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Rational Design of Urea-Based Two-Component Organogelators

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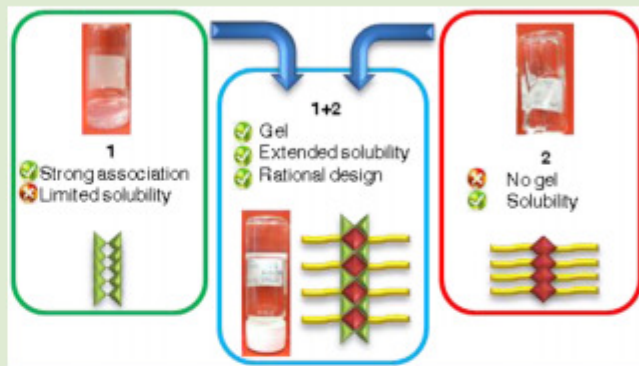
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Supporting Information

ABSTRACT: Low molecular weight gelators are versatile and responsive gel-forming systems. However, it is still a challenge to develop a new organogelator for a precise application, i.e., to gel a predetermined liquid. We propose a simple concept of a two-component gelling system that can be rationally adapted to gel liquids ranging in polarity from silicone oil to acetonitrile.



Gels are ubiquitous in our everyday life and can be obtained from a wide variety of building blocks, such as polymers, colloids, or even low molecular weight compounds. Indeed, gelation of a fluid by a limited amount (typically less than 1 wt %) of a low molecular weight gelator (LMWG) is possible if the LMWG self-assembles into anisotropic structures that interact to form a percolating network.^{1–4} Potentially these materials can be used in numerous applications, such as cosmetics, coatings, lubricants, or tissue engineering. Unfortunately, the design of an entirely new gelator molecule for a particular application (i.e., in a particular liquid) is still a difficult task. Several interesting approaches have been proposed to rationalize the gel formation by LMWGs,^{5,6} and the main required features for gel formation are known to be (i) the presence of strong self-complementary and unidirectional intermolecular interactions that enforce one-dimensional self-assembly while allowing dissolution at high temperature and (ii) the control of fiber–solvent interfacial energy to prevent bulk crystallization. Therefore, LMWGs can schematically be described as made of two parts: a part responsible for strong directional self-association and a part responsible for favorable interactions with the liquid to be gelled (Figure 1a). It is the careful balancing of these two parts that can yield an organogel. However, even with these guiding principles, the design of a new gelator for a particular liquid still requires the synthesis and testing of a large number of potential gelators before an adequate molecule is identified.

An interesting development in the field of LMWGs has been introduced with two-component gelators that allow a more flexible design.^{7–9} Several situations exist in which (1) both

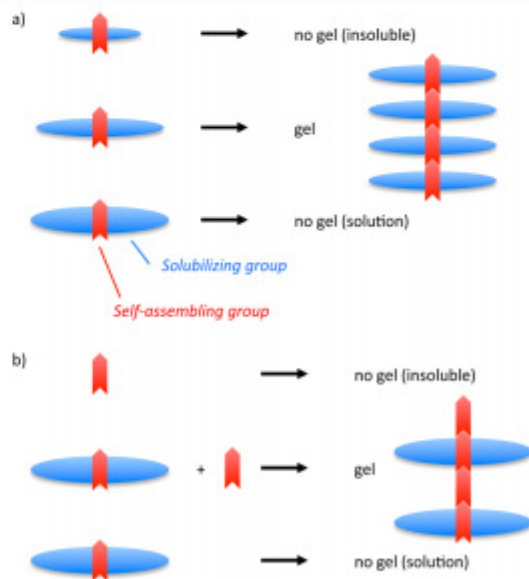


Figure 1. Schematic illustration of the adjustment of the solubility to obtain a gel from a one-component (a) or a two-component (b) gelator.

isolated components are nongelators, but when mixed together, they coassemble to yield a gel; (2) both compounds are

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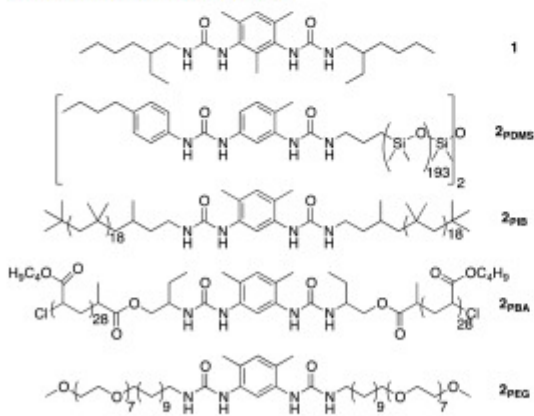
themselves gelator, and can assemble to form coiffers or self-sort resulting in two different kinds of nanofibers within the gel; or (3) one compound is a gelator, and the other molecule is a nongelating additive, designed to impact the gel properties.¹⁰ Obviously, in all cases, the presence of a second component increases the possibilities for tuning the properties of the gel such as its modulus, its shear sensitivity, or the range of liquids that are gelled. We now wish to push the two-component gel concept one step further and use it to afford a rational design of organogels, i.e., to be able to select the two components to gel a predetermined liquid, without prior testing.

The central idea is to decouple the part responsible for strong directional self-association and the part responsible for favorable interactions with the liquid to be gelled (Figure 1b). The first component should be chosen for its ability to self-assemble into anisotropic objects, irrespective of its solubility. The second component should be soluble in the liquid to be gelled and bear a moiety able to interact with the first component. A practical way to design this second component is to use an oligomer functionalized with a sticker for self-assembly^{11–13} because its solubility is mainly imposed by the nature of the oligomer, whatever the structure of the sticker. If both components coassemble (i.e., do not self-sort), then by adjusting the proportion of the two components it should be possible to tune the compatibility of the gelling system with the liquid of interest.

In this communication, we report the successful application of this concept and show that, using bisurea stickers, it is possible to rationally choose the solubilizing component and ensure gelation of any liquid ranging in polarity from silicone oil to acetonitrile.

As a first test, we describe the design of a gelator for a classical silicone oil (decamethylcyclopentasiloxane, D5). Bisurea 1 (Scheme 1) was chosen as the first component

Scheme 1. Structure of Gelators



because of its known ability to form long rodlike assemblies by hydrogen bonding.¹⁴ According to our design principle, the second component should contain (i) a bisurea sticker to allow coassembly with 1 and (ii) a macromolecular chain that is known to be soluble in D5; poly(dimethylsiloxane) (PDMS) is an obvious choice. We simply chose from a solubility table a polymer that is known to be soluble in the liquid of interest.²¹

Moreover, it is certainly possible to use a more subtle solubility parameters approach.^{22,23} Telechelic PDMS 2_{PDMS}¹⁵ with two stickers per chain, satisfies the criteria and was therefore tested. Moreover, the 2,4,6-trimethylbenzene bisurea sticker is known to lead to coassemblies with the 4-toluene bisurea sticker that are more stable than the homoassemblies.¹⁴ This complementarity between the stickers is expected to disfavor self-sorting. Figure 2 shows that it is possible to adjust the 1/2_{PDMS}



Figure 2. Middle: photograph of the gel formed by a 2/1 mixture (in sticker mole fraction) of 1/2_{PDMS} at 25 g/L in silicone oil (D5). At the same concentration, 1 is insoluble (left), and 2_{PDMS} forms a viscous solution (right).

proportion and the total concentration so that their mixture indeed forms a homogeneous and perfectly clear gel in D5. In the same conditions, 1 is insoluble, and 2_{PDMS} forms a viscous solution but not a gel.

The same approach was repeated to gel dodecane, ethyl acetate, or acetonitrile. In each case, bisurea 1 was associated with a partner containing a single bisurea sticker and an oligomer that is well-known to be soluble in the liquid of interest. Poly(isobutene), poly(butyl acrylate), and poly(ethylene glycol) were, respectively, chosen for their known solubility in dodecane, ethyl acetate, and acetonitrile.²¹ As expected, each of the resulting polymers (2_{PIB}, 2_{PBA}, and 2_{PEG}) is soluble in its, respectively, targeted liquid but does not form a gel. Remarkably, when mixed with bisurea 1, each of them forms a gel after simple adjustment of the concentrations (see Figure S1 for the exact conditions). The wide polarity range of the liquids that are effectively gelled confirms the robustness of the approach (see Table S2 for additional examples). Moreover, the number of stickers per chain (two in the case of 2_{PDMS} and one in the case of the other polymers) does not seem to be a key design feature because both structures yield gels.

The rheological properties of the gels were probed in the case of 1/2_{PIB} in dodecane, in the linear viscoelastic regime. The frequency-dependent experiment reveals the elastic character of the gel, with the elastic modulus that dominates the loss modulus over the whole frequency range (Figure 3). As expected, the elastic modulus increases strongly with the concentration and reaches a value of 100 Pa at a 1/2_{PIB} overall concentration of 15 g/L. FTIR spectroscopy (Figure S3) confirms that the bisureas are strongly hydrogen bonded.

The structure of the assemblies responsible for the gelation was then characterized in toluene because it is a good solvent for both isolated components, therefore facilitating comparisons. In this solvent, the 1/2_{PIB} mixture also forms a gel. Small-angle neutron scattering (SANS) measurements show that the 1/2_{PIB} mixture as well as the pure components are characterized by a q^{-1} dependence of the scattered intensity over one decade at low angles (Figure 4). This feature is typical of long rodlike objects. In addition, at larger angles, both 2_{PIB} and the 1/2_{PIB} mixture show a q^{-2} dependence of the scattered

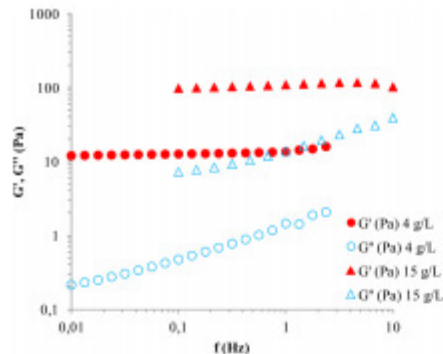


Figure 3. Frequency dependence of the elastic (G') and loss (G'') moduli for the $1/2_{\text{PIB}}$ mixture (9/1 molar fraction) in dodecane, at a total concentration of 4 or 15 g/L (25 °C).

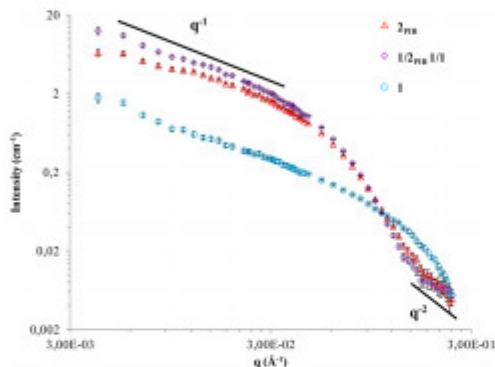


Figure 4. SANS intensity (I) versus scattering vector (q) for solutions of **1** or 2_{PIB} at a concentration of 6 g/L in toluene- d_8 and for their mixture (1/1 molar fraction) (20 °C).

intensity that is typical of polymer chains. The combination of the q^{-1} dependence at low q and the q^{-2} dependence at large q is a signature for the presence of rodlike objects that are decorated with solvated chains, i.e., hairy rods.¹⁶ Importantly, the fact that the scattered intensity for the mixture is higher than the intensities for both pure solutions proves that **1** and 2_{PIB} are coassembled. Indeed, the SANS data unambiguously show that full self-sorting is not occurring because in that case the scattered intensity of the mixture would be the average of the intensities for the pure components. However, we cannot exclude at this point the presence of partial self-sorting.

The temperature stability of the gels was investigated by rheology (Figure 5) and DSC (Figure S4). Both techniques show that the gels are thermoreversible and that there is a ca. 10 °C hysteresis between heating and cooling runs. The influence of the proportion of the constituents was probed visually (Figure S2) and by DSC (Figure S5). In the case of $1/2_{\text{PIB}}$ at 4 g/L in dodecane, gels are obtained only for mixtures containing between 10 and 50 mol % of 2_{PIB} , and the qualitative appearance of the samples indicates that the strongest gel is obtained for 10 mol % of 2_{PIB} . This means that a small proportion of 2_{PIB} is enough to induce the dissolution of **1** and then gelation and that a large proportion of 2_{PIB} is detrimental to the gel formation. This is probably related

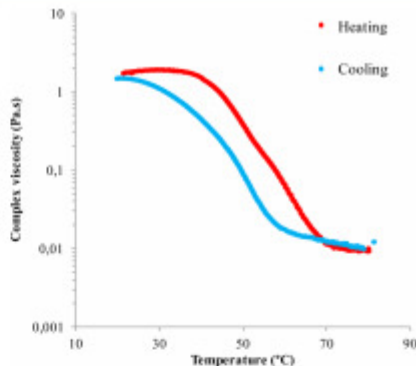


Figure 5. Temperature evolution of the complex viscosity (1 Hz) for the $1/2_{\text{PIB}}$ mixture (9/1 molar fraction) in dodecane, at a total concentration of 4 g/L. Heating/cooling rate: 1 °C/min.

to the fact that the experiments were performed at constant weight concentration (4 g/L) and that the molar mass of 2_{PIB} is 5 times larger than the molar mass of **1**. Therefore, if the proportion of 2_{PIB} is large, then the molar concentration of bisurea stickers is low. In contrast, the DSC experiments (Figure S5) show that the temperature at which the coassembly melts reaches a maximum at 50 mol % of 2_{PIB} . Therefore, the coassembly is most efficient for a 1/1 molar ratio, although the gel is stronger if the mixture is richer in the low molar mass constituent (**1**).

In conclusion, we propose a simple concept of a two-component gelling system, where the first component is chosen for its capacity to form rodlike assemblies and the second component contains (i) a sticker for coassembly with the first component and (ii) an oligomer that is rationally chosen to tune the compatibility with the liquid of interest. This concept is successfully illustrated with bisurea stickers that allow the formation of elastic and thermoreversible gels in a large variety of liquids. An important question is to know whether the successful gelation of this impressive range of liquids by the described bisurea mixtures is a unique behavior or whether it illustrates some general principle. It is obvious that any two-component system which leads to self-sorting of the components is not a suitable candidate since self-sorting of the components would lead to precipitation of the first component and thus to inhomogeneous gels. Because the second component is much more bulky than the first component, one can expect that coassembly is actually favored by the relief of steric repulsion in the coassembly. Still the choice of complementary stickers is certainly advantageous because it allows us to incorporate an additional driving force in favor of coassembly. The bias toward coassembly of the present bisurea stickers with a 2,4,6-trimethylbenzene versus a 4-toluene spacer is actually quite weak (about 1 kJ/mol).^{14,17} Therefore, it should be straightforward to find other complementary stickers (such as acid/amine,^{9,18} UPy/Napy,¹⁹ or π -donor/ π -acceptor²⁰) that also favor coassembly over self-sorting and that should therefore enable us to rationally prepare two-component gellers.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.5b00931.

Synthesis of the gelators, composition of the gels, and additional FTIR and DSC data (PDF)

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Notes

The authors declare no competing financial interest.

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