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Molecular gels formed by the self-assembly of small molecules in organic or aqueous solvents have attracted widespread attention. It is known that a common factor in all gels is the presence of a network formed by fibrous assemblies. This talk will attempt to classify molecular gels into two distinct classes based on the nature of these assemblies. In many gels, the fibers have a crystalline packing, and often the crystal structure of the fibers (in a xerogel) is identical to that of the molecules in their solid crystal. It is argued that these crystalline gels are analogous to many fibrous structures found in biology, notably the amyloid plaques that have been implicated in neurodegenerative diseases. In other gels, the fibers are completely amorphous, and in these cases, the fibers are analogous to assemblies of amphiphilic molecules such as micelles. It is further argued that these amorphous fibers are comparable to filamentous structures found in the cytoskeleton of every biological cell. Crystalline and amorphous fibers (and their gels) also show distinct properties in terms of both their structural responses (e.g., via scattering techniques) as well as in their mechanical and rheological properties.

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**Keywords:** gel, scattering, rheology

## MS.03.3

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**Dynamic covalent molecular gelators: in control of soft matter properties by dynamic covalent chemistry**

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The self-assembly of small molecules, polymers, proteins, nanoparticles and colloids under thermodynamic equilibrium conditions has been a powerful approach for the construction of a variety of structures of nano- to micrometer dimensions, like vesicles, capsules, and nanotubules. Despite these advances, the permanent nature of these synthetic self-assembled structures does not compare well to the complex spatiotemporally confined self-assembly processes seen in natural systems, which for instance allow the dynamic compartmentalization of incompatible processes, responsiveness, and self-healing. It remains a challenge to develop systems in which equilibrium and kinetics of self-assembly can be independently controlled.

In our research we focus on molecular approaches which allow independent control over interaction strength and dynamics of the self-assembling building blocks [1], [2]: (i) the development of dynamic covalent gelators, leading to new supramolecular assemblies with unprecedented control of the dynamic properties, (ii) dynamic and reversible conjugated polymers, allowing easy processing in water, and (iii) dissipative self-assembly driven by a chemical fuel [3]. I will discuss the background of our approaches together with recent results, and will suggest how dynamic self-assembling systems may lead to the next generation responsive, nanostructured or self-healing materials.

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Eelkema, J.H. van Esch, *Angew. Chem.* **49**, DOI: 10.1002/anie.201001511 **2010**

**Keywords:** supramolecular chemistry, molecular gelators, dynamic self-assembly

## MS.03.4

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**The relationship between crystallisation and gel formation in low molecular weight gelators**

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Crystallisation and gel formation of low molecular weight gelators (LMWGs) are inherently related as can be witnessed by many researchers the world over [1]. We shall present results on crystallisation within LMWGs and the conversion of LMWG gels into crystals. These results will help to rationalise the relationship between gel and crystal formation.

The use of the gel matrix to control crystallisation is a well known procedure. However, LMWGs have been scarcely looked at as the gel former in this crystallisation technique. We therefore aimed, and now shall present, the control of pharmaceutical polymorphism and morphology by testing a series of LMWGs [2]. Due to their reversible physical nature, in our case using anion tuning of gelation [3,4], LMWG crystallisation may represent an exciting new addition to the crystal growth tool kit.

Many researchers have noted that many LMWGs tend to convert from a gel to a crystalline material [5]. This process is often used to help determine the structure of the gel forming solid. We shall also present our take on this “phase” change and the possible applications of this phenomenon in the context of controlling crystallisation and the lack of crystallisation leading to stable gels. By influencing assembly and disassembly of the gel components, which is related to the underlying structure, the stability in relation to the gel to crystal transformation can be controlled. As a result of this knowledge, we are able to show post-assembly modification of a LMWG at the interface of the solid and liquid phases.

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**Keywords:** gels, gel and crystal growth, post-assembly modification

## MS.03.5

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**New insights into the polymerization and structural mechanisms of the polydiacetylene DCHD: an X-ray/MEM study**

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In this work, we studied the role of bonding and nonbonding atomic interactions in the topochemically controlled solid-state polymerization and assembly of the polymer DCHD (1,6-di(N-carbazolyl)-2,4-hexadiyne). For this we carried out a high brilliance SPring-8 (Hyogo, Japan) synchrotron X-ray study of DCHD monomer and polymer crystals in the temperature range from 20 to 420 K. Since topochemical polymerization is interplay of the monomer and polymer lattices, a comparative analysis of the both monoclinic structures allows us to uncover important insights into the structural machinery controlling formation and stability of polymer DCHD.

For advance details, we examined the structures on a charge density level using Maximum Entropy Method (MEM) upgraded to determine the electrostatic potential, electric field and atomic polarization in structure [1], [2]. The MEM maps based on highly reliable polyDCHD x-ray data viewed the hydrogen bond as electron density path bridging acceptor-donor atoms, linkage of electrostatic potential contour and flux of electric field vector from donor to acceptor sites. They allow us to reveal that polyDCHD assembled by networks of unconventional H-bonds, C-H $\cdots\pi$ (C $\equiv$ C) between sidechain C-H and  $\pi$ -electron clouds of the triple bond segment of nearby backbone in layer and C-H $\cdots\pi$  amongst the interlayer carbazolyl rings packed in a herringbone motif.

In the monomer form, C-H $\cdots\pi$ (C $\equiv$ C) links the monomer's carbazolyl to the triple bond segments of the nearby monomers. The arrangement of the inter-monomer H-bonds is changed from the low-temperature trifurcated (four-centered) to the bifurcated (three-centered) at temperatures above  $T_p \sim 140$ K. As we find, the trifurcated H-bond provides conformational constraint preventing twist of monomer rods to the reactive state for the solid-state polymerization. Supposedly, it makes DCHD non-polymerizable under  $\gamma$ -ray or other radiations below  $T_p$  [3]. Declining of that constraint above  $T_p$  resulted in non-planar bifurcated H-bond arrangement which may accommodate the "monomer rods" to "polymer backbone" switch. In the resulted polymer phase, the chains strengthened by linear (two-centered) H-bonds.

Thus, in the DCHD system unconventional C-H $\cdots\pi$ (C $\equiv$ C) interactions of trifurcated and linear geometries direct the structural stability for the monomer and polymer forms, respectively, while bifurcated one triggers the solid-state monomer-to-polymer reactivity.

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**Keywords:** electron density, hydrogen bond, polymerization

## MS.04.1

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**Small-angle neutron scattering studies on catalyst ink of fuel cell**  
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Development of fuel cells has been a hot topic in materials science. The performance of fuel cells depends greatly on the microscopic structure of electrodes [1], [2]. Electrodes of fuel cells are manufactured from catalyst ink. Catalyst ink is a multi-component system, consisting of carbon, platinum, water, and ionomers. Contrast-variation small-angle neutron scattering (CV-SANS) is a powerful technique to study the structure of multi-component materials since it allows one to decompose scattering intensity functions to partial scattering functions [3]. In this study, we employed CV-SANS to unveil the structure of

catalyst ink and discuss the relationship between the structure and performance of fuel cells.

Various types of catalyst ink were prepared by varying the size and porosity of carbon in water with various compositions of D<sub>2</sub>O/H<sub>2</sub>O. CV-SANS was conducted at the small-angle neutron instrument, SANS-U, JRR-3 [4]. Contrast-variation SANS revealed the following: (1) The partial scattering functions for carbon-carbon,  $S_{cc}(q)$ , polymer-polymer,  $S_{pp}(q)$ , and carbon-polymer correlations,  $S_{cp}(q)$ , were successfully obtained by CV-SANS. (2) The microscopic structure of the catalyst ink consists of dendric clusters of carbon particles surrounded by ionomers. (3) Ionomers have an ionic cluster peak around  $q \approx 0.1 \text{ \AA}^{-1}$ , which maintain its structure even in the ink mixed with carbon/Pt. (4) The cross term, i.e.,  $S_{c}(q)$ , indicates that ionomers are concentrated on a surface of carbon clusters.

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## MS.04.2

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**Industrial SAS activities at European facilities ESRF and ILL**  
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Large scale synchrotron and neutron facilities offer very efficient tools to analyze the structure of materials using the small-angle scattering technique (SAS). In short, the modern synchrotron rings deliver several million times more intense X-ray beams than those emitted by conventional laboratory sources, allowing the follow-up of real-time evolutions. In addition, the low divergence leads to a sub-micrometer spatial resolution for the micro-analysis and the imaging techniques. SAS using a neutron source opens the possibility to match the contrast for organic materials working with deuterated samples. SAS beamlines at large scale facilities are today used for industry-driven projects, either directly by engineers from companies or by public institutes. The projects concern the various phases of a product life-cycle, mainly for the research and development phases, but also the engineering and the control of quality. A few examples in various domains will be presented, among which: the ageing of the structural components of nuclear reactors under neutron and gamma irradiation, the molecular structure of epidermis and hair in relation with cosmetics, the development of new polymers and composites.

However, despite the obvious interest of the SAS measurements for applied activities using large facilities' equipment, the rate of industrial use is low compared to that of other techniques. The main reasons for this situation are probably: an insufficient communication and commercial effort, the cost and the delays for getting access to the beamlines, the lack of optimized equipment and scientific expertise for industrial issues.

In order to improve the interface between their equipment for the analysis of soft-condensed matter, including SAS, and the communities of users, academic as well as industrial, the ESRF and the ILL have recently launched the *Partnership for Soft Condensed Matter* (PSCM). The PSCM will be established in a step-by-step process, initially as a support facility for the better exploitation of neutron and synchrotron scattering instruments in Soft Matter Research. The PSCM, in the medium term, will provide a platform for promoting the complementary aspects of neutron and synchrotron techniques. The long-term mission