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Polyaniline superstructures created by a templating effect of organogels†

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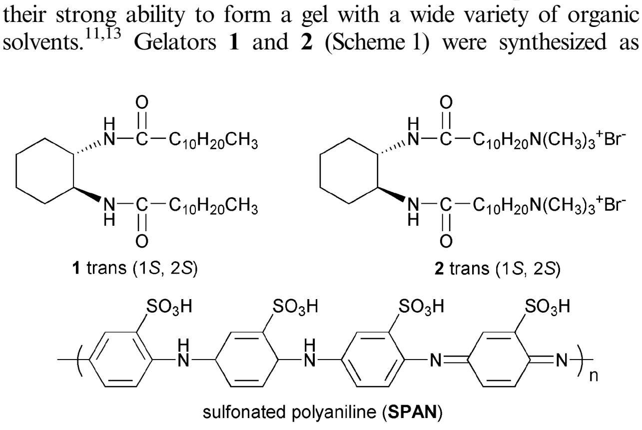
The use of organogelators to template chiral and achiral polyaniline superstructures *via* the electrostatic interaction between anionic sulfonated polyaniline and a cationic gelator is described.

The architecture of conducting polymer-based nanostructures has become a topic of increasing interest due to their potential applications to electrical, optical and sensor devices.[1] Various techniques and methods have been developed for the construction of these novel structures, such as nanolithography,[2] the Langmuir–Blodgett technique,[3] chemical or electrochemical polymerization of monomers using nanoporous membrane filters,[4] porous silica,[5] surfactant aggregates,[6] liquid crystals[7] and carbon nanotubes as templates.[8] Moreover, it is also well documented that various conjugated polymers and oligomers can self-assemble into supramolecular structures both in solution and at interfaces.[9]

Thermoreversible physical gels (organogels) attract attention in view of their remarkable self-assembled structures and many potential applications.[10] Recently, we and others have explored a new method to transcribe various organic superstructures formed by organogelators into inorganic materials by a sol–gel reaction of metal alkoxides, by which one can control the morphology of inorganic compounds and create various new superstructural inorganic materials.[11,12] The driving force in this templating sol–gel reaction is considered to be electrostatic[11] and/or hydrogen-bonding[12] interactions between silica nanoparticles and organic assemblies acting as templates. In the present work, our attention has been focused on extending this novel concept into the creation of new conducting polymer superstructures by the organogel templates. Herein, we report superstructures of sulfonated polyaniline (SPAN, Scheme 1) created in chiral diaminocyclohexane-based organogel systems.

Diaminocyclohexane derivatives were used as templates due to their strong ability to form a gel with a wide variety of organic solvents.[11,13] Gelators **1** and **2** (Scheme 1) were synthesized as reported previously.[11,13] It is known that the neutral **1** is a versatile gelator for many solvents such as alcohols, aprotic, and apolar solvents.[13] On the other hand, cationic **2** can gelate a limited number of solvents such as acetone, acetonitrile, THF and DMF,[11] indicating that the gelation ability is diminished by introduction of cationic charges. First, we checked the solubility and gelation ability of SPAN and a SPAN/**2** complex formed by electrostatic interaction in organic solvents. It was found that they show poor solubility in most organic solvents due to the rigid main chain structure of SPAN, whereas they show good solubility in DMSO but cannot form the organogel even at high concentrations. In this work, therefore, mixtures of neutral gelator **1** and cationic gelator **2** were used to prepare the template in DMSO because the presence of the cationic charge is indispensable to the efficient interaction of the gel fibers with anionic SPAN.



Scheme 1 Chemical structures of diaminocyclohexane-based neutral (**1**) and cationic (**2**) organogelators and sulfonated polyaniline (SPAN).

To check the templating effect of organogelators, two series of samples were investigated as shown in Table 1, in which the molar ratio of SPAN (repeat unit) to cationic and neutral gelators was 2 : 1 : 5. For samples prepared at higher concentrations (A–D), the gel phase was formed except for sample D; whereas at lower concentrations (E–H), all samples existed as the sol phase in appearance.

In order to obtain a picture of the aggregation mode of SPAN in the gel and sol phases, all samples (A–H) were submitted to transmission electron microscopy (TEM) measurements (without staining).‡ The aggregated structures of SPAN were easily distinguished by TEM since SPAN has a higher electron density than gelators. Fig. 1 shows the TEM images of SPAN/**2**/**1** xerogel obtained from DMSO (sample A) and its film cast from dilute DMSO solution (sample E). It is clearly seen from Fig. 1 that the straight fibrous structures are constructed from SPAN in the gel phase, whereas the minute helical structures appear in the sol phase, which indicates that polyaniline superstructures were formed even in the sol-forming concentration range ($c >$ critical aggregation concentration (*cac*)). This phenomenon has been well addressed previously.[14] The helicity of the SPAN fibers created by a mixture of (*S*)-**1** and (*S*)-**2** shows a right-handed helical motif, which is consistent with that of helical silica obtained using the same gelator mixture as a template.[11] These results indicate that SPAN can form novel superstructures in DMSO with the aid of cationic and neutral

Table 1 The appearance and morphology of SPAN/**2**/**1** in samples with different component concentrations

Sample	SPAN/mM	**2**/mM	**1**/mM	Appearance	TEM[a]
A	12	6	30	gel	fiber
B	12	—	30	gel	agg
C	—	6	30	gel	ns
D	12	6	—	sol	agg
E	0.2	0.1	0.5	sol	fiber
F	0.2	—	0.5	sol	agg
G	—	0.1	0.5	sol	ns
H	0.2	0.1	—	sol	agg

[a] Without staining; agg: aggregates without defined morphology, ns: no structure.

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† Electronic supplementary information (ESI) available: transmission electron microscopy images and the gel–sol phase transition temperature. See http://www.rsc.org/suppdata/cc/b4/b408893j/

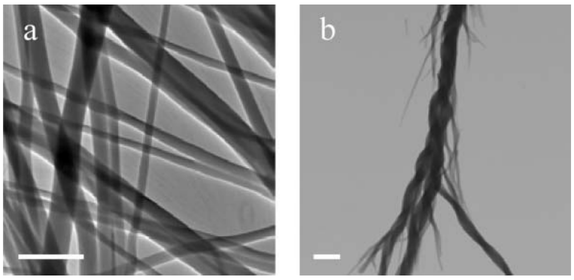

Fig. 1 TEM images of the SPAN/**2**/**1** xerogel prepared from DMSO (sample A) (a), and the film cast from its dilute solution in DMSO (sample E) (b), without staining (note that the shadows are attributed to SPAN but not to gelators); [**1**] = 1.5 wt% and the molar ratio SPAN : **2** : **1** is 2 : 1 : 5; scale bar = 1 μm.

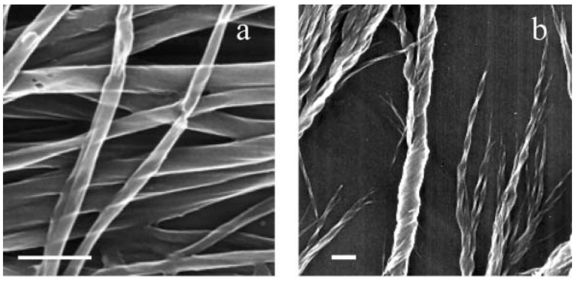

Fig. 2 SEM images of the SPAN/**2**/**1** xerogel prepared from DMSO (sample A) (a), and the film cast from its dilute solution in DMSO (sample E) (b); [**1**] = 1.5 wt% and the molar ratio SPAN : **2** : **1** is 2 : 1 : 5; scale bar = 1 μm.

organogelators. In addition, the scanning electron microscopy (SEM) pictures of samples A and E (Fig. 2) also reveal the fibrous structures for the gel phase and a characteristic right-handed helical structure for the sol phase.

To further corroborate that the organogel structure really acted as a template for creation of the SPAN superstructures, the TEM pictures for three reference systems were taken. For an organogel formed by neutral gelator **1** and SPAN, some aggregates without defined morphology were detected (Fig. S1†), which would be due to the dispersion of SPAN in the gel phase. The difference indicates that cationic gelator **2** is necessary to induce the formation of an ordered SPAN structure. When neutral **1** was not added, the SPAN/**2** complex could not form an organogel in DMSO and no ordered structure was observed by TEM. Of course, we could observe nothing for the organogel formed only from gelators **1** and **2** without staining, indicating that the shadows observed in the TEM images are ascribed to SPAN superstructures.

X-ray powder diffraction patterns of the xerogels prepared from **2**/**1** and SPAN/**2**/**1** were recorded to ascertain the molecular packing of gelators in the gel phase and the influences of added SPAN on the structure (Fig. 3). The small angle reflection peak of **2**/**1** xerogel ($2\theta = 2.6°$, $d = 33.9$ Å) is ascribed to the bilayer thickness, which is slightly smaller than twice the bimolecular length with an extended conformation estimated from a CPK model, indicative of a tilted bilayer packing structure. In the wide angle, a distinct interchain distance of 4.3 Å ($2\theta = 20.2°$) was observed, which corresponds to the distance between the intermolecular H-bonding packing structures. The xerogel of SPAN/**2**/**1** gave similar patterns and d values as **2**/**1** except for their much weaker intensities. These results indicate that introduction of SPAN somewhat disorders the packing mode of the gelators. This proposal is consistent with a change in the gel–sol phase transition temperature (T_{gel}): that is, with increase in the amount of SPAN, the T_{gel} for the gels decreases gradually from 83 °C to 74 °C (Fig. S2†).

In conclusion, the present work has demonstrated that the new superstructural morphology of polyaniline can be created by using organogelators as a template through the electrostatic interaction between sulfonated polyaniline and a cationic gelator with the aid of a neutral gelator matrix. We believe that the results shown here would open a way to obtain novel conducting polymer superstructures.

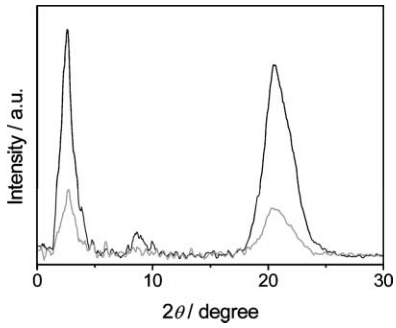

Fig. 3 X-ray powder diffraction diagrams of xerogels prepared from **2**/**1** (black line) and SPAN/**2**/**1** (grey line); [**1**] = 1.5 wt% and molar ratio SPAN : **2** : **1** is 2 : 1 : 5.

Notes and references

‡ For TEM and SEM measurements, a piece of the gel was placed on a carbon-coated copper grid and removed after 30 s, leaving some small patches of the gel on the grid, which was then dried at reduced pressure.

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