assemble within the monomeric mixture to realise the gelating properties of the gelator;
- initiating polymerisation of the mixture to form a polymeric composition having a network of gelator embedded therein;
- wherein the gelator comprises gelator components comprising two head groups linked by a spacer molecule, wherein the head groups compromise a multiplicity of hydrogen-bondable species to provide a multiplicity of hydrogen bonding interactions, and/or the head groups are selected so as to provide stabilising interactions such as pi-stacking.

The method may include the optional step of:

- washing the polymerised material to remove the gelator and thereby generate a polymeric composition comprising nanostructured cavities.
The hydrogen bondable species may suitably comprise oxygen, nitrogen or fluorine. The term "hydrogen-bondable species" relates to a moiety which is capable of entering a hydrogen bonding interaction. Typically such a moiety will comprise at least one comparatively electronegative atom, for example those preferable atoms listed above.

Suitably the two head groups of the gelator component have the same structure. Alternatively the two head groups may have a different structure. The head groups of the gelator component comprise a branched carbon backbone which may or may not be dendritic. The term "dendritic" is used herein to mean a hyper-branched group. Dendritic groups may also comprise an average of at least one polymerisable site, such as double bond, per molecule. Suitably the head groups comprise at least three polymerisable sites per molecule, typically at least five polymerisable sites per molecule. Advantageously both of the head groups are dendritic.

The carbon backbone of the head groups may be saturated or unsaturated. The head groups may comprise one or more unsaturated groups at their periphery.

The carbon backbone of the head groups may be substituted or unsubstituted. More suitably the carbon backbone of each head group is substituted with more than one hydrogen bonding or pi-stacking group. Suitably the carbon backbone is substituted with more than one hydrogen bondable electronegative atoms; in particular oxygen, nitrogen or fluorine atoms. Suitably the branched carbon backbone is substituted with one or more amine, amide, carbamate, urea, thiourea, aryl, ether and/or ester group. Additionally, or alternatively, the carbon
backbone of the head groups may be substituted with one or more aromatic compounds.

The head groups may incorporate chiral centres. Most suitably the gelator components used in the method are in homochiral form, although in certain preferred embodiments racemates may be used.

According to one embodiment the head groups are hydrogen bonding head groups. Suitably the hydrogen bonding head groups comprise one or more functional groups such as amides or carbamates. These head groups are typically based on the structure of lysine.

Typically each head group comprises at least five hydrogen-bondable species; suitably at least seven; more suitably at least ten hydrogen-bondable species. Typically one or both head groups comprise peptides; generally one or both head groups consist of peptides. In one embodiment both head groups consist of peptides.

The spacer molecule linking the two head groups may be alkyl or aromatic, most suitably alkyl. Advantageously the spacer molecule is alkyl. Suitably the spacer molecule has a carbon backbone of 6 to 25 carbon atoms, more suitably 9 to 15 carbon atoms, advantageously 12 carbon atoms. The spacer molecule may be substituted or unsubstituted. The spacer molecule is suitably substituted providing the gel structure is not disrupted. The spacer molecule may be substituted with one or more hydrocarbon groups, (particularly alkyl or aryl groups having 1 to 25 carbon atoms), halogen, ether, amine, aldehyde, ketone, ester or amide groups.
Suitably the spacer molecule is a diamine alkyl spacer molecule. In one embodiment the diamine alkyl spacer molecule comprises an amine group at both ends of the carbon backbone.

The head groups may be linked to the spacer molecule through covalent or non-covalent interactions.

A schematic structure of a typical gelator component is shown in Figure 9.

The gelator components of the present invention provide several significant advantages over the dendron-rod-coil (DRC) molecules disclosed by Stupp and his co-workers [11]. The gelator components of the present invention are constructed primarily from amino acid building blocks and accordingly have a high associated bio-compatibility. They are also compatible with the monomeric mixture typically resulting in a substantially even dispersion of the gelator components throughout the polymeric composition. The effects of the gelator network are thus substantially consistent throughout the polymeric composition of the present invention.

The gelator components of the present invention are generally smaller than the DRC molecules of Stupp meaning they can be washed out more easily from the polymeric composition formed. It is likely that the polymeric composition of Stupp would have to be damaged to remove the DRC molecules disclosed therein. Furthermore the relatively small gelator components of the present invention may be broken down more easily.

The gelators of the present invention have a different associated thermal transition from gel to liquid compared to the DRC molecules of Stupp.

Importantly, the thermal transition from gel to sol can easily and simply be
changed by modifying the structure of the gelator component - giving easy
tunability of the thermal behaviour of the materials. It also provides a
simple method for introducing added functionality to the materials
generated in this way.

Additionally, the gelators of the present invention are generally easier to
synthesize than the DRC molecules of Stupp.

In one embodiment the gelator component has one of the following
structures:

1. 
2. 
3. 
4. 
5. 

\( R = \text{(e.g.) (CH}_2)_n-\text{CH}=-\text{CH}_2 \)
The R group of structure 5 is suitably a hydrocarbon group, typically a hydrocarbon group comprising 1 to 25 carbon atoms; more suitably 8 to 12 carbon atoms. In one embodiment the R group has the structure (CH2)8CH=CH2.

It has been found that where the head groups are associated with the spacer group through acid/base interaction only, the gelator may be unable to maintain its gelled structure throughout the polymerisation process. In this case, the head groups can detach from the spacer molecule and partially phase separate. However, when the head groups are attached to the spacer molecule through covalent bonds, the structure of the gelator is maintained. Accordingly, the head groups of the gelator components are advantageously attached to the spacer molecule through covalent bonds.

The gelator components for use in the present invention suitably have a relatively low molecular weight. The molecular weight of the gelators may be 400 to 5000 amu.

The monomeric mixture of the method of the present invention may comprise one or more different monomeric compounds. Any monomeric compound which may undergo free-radical polymerisation is suitable for use in the monomeric mixture. Suitability is determined by the ability to solvate the gelator and then allow the self-assembly of the gelator to occur. Consequently not all monomers are suitable with all gelators. It is necessary that the gelator system is soluble in the uncured monomeric mixture and exhibits a convenient gel temperature. An example of this is provided in Example 1, where the monomeric mixture employed is a mixture of styrene and divinylbenzene. Suitably the monomeric mixture comprises one or more of styrene and divinylbenzene (DVB).
embodiment the monomeric mixture may comprise styrene and DVB, suitably in the ratio of approximately 90:10.

In general the monomers act as solvents, dissolving the gelator at elevated temperature and on cooling, the gelator molecules assemble into nano- or micro-scale aggregates in the form of a gel. The properties of the mixture may be modified to modify the properties of the gel and/or the resulting polymeric composition formed. Typically the properties of the composition may be altered in a controllable and predictable manner by altering the properties of the mixture.

A number of monomer species may be used, singly or in combination, as the host system (i.e. monomeric mixture) provided that gelator employed can be dissolved within this host system then undergo a transition into the self-assembled state. The host system may be compatible with addition polymerisation or copolymerisation; suitable reactive functionality includes acrylates, methacrylates, styrenics, maleimides, and vinylics where the gelator employed can be dissolved within this host system then undergo a transition into the self-assembled state. Alternatively, host condensation polymerisable species may be found which allow the gelator to self-assemble; potentially suitable chemistries include epoxide-hardener systems, phenolic systems, cyanate esters, precursors for formation of polyesters, polyanhydrides, polyacetals, polyamides, polyurethanes or polyureas.

Prior to initiation of polymerisation the rheology of the monomeric mixture is suitably modified through addition of the gelator; generally the viscosity of the monomeric mixture is substantially increased. The benefit here is that the viscosity of the monomeric mixture is only increased when the temperature is below the gel temperature. After initiation of polymerisation
the properties of the polymeric composition formed are generally modified compared to the properties of a polymeric composition which has not been benefited from the addition of the gelator. Typically one or more of the thermomechanical, optical, mechanical and electrical properties are altered. The thermomechanical properties of the polymeric composition are suitably altered according to the gel phase transition temperature. The opacity of the polymeric composition may be modified; generally the opacity is increased. Electrical properties, such as the dielectric constant of the polymeric composition may also be modified through the method of the present invention. Typically the permeability of the polymeric composition is also increased.

In one embodiment mechanical properties such as modulus, toughness and elongation to break may be favourably modified.

Suitably the morphology of the polymeric compositions of the present invention differs from the morphology of known polymeric compositions, for instance, the polymeric composition of the present invention may display a structured multi-phase morphology.

The morphology of the polymeric composition may be altered by modifying the structure of the gelator. Examples of morphologies which would be formed in this way include fibres, ribbons, plates, bundles, platelets, worm-like micelles or other micro or nano-scale networks.

Suitably up to 10% wt/vol gelator is added to the monomer mixture; more suitably 0.5-2% wt/vol.
Polymerisation of the monomeric mixture may be initiated through the addition of any suitable initiator compound such as, but not limited to, classic peroxides well known for use as initiators or redox compounds.

The mixture may also comprise a sensitizer such as 4,4'-bis(dimethylamino)benzophene. Alternatively, or additionally, the mixture may also include an initiator such as 4,4'-bis(dimethylamino)benzophene.

Suitably the monomeric mixture is subjected to thermal, photochemical and/or chemical stimuli to initiate polymerisation. In particular polymerisation may be initiated by subjecting the monomeric mixture to UV-visible radiation. If required the polymerisation reaction may take place under an inert atmosphere, such as a nitrogen atmosphere.

The method may include the step of cooling the mixture during polymerisation, in particular the mixture may be cooled to prevent heating effects from damaging or destroying the gelator network during polymerisation. Suitably the mixture is cooled by water flow to maintain the temperature, particularly in the initial stage of the curing process.

In one embodiment the polymeric composition formed according to the method of the present invention comprises a network of gelator components embedded therein. In general the gelator components are not polymerised during the polymerisation reaction. Suitably the structure of the gelator components does not alter during the polymerisation reaction and the gelators embedded in the polymeric composition have the same structure as the gelator components contacted with the monomeric mixture.
In a second embodiment the gelator components may have functional
groups and the gelator may react with the monomeric mixture during the
polymerisation reaction. Typically, the gelator may react with the
monomeric mixture to produce fibrils that are covalently bonded to the
polymeric composition formed during polymerisation of the monomeric
mixture.

The method of the present invention may include the step of washing the
polymeric composition to remove the embedded network of gelator. A
polymeric composition comprising nanostructured cavities is suitably
formed following the washing step. The nanostructured cavities are
suitably in the form of a series of channels imprinted in the polymeric
composition corresponding to where the embedded network of gelator had
been. Suitably the polymeric composition is washed with a solvent such
as methanol to generate a micro- or nano-channelled networked structure.

This networked structure may be applied as a host to provide a template
for infilling with additional moieties to provide new functionality such as
electrical conductivity, ion permeability and encapsulation and release or
optical and colouration effects. For use in such applications as electronic
materials, including batteries and transparent conductors or biomechanical
applications such as diagnostics and controlled release.

The structure of the gelator removed through the washing step is typically
the same as the structure of the gelator contacted with the monomeric
mixture indicating that the structure of the gelators may be maintained
throughout the polymerisation process. This structure may or may not be
chiral.
Where the gelator component comprises functional groups, the functional groups typically remain attached to the gelator throughout the polymerisation process and may be removed through the washing step.

According to a further aspect of the present invention there is provided a method of forming a polymeric composition whose properties have been modified, said method comprising the steps described above.

According to a further aspect of the present invention there is provided a polymeric composition obtainable or obtained according to either of the methods described above.

According to a further aspect of the present invention there is provided a polymeric composition comprising a network of gelators embedded therein wherein the gelator comprises gelator components comprising two head groups linked by a spacer molecule; wherein both head groups comprise a multiplicity of hydrogen bondable species providing a multiplicity of hydrogen bonding interactions, and/or the head groups are selected so as to associate providing stabilising interactions such as pi-stacking.

Suitably the polymeric composition may be obtainable or obtained according to either of the methods described above.

The polymeric composition of the present invention comprises a network of gelator embedded therein. The network of gelators is suitably distributed substantially homogenously throughout the polymeric composition.

The network of gelator is typically in the form of a network of supramolecular structures. The dimension of the gelator components
forming the nanoscale network depends upon the structure of the molecules used. Typically the dimensions of the gelator components are 1-4 nm in diameter. These generally assemble into fibrils with approximately molecular-scale dimensions. The fibrils then assemble into bundles, referred to as fibres, which form the basis of the network of gelator embedded in the polymeric composition.

In principle the gelator may comprise any functional groups, including but not limited to amides or carbamates, which provide a multiplicity of hydrogen bonding and/or pi-stacking interactions and the network of gelator is suitably in the form of a functional assembly embedded within the polymeric composition.

The network of gelator is preferably not permanently cross-linked into the polymeric composition, and may be removable for instance upon contact with a solvent such as methanol.

The properties of the polymeric composition of the present invention are suitably modified compared to known polymeric compositions comprising the same polymer or polymers.

As noted above, the polymeric composition obtainable according to the method described above may be washed to remove the gelator, generating a polymeric composition comprising cavities. These cavities may be in the nano-scale to micro-scale range.

According to a further aspect of the present invention there is provided a polymeric composition comprising nanostructured cavities. The nanostructured cavities are defined by the spaces left following removal of a gelator which was embedded within the polymeric composition. Suitably
the nanostructured cavities are in the form of a series of channels and/or cavities imprinted through the polymeric composition. The series of channels and/or cavities is suitably in the form of a structured architecture.

Suitably the polymeric composition comprising nanostructured cavities is obtainable or obtained according to the methods described above.

The gelators of the present invention may be synthesised using standard methods such as those disclosed in reference 12. The gelators of the present invention may be synthesised using a combination of the methods disclosed in reference 12 and reference 13.

The present invention will now be described by way of example only with reference to the accompanying drawing in which:

- Figures 1a, 1b and 1c show SEM images of gels formed through a combination of styrene/divinylbenzene (90/10) and Gelators 1, 2 and 3 respectively, all gels were allowed to dry under ambient conditions;
- Figure 2 shows a TEM image of a cross section of the polymeric composition formed in the presence of Gelator 1, the upper surface is at the bottom of the image;
- Figure 3 shows an SEM image of a polymeric composition formed in the presence of Gelator 2;
- Figure 4 shows representative nano indentation studies performed on a polymeric composition comprising no gelator and a polymeric composition comprising Gelator 2 at 20 nM;
- Figure 5 shows a TEM image of a polymeric composition formed in the presence of Gelator 3;
- Figures 6a and b show DMTA data for a polymeric composition comprising no gelator and a polymeric compositing comprising Gelator 3 at 20 nM respectively;
Figure 7 shows a SEM image of a polymeric composition formed in the presence of Gelator 3 following washing with MeOH and sonication;

Figure 8 shows a schematic overview of the gel based nanofabrication method of the present invention for the production of nanostructured polymeric materials.

Figure 9 shows a schematic representation of a gelator component according to the present invention.

Example 1

Gelator components having the following structures were formed:

![Chemical structures](image)
Gelator components 1 and 2 were synthesised using standard methods as reported in reference 12. Gelator component 3 was synthesised as detailed below.

**Synthesis of Gelator 3**

Compound (Boc)_2Lys-NH(CH_2)i2NH-Lys(Boc)_2 [12b] (0.30g, 0.35 mmol) was dissolved in dichloromethane (1.5 mL) and trifluoroacetic acid (1 mL) was added. The solution was stirred under nitrogen for a period of 30 min before the excess solvent and trifluoroacetic acid were removed by rotary evaporation. The sample was then subject to high vacuum for 10 minutes to dry. To dissolve the deprotected intermediate and therefore produce the free amine, ethyl acetate (15 mL) and triethylamine (0.74 mL, 0.51 g, 5.02 mmol) were added. To the reaction mixture the carboxylic acid of the building block reported in reference 13 (0.58g, 2.21 mmol, 6.3 eq.) was added and the solution stirred under nitrogen for 2 min. The solution was cooled to 0°C before the addition of hydroxybenzotriazole (HOBt, 0.89g, 4.25 mmol) and dicyclohexylcarbodiimide (DCC, 0.58g, 4.25 mmol) as a mixture of solids. The reaction mixture was left to warm to room temperature and then stirred for a period of 90 h. The precipitate containing the product was filtered of and washed with ethyl acetate. The precipitate was dissolved in a minimum amount of dichloromethane and placed in the freezer for an hour. The insoluble material was then filtered off and purified by size-exclusion chromatography (Biobeads, DCM: MeOH 90:10) to give a yield of 0.870g (0.61 mmol, 34.5%).
Formation of Polymeric Material Using Gelator 1, 2 or 3

All three gelators formed gels in a monomeric mixture of styrene/divinylbenzene (DVB) (90/10) acting as solvent. Samples of these gels were allowed to dry and subsequently imaged using field emission gun scanning electron microscopy (SEM). As expected, the gels have fibrillar morphologies (Fig 1). Gelators 2 and 3 exhibited thinner fibres than gelator 1.

Polymerisation of the solvent in these gels, and of a model system in the absence of gelator, was achieved using UV initiation, at wavelengths of less than 300 nm, with 4,4'-bis (dimethylamino) benzophenone as sensitizer. The polymerisation reactions were performed in a flat glass mould under nitrogen to produce polymer wafers with dimensions of approximately 5 cm x 5 cm x 200µm. The mould was water-cooled in order to prevent heating effects from destroying the self-assembled gel-phase network during polymerisation. After polymerisation, the polymer wafers were analysed by x-ray photoelectron spectroscopy (XPS), and fractured cross sections of the polymers were subjected to electron microscopy methods.

In the absence of gelator, the polymerisation of styrene/DVB (90/10) gave rise to a polymer standard - a homogeneous material with a featureless transmission electron microscopy (TEM) profile. However, in the presence of Gelator 1, TEM imaging of a cross section of the polymer demonstrated high levels of contrast between darker and lighter areas (see Fig 2). It appears that the dendron groups of the gelator molecule migrated towards the upper surface (N₂ interface) of the polymer wafer and away from the lower surface (glass interface).
XPS studies on the lower and upper surface of the polymer wafer confirmed that this type of migration process had taken place. The styrene/DVB polymer is only composed of C/H whilst the gelator is composed of C/H/N/O. The presence of nitrogen therefore provides a distinctive XPS fingerprint for the presence of the self-assembling gelator. In this case, no nitrogen was present at the lower surface of polymer, but it was present at the upper surface.

It appears that Gelator 1 is unable to maintain its self-assembled nanostructure during the polymerisation step. It is likely that the acid base interaction between the two components in the gelator complex of Gelator 1 breaks down during the polymerisation process. The dendron groups of Gelator 1 then migrate to the upper surface (N$_2$ interface), and phase separation between the diamine groups of the space molecule of the gelator and the polymer takes place. As a result, nitrogen is observed at the upper surface (N$_2$ interface), but not the lower surface (glass interface) of the polymer wafer.

Gelator 2 was employed in an attempt to prevent the degradation and migration of the gelator during polymerisation. The sub-units of Gelator 2 are permanently connected through a covalent bond. SEM imaging of the polymer formed in the presence of Gelator 2 indicated an homogeneous product, with no obvious phase separation (Fig 3A). Importantly, XPS spectroscopy indicated equivalent levels of nitrogen content on both the upper and lower faces of the polymer. These results indicate that degradations of the gelator and migration of the dendron groups does not occur using Gelator 2.

Some preliminary mechanical studies of this polymer were performed using nano indentation. Using this technique, a tip was pushed into the
material with constant force, and the depth of indentation measured as a function of the time for which the force was applied (Fig 4). Interestingly, samples of polymer with embedded Gelator 2 were indented significantly less than the polymer standard in the absence of gelator. This could be due to the presence of a self-assembled gelator network in the polymer, providing "scaffolding", and hence strengthening the polymer against applied stress.

TEM was performed on the polymeric material formed using Gelator 3 the polymerised materials using an OsO₄ stain (which reacts with any free double bonds and provides good contrast in the image). No large scale migration to the interfaces was observed during polymerisation, and the nanoscale fibres embedded within the polystyrene/DVB sample could be unambiguously imaged using TEM techniques (see Fig 5). Some extended fibres can be observed in the TEM image of Fig 5, whilst the dark spots represent fibres viewed in cross-section after fracturing of the polymer.

Preliminary dynamic mechanical thermal analysis (DMTA) studies were performed on the standard polymer formed without any gelator (Fig 6A), and on the polymer formed in the present of Gelator 3 (Fig 6B). In the presence of the nanoscale gelator network, the T₉ value of the polymer was measured as increasing from approximately 80°C to 100°C. Furthermore, the degree of damping at the T₉ value, as given by tan delta, was observed to decrease from 0.285 to 0.235. In addition, the modulus of the standard polymer at 20°C was 4.0 x 10⁹ Pa, whilst in the presence of embedded gelator, the modulus increased to 1.95 x 10¹⁰ Pa. These results indicate significant stiffening of the polymer and this is consequence of the presence of a nanoscale structured network, which reinforces the polymer.
Investigation as to whether the double bonds on the gelator may themselves polymerise were conducted. Polymerisation of the double bonds would lead to the gelator being cross linked into the overall polymer network. However, the fact that the double bonds of the gelators reacted with OsO$_4$ prior to TEM imaging indicates that polymerisation of the gelators does not occur. Furthermore, washing the polymer with MeOH removed essentially all of the gelator from the polymeric sample and this was evidenced through TEM imaging. The gelator was washed out in monomeric form (as demonstrated by mass spectrometry), proving that Gelator 3 is not permanently cross-linked into the polymer.

Interestingly, the polymeric material from which the gelators have been washed out maintains its nanoscale ordering (SEM, Fig 7) and appears to contain "washed out" fibrillar architectures. This indicates that this gel-polymerisation-washing approach has potential for the generation of nano-imprinted polymeric material. The overall process is illustrated schematically in Fig 8.

All documents referred to in this specification are hereby incorporated by reference. Various modifications and variations to the described embodiments of the invention will be apparent to those skilled in the art without departing from the scope and spirit of the invention. Although the invention has been described in connection with specific preferred embodiments, it should be understood that the invention as claimed should not be unduly limited to such specific embodiments. Indeed, various modifications of the described modes of carrying out the invention which are obvious to those skilled in the art are intended to be covered by the present invention.
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CLAIMS

1. A method of forming a polymeric composition comprising the steps of:
   - contacting a monomeric mixture with a gelator to form a mixture;
   - allowing the gelator to self-assemble within the monomeric mixture to realise the gelating properties of the gelator;
   - initiating polymerisation of the mixture to form a polymeric composition having a network of gelators embedded therein;
   - wherein the gelator comprises gelator components comprising two head groups linked by a spacer molecule, wherein the head groups comprise a multiplicity of hydrogen-bondable species to provide a multiplicity of hydrogen bonding interactions, and/or the head groups are selected so as to provide stabilising interactions such as pi-stacking.

2. The method of claim 1 wherein both head groups comprise a multiplicity of hydrogen-bondable species to provide a multiplicity of hydrogen bonding interactions.

3. The method of either one of claim 1 or 2 wherein the hydrogen-bondable species comprise an electronegative atom.

4. The method of claim 3 wherein the electronegative atom is oxygen, nitrogen or fluorine.

5. The method of preceding claim wherein each head group comprises at least five hydrogen-bondable species.
6. The method of any preceding claim wherein both head groups consist essentially of peptides.

7. The method of any preceding claim wherein the head groups have a structure based on the structure of lysine.

8. The method of any preceding claim wherein the spacer molecule is an alkyl molecule.

9. The method of any preceding claim wherein the spacer molecule is an alkyl molecule having a substituted carbon backbone of 6 to 25 carbon atoms.

10. The method of any preceding claim wherein the spacer molecule is a diamine molecule.
11. The method of any preceding claim wherein the gelator component has one of the following structures:
12. The method of any preceding claim wherein the head groups are attached to the spacer molecule through covalent bonds.

13. The method of any preceding claim wherein the gelator has a molecule weight of 400 to 500 amu.

14. The method of any preceding claim wherein the monomeric mixture comprises a self-polymerisable species.

15. The method of any preceding claim wherein the monomeric mixture comprises monomers compatible with addition polymerisation or copolymerisation.

16. The method of claim 15 wherein the monomers comprise functionalities selected from acrylates, methacrylates, styrenics, maleimides or vinylics.

17. The method of any preceding claim wherein the monomeric mixture comprises monomers compatible with condensation polymehsable species.

18. The method of claim 17 wherein the monomeric mixture comprises monomers suitable for epoxide-hardener systems, phenolic systems, cyanate esters, precursors for formation of polyesters, polyanhydrides, polyacetals, polyamides, polyurethanes or polyureas.

19. The method of any preceding claim wherein the monomeric mixture comprises a self-polymerisable species selected from epoxy, acrylate, methacrylate, maleimide, bis-maleimide, norbornene derivatives or vinyl.
20. The method of any of the claims 1 to 16 wherein the monomeric mixture comprises one or more of divinylbenzene and styrene.

21. The method of any preceding claim wherein the monomeric mixture comprises divinylbenzene and styrene.

22. The method of any preceding claim wherein the monomeric mixture consists essentially exclusively of divinylbenzene and styrene.

23. The method of any preceding claim wherein the monomeric mixture consists essentially exclusively of divinylbenzene and styrene at a molar ratio of 90:10.

24. The method of any preceding claim wherein the tensile strength of the polymeric composition is increased relative to polymeric compositions consisting of the same polymer or polymers in the absence of the gelator.

25. The method of any preceding claim wherein the mechanical strength of the polymeric composition is increased relative to polymeric compositions consisting of the same polymer or polymers in the absence of the gelator.

26. The method of any preceding claim wherein the modulus of the polymeric composition is increased relative to polymeric compositions consisting of the same polymer or polymers in the absence of the gelator.
27. The method of any preceding claim comprising the step of washing the polymeric composition to remove the network of gelator embedded therein and form a washed polymeric composition, wherein a structured architecture of channels and/or cavities is imprinted into the washed polymeric composition, said structured architecture corresponding to the location of the embedded network of gelator prior to washing.

28. A method of forming a polymeric composition having modified properties said method comprising the steps of any preceding claim.

29. A polymeric composition obtainable or obtained according to the method of any one of claims 1 to 28.

30. A polymeric composition comprising a network of gelator embedded therein, said gelator comprising gelator components comprising two head groups linked by a spacer molecule, wherein the head groups compromise a multiplicity of hydrogen-bondable species to provide a multiplicity of hydrogen bonding interactions, and/or the head groups are selected so as to provide stabilising interactions such as pi-stacking.

31. The polymeric composition of claim 30 wherein said polymeric composition is obtainable or obtained according to the method of any one of claims 1 to 28.

32. The polymeric composition of any one of Claim 30 to 32 wherein the network of gelator is substantially homogenously distributed throughout the polymeric composition.
33. A polymeric composition comprising nanostructured channels and/or cavities, the nanostructured channels and/or cavities being defined by the spaces left following removal of a gelator which was embedded within the polymeric composition.

34. A polymeric composition according to claim 33 wherein the nanostructured channels and/or cavities are in the form of a series of channels and/or cavities imprinted through the polymeric composition.

35. A polymeric composition according to claim 33 or 34 wherein the polymeric composition comprised a structured architecture of channels and/or cavities.
Fig. 2

Fig. 3

Substitute Sheet (Rule 26)
Fig. 4

Fig. 5
**Fig. 7**

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monomer solvent                  gelator                  polymerise                  wash
              |                             |                           |
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**Fig. 8**

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solid polymer containing self-assembled nanostructures

nanoscale imprinted polymer
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Covalent Bond or Non Covalent Interaction

Head groups typically composed of peptides
Spacer typically a diamine

Head Group  Spacer  Head Group
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

According to International Patent Classification (IPC) or to both national classification and IPC:

B. FIELDS SEARCHED

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched:

Electronic data base consulted during the international search (name of data base and, where practical, search terms used):

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No</th>
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Further documents are listed in the continuation of Box C

See patent family annex

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Date of the actual completion of the international search:
30 March 2009

Date of mailing of the international search report:
03/04/2009

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Hammond, Andrew
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**C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT**

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Form: FCT/ISA/210 (continuation of second filed) (April 2006)

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