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A photo-responsive organogel

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A photo-responsive organogel has been made by addition of a novel stilbene-containing photo-surfactant to toluene: exposure to UV light led to a gel-to-sol transition with spatial control.

Gels are important materials with diverse applications.[1] Tanaka *et al.* reported the first example of "smart" or "intelligent" gels (stimuli-responsive gels),[2] and since then much effort has been made to develop these novel materials (*e.g.* refs. 2–10). Advantages of smart gels arise from their many potential applications, for example: delivery systems, sensors, actuators, chemical valves and switches, industrial separators, micromachines, mechanical transducers and artificial muscles. Recent developments have employed various triggers: solvent composition (*e.g.* ref. 2) pH (*e.g.* ref. 3), magnetic fields (*e.g.* ref. 4), addition of salts (*e.g.* ref. 5), electric fields (*e.g.* ref. 6), addition of sugars (*e.g.* ref. 7), IR (*e.g.* ref. 8) and UV light (*e.g.* refs. 9 and 10) Only one study[10] involves a surfactant, but it is an inert cationic compound, the photo-responsive component is anthracene-9-carboxylate. Here is reported a new photo-responsive organogel, which displays a UV-induced gel-to-sol transition. The gel is formed by stilbene-containing gemini photo-surfactant E-SGP (Fig. 1), toluene and trace amounts of dimethyldodecylamine. The synthesis and UV-induced changes in adsorption and aggregation behaviour of SGP in water has been previously reported,[11] and irradiation drives changes in surface tension and a vesicle-to-charged spherical micelle transition.

The organogel was prepared by refluxing for several hours a sample containing 8% E-SGP and 0.4% of *N*,*N*′-dimethyldodecylamine (Aldrich, 97%) in toluene-d$_8$ (Cambridge Isotope Laboratories, 99.6%), then cooling slowly to room temperature. A sample at 4% E-SGP and 0.2% *N*,*N*′-dimethyldodecylamine in toluene-d$_8$ gave similar results. Reproducibility was checked by repeating all the experiments described here with freshly synthesised, and newly made up, samples over a six month period. Gels were irradiated in rectangular quartz cells (1 mm path length, Hellma) with a 100 W high-pressure Hg lamp (LPS-220/250 power supply from PTI; lamp housing from HI-TECH Scientific and Mercury short-arc photo optic lamp HBO® 103 W/2), polychromatic to maximise the photon flux. The irradiation time was 1 hour for all samples.

Fig. 2 shows the gel-to-sol transition seen for this system after irradiation with UV light: initially, as the opaque gel (a), and after irradiation (b) when a transparent low viscosity solution was formed from the gel. Interestingly, when the system was irradiated trough a mask, only the illuminated areas were converted to the sol, as shown in (c), demonstrating some degree of spatial control.

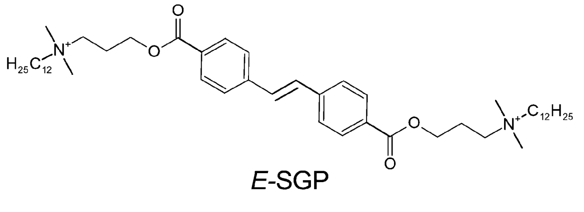

Fig. 1 Stilbene-containing gemini photo-surfactant (SGP).

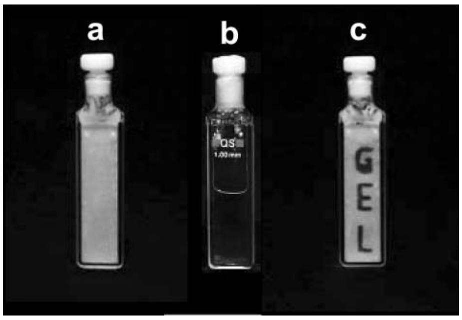

Fig. 2 Photo-induced gel-to-sol transition of an 8% SGP–*N*,*N*′-dimethyldodecylamine–toluene-d$_8$ organogel: initial gel state (a); after irradiation (b) and after irradiation through a mask (c).

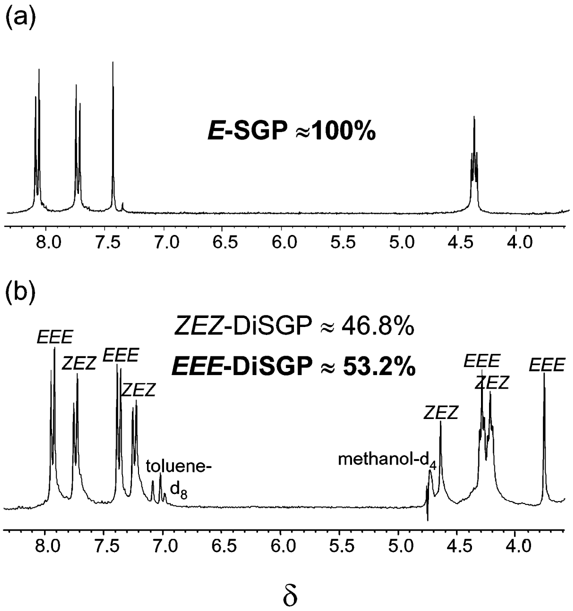

Fig. 3 Partial ^{1}H NMR spectra of SGP-toluene system: before irradiation (a) and after irradiation (b).

It is known that photo-dimerization of such stilbenes occurs, yielding either *cis,anti,cis* dimer (*ZEZ*-DiSGP) or the *all-trans* dimer (*EEE*-DiSGP).[11] Fig. 3 shows ^{1}H NMR spectra in the δ region of interest. The starting *E*-SGP isomer displays a peak at around δ 7.4 (Fig. 3(a)), characteristic of CH=CH between the aromatic ring; singlets in Fig. 3(b) at around δ 4.6 and 3.7 correspond to the protons in the cyclobutane region of *ZEZ*-DiSGP and *EEE*-DiSGP, respectively. Triplets appearing around δ 4.2 and 4.3 correspond to methylene protons next to the ester group of *ZEZ*-DiSGP and *EEE*-DiSGP, respectively. These NMR spectra suggest that the reaction is essentially complete after irradiation, with little remaining *E*-SGP and a photostationary state corresponding to a composition of 47% of *ZEZ*-DiSGP and 53% of *EEE*-DiSGP. Apparently these changes in the molecular geometry are linked to the state of aggregation (Fig. 2), which was further investigated by small-angle neutron scattering (SANS),† shown on Fig. 4. These

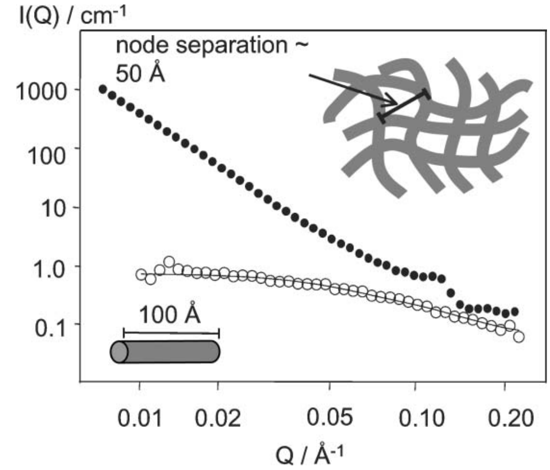

Fig. 4 SANS data for the 8% h-SGP–toluene-d_8 system: before irradiation of the gel (●) and after irradiation (○), fitted to the cylinder micelle model with $R = 13$ Å and $L = 100$ Å shown as a line as a possible interpretation.

SANS experiments were repeated on two occasions, separated by about six months to ensure reproducibility. In Fig. 4(a) it is clear that strong Q^{-3} scattering is present in most of the Q range, characteristic of convoluted internal surfaces such as found in gels and meshes.[12–15] Furthermore, a high Q correlation peak is present at $Q \sim 0.126$ Å^{-1}, which would correspond to a node-to-node separation of $\sim$50 Å.

Although the data could not be fitted completely,† in general they follow a profile similar to those found in classic gel networks (*e.g.* refs. 12–15). UV irradiation causes a dramatic decay of the SANS signal (Fig. 4), and these data could be adequately fitted,† by a model for dilute non-interacting rods, 13 Å in radius and of length 100 Å.[16] Since after UV the SANS is quite weak, it is important not to place too much emphasis on the exact self-assembly structure as determined by data fitting. However, the large differences between the pre- and post-irradiated SANS signals are consistent with a dramatic UV-induced change in aggregation, from an interconnected network to anisotropic non-interacting reversed micelles.

This switch in aggregation is consistent with molecular changes (simulations shown elsewhere[11]). For the initial *E*-SGP π–π stacking interactions may promote aggregation, with the organophilic pendant chains protecting central polar moieties from solvent, in a similar fashion to classic organogelators.[14,15] On the other hand, the UV-produced photodimers are sterically hindered[11] resulting in much weaker intermolecular association and reduced aggregation.

A novel surfactant-containing photo-responsive organogel has been described, for which a gel-to-sol transition can be induced by irradiation with UV light. Spatial control of this phenomenon within the sample itself has been demonstrated. NMR shows that these responses are due to the formation two types of photo-surfactant dimer (*all trans* and *cis*,*anti*,*cis*). Large photo-induced changes in aggregation were confirmed by SANS. This study complements work on aqueous properties of SGP,[11] demonstrating the versatility of such stilbene photo-surfactants, and pointing to new applications.

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Notes and references

† SANS was carried out on the time-of-flight LOQ instrument at ISIS, UK as described elsewhere.[11] Toluene-d_8 was used to contrast the h-SGP surfactant. SANS data were analysed using the interactive FISH program as described elsewhere (ref. 11 and references therein). Attempts were made to fit non-irradiated gel data included analysis using either the Kotlarchyk–Ritzau model,[12] which represents randomly oriented lamellar stacks with a one-dimensional paracrystalline distortion, or the Lorentz plus Debye–Bueche model for gel networks, as proposed for aqueous gelatin by Pezron *et al.*[13] Both methods reproduced the low Q region <0.07 Å^{-1} well, but failed at high Q. Similar tests of the model described by Terech *et al.* for cholesterol-based organogels[14,15] were carried out with limited success. The SANS from post-irradiated samples was tested against various possible form factors, including dilute non-interacting monodisperse and also polydisperse spheres. These models for isotropic particles did not result in convincing fits. However, it was found that form factors for homogeneous cylinders[16] and/or ellipsoids (aspect ratio $\sim$4) gave a good descriptions of the post-irradiated SANS. This is consistent with the data decaying as approximately Q^{-1} in the range $0.03 < Q < 0.15$ Å^{-1}.

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