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Tuning reversible supramolecular polymer properties through co-monomer addition

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Unlike most low molar mass organogelators, which form strong gels due to the entanglement of strong molecular aggregates such as crystalline fibres, a few reversible supramolecular polymers form viscoelastic solutions due to the formation of both rigid and dynamic filaments. By using three different bisureas which self-assemble according to the same hydrogen-bonding pattern and form such rigid reversible supramolecular polymers, we have shown that it is possible to finely tune the properties of the resulting solutions. The critical temperature below which viscoelastic solutions are obtained and the viscosity of the dilute solutions can be adjusted by changing the co-monomer content. This clearly facilitates gel formulation, which is an important step as far as applications are concerned.

Keywords: supramolecular polymer; organogelator; hydrogen bond; bisurea

Introduction

A large variety of low molar mass compounds are known to form thermoreversible gels at low concentrations in organic solvents (*1*). The overwhelming majority of these organogels are obtained by cooling a hot solution of the organogelator below a critical temperature, where molecular aggregation or even crystallisation occurs. If the crystals obtained are highly anisotropic, they can form a percolating network, which effectively entraps the solvent. These classical organogels are intrinsically metastable because close packing of the crystalline fibres, which is a thermodynamically favourable process, leads to a macroscopically biphasic system. However, in some cases this process is kinetically trapped and the gels obtained are effectively stable for months and can be used in various applications (*1*). In contrast to these materials, a few hydrogen-bonded low molar mass compounds have been reported to form thermodynamically stable viscoelastic solutions (*2–5*). Rather than thick crystalline fibres, these reversible polymers (*6*) form filaments with a cross-section close to the molecular dimension of the monomer, so that a dynamic exchange between the filaments is possible at room temperature. If the filaments are sufficiently rigid, they can entangle at low concentrations and yield elastic properties at high frequencies. On the other hand, the dynamic nature of the filaments is responsible for viscous flow at low frequencies, because of the reversible breaking of the filaments. The dynamic nature of the filaments is also responsible for the thermodynamic stability, for the self-healing behaviour, and even for the easily tunable properties of the viscoelastic solutions. Indeed, for a thermodynamically stable system, a small incremental change can be expected to lead to a small property variation. This is in contrast to classical organogels, which can be totally disrupted even by a small incremental change, because of their metastable condition. The purpose of this article is to show that tuning the properties of rigid reversible supramolecular polymers by adding co-monomers is indeed a straightforward and efficient methodology (*7*).

Experimental

The synthesis of bisureas was described previously (*8*). Solvents were used as received. Solutions were prepared by stirring or shaking, at least 1 week prior to use. Heating at 50°C accelerated the dissolution process, but did not affect the measurements.

IR spectroscopy

Infrared spectra were recorded on a Nicolet Avatar 320 spectrometer in a KBr cell of 0.1 cm path length. The temperature was controlled with a heating device (P/N21525) from Specac. Consecutive measurements were separated by at least 10 min, to allow for thermal equilibration. Thermal expansion of the solutions was not corrected.

ITC

Heats of dissociation were measured using a MicroCal VP-ITC titration microcalorimeter (*9*). The sample cell

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(1.435 cm^3) was filled with pure toluene. A relatively concentrated bisurea solution in toluene was placed in a 0.295 cm^3 syringe that was continuously stirred (270 rpm). A first 2 μl aliquot was injected, without taking into account the observed heat, to remove the effect of solute diffusion across the syringe tip during the equilibration period. Subsequent aliquots of the solution (5 μl) were automatically injected into the sample cell every 360 s, until the syringe was empty.

Viscometry

Measurements were performed with Cannon-Manning semi-micro capillary viscometers. The solutions were not filtered.

Rheology

The measuring conditions for EHUT were as described previously (*10*). The measurements for DMHUT were performed on a strain-controlled TA Instrument (ARES-LS1) equipped with a stainless steel Couette cell (diameter, 16.5–17 mm and height, 13 mm). In order to obtain reproducible results, the sample was first heated to 70°C for 1 h and poured in the Couette geometry regulated at 20 or 35°C. The measurements were performed after 20 min of equilibration. The protocol for each sample was the following: first, the sample was submitted to a strain sweep at 1 Hz in order to determine the viscoelastic regime, before reaching the non-linear regime the strain sweep was stopped in order to preserve the sample. The strain sweep was followed by a frequency sweep.

Results and discussion

Reversible homopolymer structure and properties

Three bisurea-based monomers (Figure 1) were considered for this study. The self-assembly of monomer EHUT has been previously characterised by FT-IR spectroscopy, small angle neutron scattering (SANS) and rheology (*8*,*10*,*11*). At room temperature, in toluene or dodecane solution, EHUT forms thick and probably tubular filaments with about three molecules in the cross-section. This supramolecular structure is responsible for the strong viscoelasticity of the solutions (see below). The three monomers considered here (Figure 1) contain the same associating bisurea unit and thus behave similarly: SANS analyses have shown that all three monomers self-assemble to form thick filaments with the same diameter and the same number of molecules in the cross-section (Table 1; (*8*)).

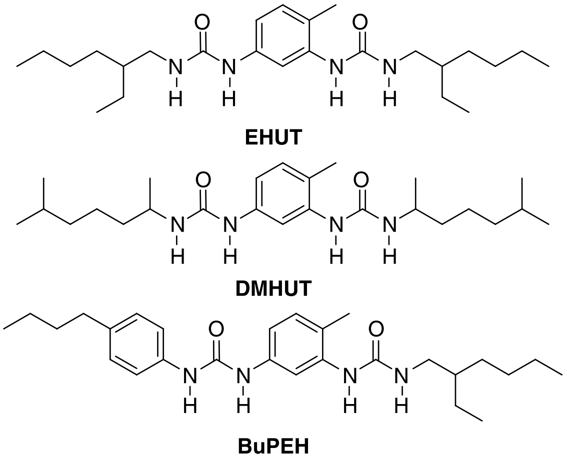

Figure 1. Structure of the studied bisureas.

At high temperatures or at low concentrations, the thick structure disappears in favour of thinner filaments containing a single molecule in the cross-section (*8*,*12*). The thin filaments do not show viscoelasticity, due to faster dynamics and reduced rigidity of the filaments. The thermal stability of the thick filaments has been tested by FT-IR spectroscopy (*8*). The values of the transition temperature above which the thick filaments are unstable (T^{**}) are mentioned in Table 1; the thermal stability of the thick filaments increases in the order BuPEH < EHUT < DMHUT.

The stability of the thick filaments to dilution can be conveniently tested by isothermal titration calorimetry (ITC; (*9*)). The principle of the technique is to measure the heat evolved while aliquots of a relatively concentrated bisurea solution are injected into the pure solvent (placed in a calorimetric cell, at a fixed temperature). Figure 2(a) shows the heat-flow curves obtained when a 0.24 mM bisurea solution in toluene is incrementally injected into pure toluene at 25°C, and Figure 2(b) shows the enthalpograms deduced from the heat-flow curves after integration. The three bisureas show qualitatively the same behaviour, but some significant differences are visible. First, the dissociation of the thick filaments

Table 1. Characteristics of bisurea self-assembly in toluene.

Bisurea	L^a (Å)	$d^{b,c}$ (Å)	$M_L{}^{c,d}$ (g mol^{-1} Å^{-1})	$n^{c,e}$	T^{**f} (°C)	$C^{**} \times 10^{-5g}$ (mol L^{-1})
DMHUT	25	25	790	2.5	63	1.8
EHUT	25	26	800	2.5	43	2.9
BuPEH	27.5	30	910	2.3	35	3.7

[a] Largest dimension of the fully extended monomer.

[b] Diameter of the filament cross-section.

[c] Derived from SANS measurement (*8*) of a 22 mM solution in d_8-toluene, at 22°C.

[d] Mass per unit length of the filament.

[e] The number of bisurea molecules in the cross-section, assuming a repeat distance of 4.6 Å.

[f] Transition temperature between thick and thin filament structures, determined by FT-IR measurement (*8*) of a 12.5 mM solution in toluene.

[g] Concentration corresponding to the transition between thick and thin filament structures at 25°C, determined by ITC (see Figure 2(b)).

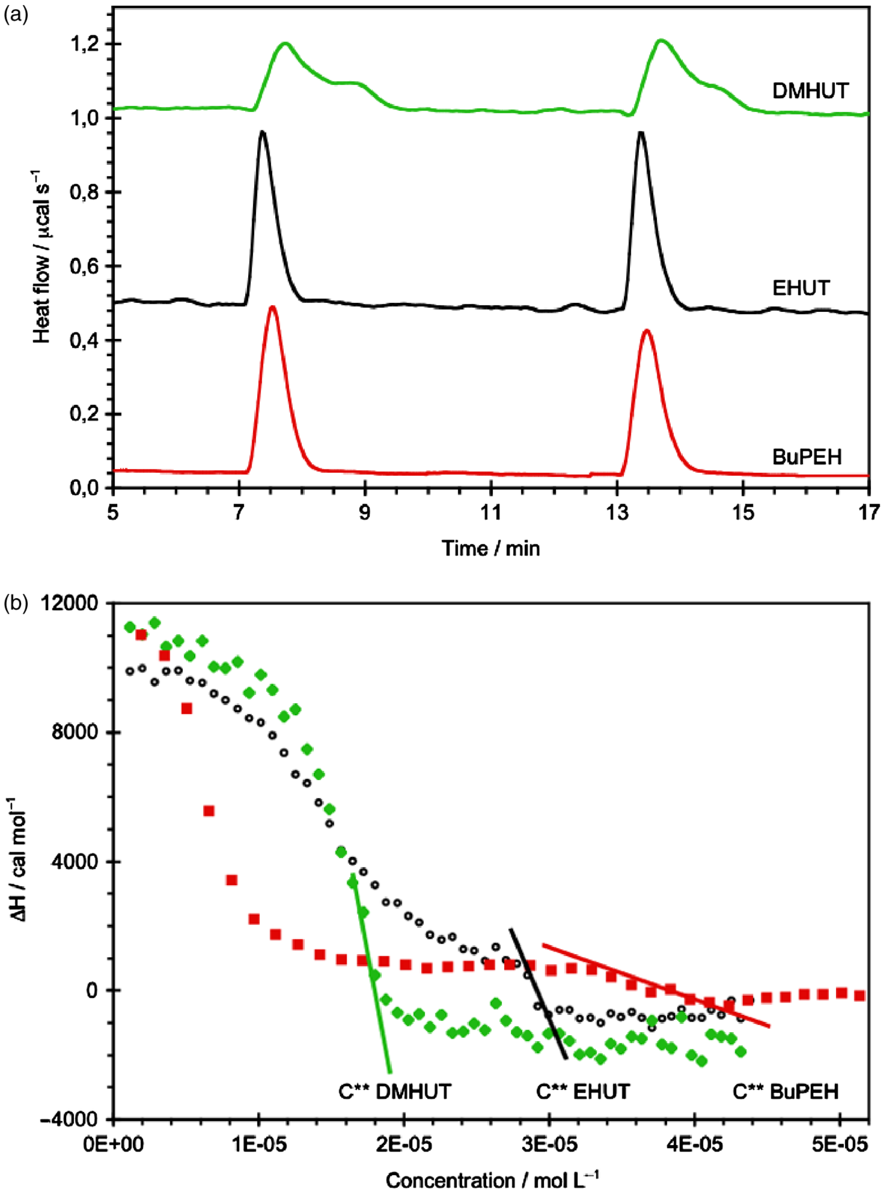

Figure 2. Heat effect produced by injecting a 0.24 mM toluene solution of bisurea into toluene at 25°C (5 µl aliquots). (a) Heat flow produced by the first two injections. (b) Enthalpogram for the whole experiment.

is an endothermal process for all three bisureas, but Figure 2(a) shows that the dissociation of the thick filaments is a slower process for DMHUT than for the other bisureas. Second, each enthalpogram (Figure 2(b)) displays two thresholds which are as follows (*8*). The low-concentration threshold corresponds to the transition between the thick filaments and the monomers and is not of interest for the present discussion. The second threshold corresponds to the transition between the thick filaments and the thin filaments: its position gives the critical concentration (*C***) below which the thick filaments are unstable.[1] The values of *C*** are mentioned in Table 1 and they show that the stability towards dilution follows the same trend as the thermal stability: the thick filament stability increases in the order BuPEH $<$ EHUT $<$ DMHUT.

A simple visual inspection reveals that all three monomers form gels in toluene. Consequently, rheology was used to see whether the quantitative differences in the strength of the self-assembly have measurable consequences on the material properties. The experiments were performed in dodecane to avoid artefacts due to solvent evaporation. The stability of the thick filaments is enhanced in dodecane, compared with toluene, but no precise values for *T*** and *C*** could be obtained. Figure 3 shows the frequency dependence of the storage and loss moduli for EHUT and DMHUT solutions.[2] The results for

EHUT (Figure 3(a)) prove the viscoelastic nature of the solution. At low frequencies, the mechanical response is dominated by the loss modulus. At higher frequencies the storage modulus is predominant and reaches a plateau value. This signature has previously been interpreted to be due to the entanglement of long and semi-flexible filaments presenting a fast scission and recombination process (*5*,*10*). DMHUT also shows this characteristic signature, but only at a higher temperature (Figure 3(c)). A comparison of data at the same temperature and concentration (Figure 3(a) and (b)) shows that the characteristic relaxation time (the crossing point of G′ and G″) for the DMHUT solution is at least two orders of magnitude smaller than that in the case of the EHUT solution. This means that the filaments present in the DMHUT solution have slower dynamics. This effect is probably related to the slow dissociation revealed by ITC (Figure 2(a)).

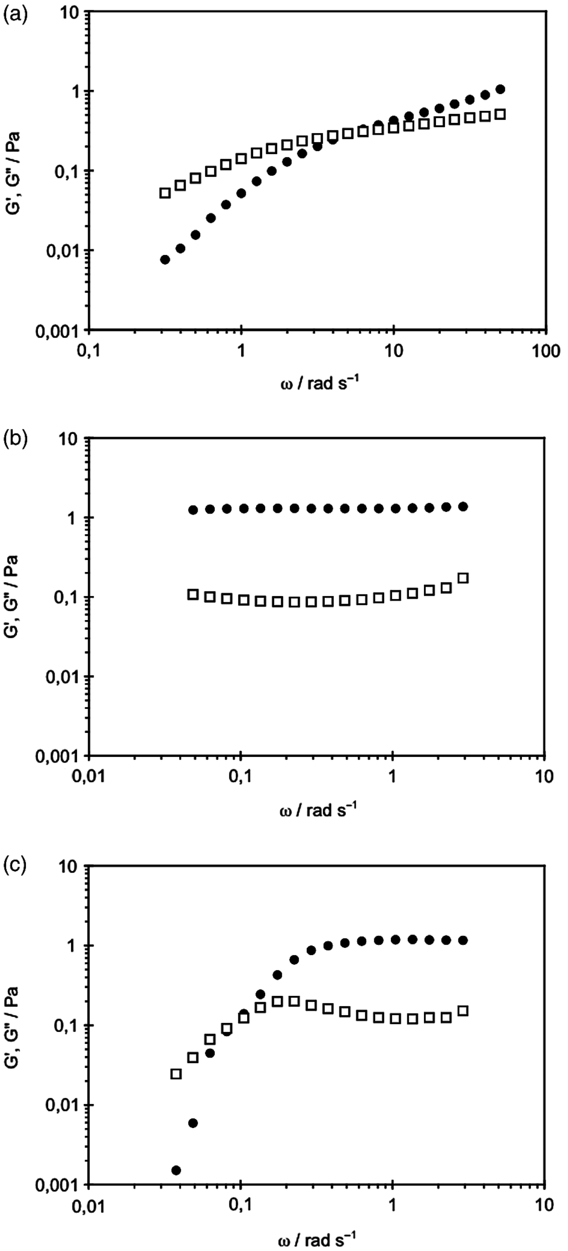

Figure 3. Storage G′ (•) and loss G″ (□) modulus vs. frequency for bisurea solutions in dodecane, at a concentration of 1 g/l (2.3 mM). (a) EHUT, 20°C; (b) DMHUT, 20°C; and (c) DMHUT, 35°C.

Influence of co-monomer composition on transition temperature

Because of the difference in filament stability between the three monomers, it is of interest to mix them and see whether tuning of the properties is possible. Figure 4 shows the evolution of the ratio of FT-IR absorbances for EHUT/DMHUT mixtures in toluene. This ratio measures the shape of the vibration band for hydrogen bonded N—H groups and is a characteristic of the filament structure: a high value (*c.* 1.25) is attributed to the thick filament structure, whereas a low value (*c.* 1.1) is attributed to the thin filament structure (*8*). Figure 4 shows that the monomer mixtures behave similar to the pure components, but with a gradual shift in the transition temperature. This means first that copolymers are indeed obtained; if a non-interacting mixture of EHUT and DMHUT filaments were obtained, then two transitions should be detected. A second point worth noting is that the slope of the curves (that is, the cooperativity of the transition) is the same in the case of the copolymers as in the case of the homopolymers. This observation may seem surprising, because based on the monomer structures, statistical copolymers are expected, which means that a broadening

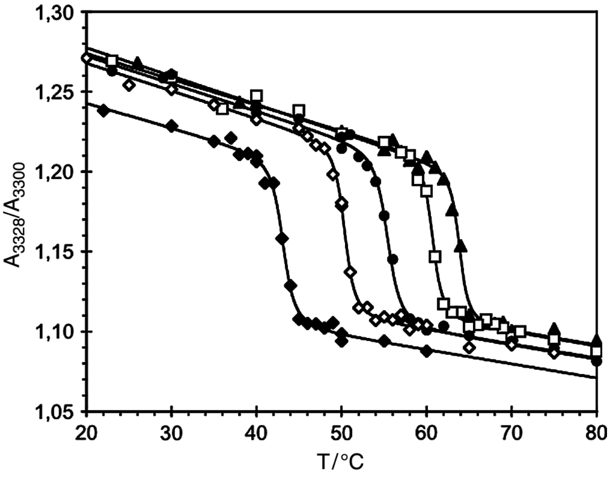

Figure 4. The ratio of absorbances at 3328 and 3300 cm^{-1} for 12.5 mM toluene solutions of EHUT/DMHUT mixtures (◆, 100/0; ◇, 75/25; •, 50/50; □, 25/75; ▲, 0/100) vs. temperature. Both heating and cooling runs are represented, showing the absence of hysteresis.

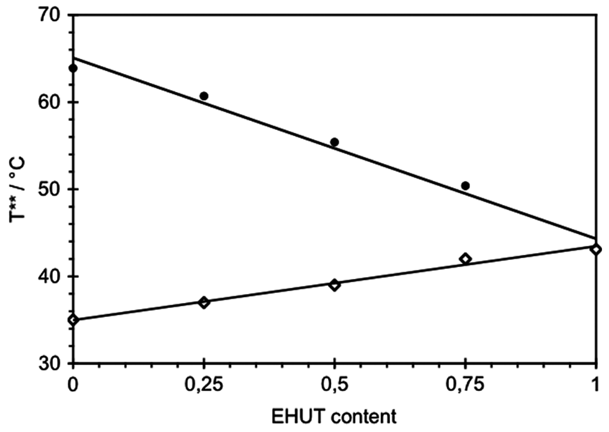

Figure 5. Transition temperature between thick and thin filaments, for 12.5 mM EHUT/DMHUT (●) and EHUT/BuPEH (◇) solutions in toluene vs. EHUT molar content.

of the transition could be expected because of compositional heterogeneity within a copolymer sample. Indeed, in a given mixture, the filaments with a content in EHUT higher than average should present a transition temperature at a lower temperature than the average. However, due to the great length of the filaments, the probability to find a pure EHUT filament in an equimolar EHUT/DMHUT solution is vanishingly small. Consequently, the sharpness of the transition for a mixture means that all the filaments in the sample have a very similar overall composition (the average composition). Compositional fluctuations along the filament most probably occur, but do not affect the slope of transition because the fluctuations are averaged out over the very long filaments.

Finally, Figure 5 shows that, for both monomer mixtures EHUT/DMHUT and EHUT/BuPEH, the transition temperature is close to a linear function of the composition. From a practical point of view, this point is particularly useful because it means that the temperature above which the viscoelastic properties of the solution disappear, can be finely tuned.

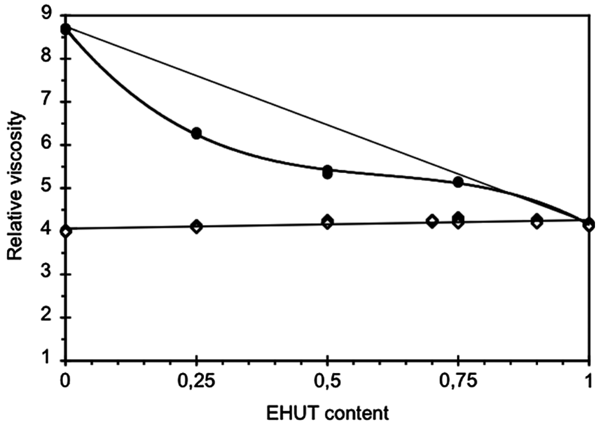

Figure 6. Relative viscosity (η/η_0), for 0.8 mM EHUT/DMHUT (●) and EHUT/BuPEH (◇) solutions in toluene, versus EHUT molar content (25°C).

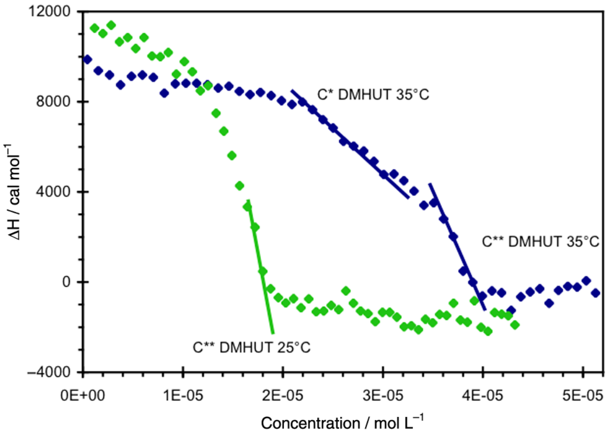

Figure S1. Enthalpogram produced by injecting a 0.24 mM toluene solution of DMHUT into toluene at 25 or 35°C (5 μl aliquots). At 35°C, two transitions (*C*∗ and *C*∗∗) are visible; at 25°C, the two transitions coincide.

Influence of co-monomer composition on dilute solution viscosity

In order to check if the co-monomer composition also has an influence on properties far from the transition temperature, dilute solution viscosity measurements were performed at 25°C. Figure 6 shows that the viscosity of the DMHUT solution is much larger than the EHUT solution: the increased stability of the DMHUT filaments probably means that they are longer than the EHUT filaments, explaining the higher viscosity. As a consequence, the viscosity of EHUT/DMHUT mixtures is strongly influenced by composition. The variation is monotonous, but significantly non-linear. In the case of EHUT/BuPEH mixtures, the effect is much less visible: the EHUT solution ($\eta/\eta_0 = 4.2$) is only slightly more viscous than the BuPEH solution ($\eta/\eta_0 = 4.0$). Consequently, the viscosity of EHUT/BuPEH mixtures is nearly independent of composition.

Conclusion

By using three different bisureas which self-assemble according to the same hydrogen-bonding pattern, we have shown that it is possible to finely tune the properties of the resulting solutions. First, the critical temperature below which viscoelastic solutions are obtained (*T*∗∗) varies linearly with the co-monomer composition and can thus be adjusted rationally. Second, the viscosity of the dilute solutions can also be finely tuned by changing the co-monomer content. This clearly facilitates formulation, which is an important step as far as applications are concerned. Moreover, such a smooth behaviour is difficult to achieve with classical organogelators, which rely on crystalline fibre formation, because it is not a trivial task to find several compounds that can co-crystallise without morphological changes or self-sorting effects (*13*,*14*).

Acknowledgements

C. Rossi and F. Dubut are thanked for their contribution to this project.

Notes

1. In the case of DMHUT, both transitions occur at very similar concentrations. This can be deduced from the value of the enthalpy change on Figure 2(b), and is unambiguously proved by comparison with the result for the same experiment performed at 35°C (Figure S1). At this temperature, the two transitions are clearly separated.
2. Insolubility of BuPEH in dodecane prevented its rheological characterisation.

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