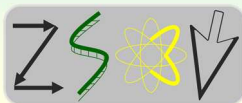


ORGANOGELES AS HYBRID AND FUNCTIONAL NANOMATERIALS

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In last ten years a special attention attracted a group of compounds capable to gelate different organic solvents and water. A new series of bis (Leu) -bisoxalamide and -bisurea gelators with different length of aliphatic chain between two nitrogens were synthesized. These series of chiral low molecular weight gelators are designed on the basis of the self-complementary oxalamide and urea units as the persistent intermolecular hydrogen bonding motif. We examined the effects of aliphatic chain length, change of the hydrogen bonding units (oxalamide or urea) and change of terminal functional groups ($R = \text{OCH}_3, \text{OH}$) on gelation properties. OXALAMIDE derivatives exhibit gelation of various organic solvents, solvent mixtures and water independently of the length of the methylene spacer.

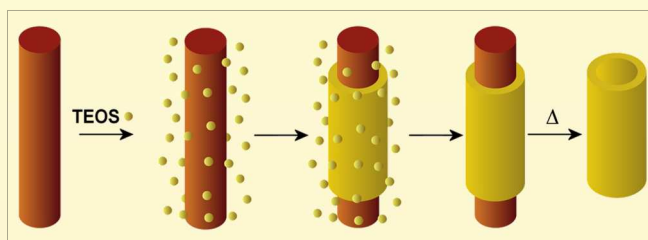
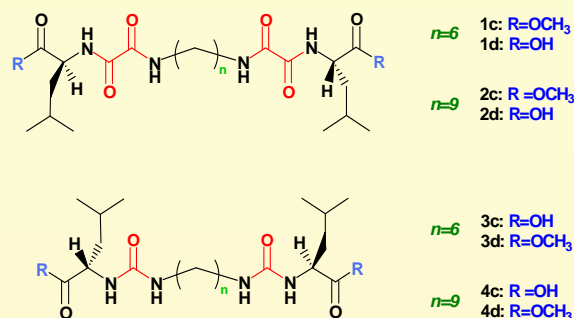


Figure 1. Scheme of sol-gel polymerization of organogel fibers

It was found that the variation of terminal functional groups ($R = \text{OCH}_3$ or OH) had the most pronounced effect on fiber morphology. The gel network can serve as template for sol-gel transcription of fibers in inorganic materials (Figure 1). To transcribe the structures formed in the organogel into their analogous SiO_2 structures, we carried out sol-gel polymerization of $\text{Si}(\text{OEt})_4$ in a gel of **2d** and **2c** in different solvents. When polymerization was completed, the product was calcined and organogelator removed from silica structure by calcination at 200°C for 2 h, then at 500°C for 2h under a nitrogen atmosphere and 500°C for 4 h under aerobic conditions (Figure 3 and 5).

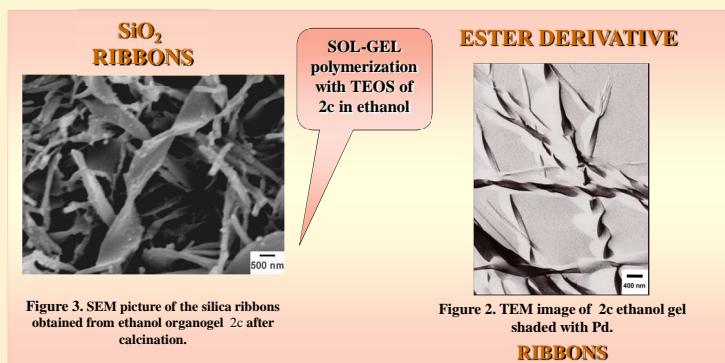


Figure 3. SEM picture of the silica ribbons obtained from ethanol organogel **2c** after calcination.

Figure 2. TEM image of **2c** ethanol gel shaded with Pd.

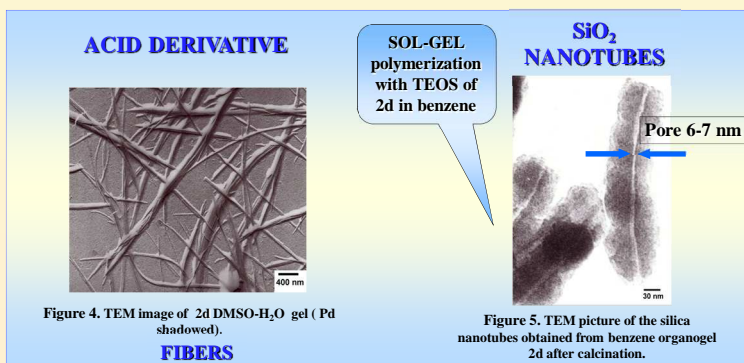


Figure 4. TEM image of **2d** DMSO-H₂O gel (Pd shadowed).

Figure 5. TEM picture of the silica nanotubes obtained from benzene organogel **2d** after calcination.

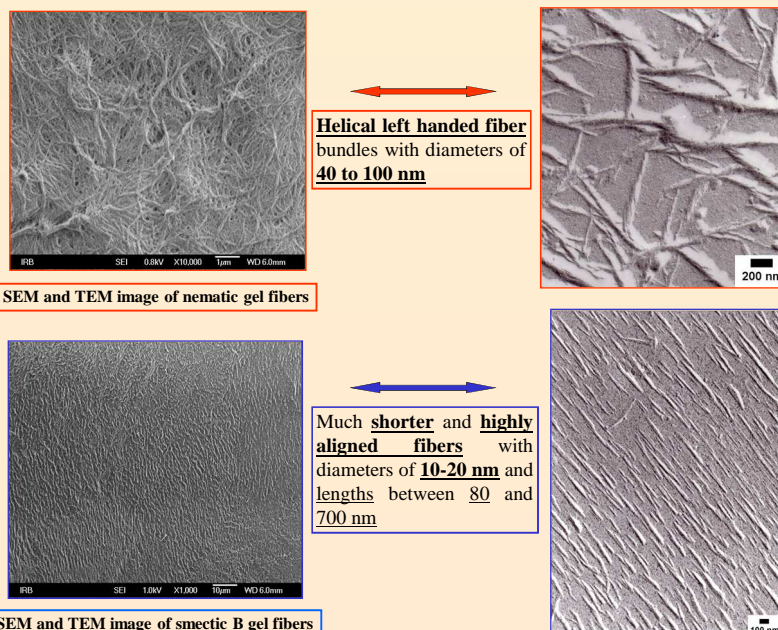
The fiber morphology determined by TEM and SEM investigations is found to be dependent on the type of terminal groups. Small changes in the chemical structure can lead to drastically different internal gel morphologies. Various silica nano-structures (nanotubes, hollow ribbons, helical SiO_2 structures) can be prepared by transcription using various superstructures in organogels as a template.

In addition, formation of liquid crystalline gels (LC gels) where a liquid crystalline phase was gelled playing a role of an ordinary solvent, represent a new type of soft materials and may possess induced or enhanced electro-optical, photochemical and electronic properties useful for construction of supramolecular devices for advanced applications. LC gels represent more complex systems consisting of a mesogen and a gelator each capable of giving different type of supramolecular organization at specific temperature.

We found that chiral gelator **2c** shows remarkable gelation capacity of the liquid-crystalline (LC) phases of *trans*-4-heptylcyclohexanecarboxylic acid. It is known that pure acid displays two mesophases, nematic and smectic B phase. When **2c** is present in the concentrations higher than 0.55 wt% it induces first the transformation of nematic into a chiral nematic (cholesteric) phase which upon further cooling is gelled by gelator **2c**.

In contrast, with **2c** present in the concentration range of 0.025 – 0.5 wt% neither chiral induction nor gelation of nematic phase could be observed. However, the subsequent transition at lower temperatures of nematic phase containing **2c** into homeotropically oriented smectic B phase triggers instantaneous self-assembly of gelator molecules into aligned fibrous aggregates.

The results described herein may open new possibilities for the preparation of LC phase-controlled self-assembled systems and production of unidirectionally aligned assemblies.



SEM and TEM image of smectic B gel fibers