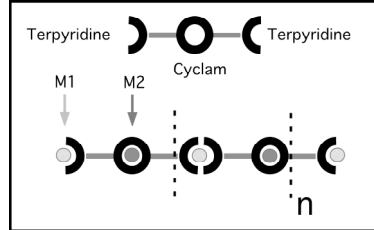


Multiresponsive metallo-supramolecular polymers (SC2197).

A series of metallo-supramolecular polymer systems were investigated in which the type of metal ion, the location of metals in the 2 coordination sites available (cyclam and terpyridine grafts-see Scheme 1), the type of solvent and counter-ion, the redox state were varied. In the present experimental report, we analyze a first selection of data that aims at characterizing the non-aggregated *versus* aggregated states of the system under the above mentioned conditions.



Scheme 1: The two coordinations sites used to form homo or hetero metallic sequences.

Once the coordination sites are occupied, a linear aggregation phenomenon develops. If the length turns to be large enough, the macroscopic flowing properties of the systems become that of supramolecular gels. Apart from this simple description, more sophisticated situations may occur that require a refined analysis (under progress). Indeed, the cyclam site may adopt 5 different conformations that may also favor some lateral aggregation or entanglement mechanisms between the genuine fibrils. The length of such "equilibrium polymers" are classically governed by the concentration, temperature but also by the stoichiometry (number of metallic equivalent per monomer), type of metallic element and its redox state, type of counterion and solvent. The analysis uses the single-particle approximation (expression 1) since the low concentrations that are used ($\sim 0.3\%$) favor a clear identification of the typical scattering features for a 1D aggregate (Q^{-1} low- Q decay associated to a Guinier behavior and a form-factor oscillation at large Q).

$$I(Q) = \left| 4\pi L r^2 \Delta\rho \int_0^{\pi/2} \frac{\sin(QL \cos\theta)}{QL \cos\theta} \frac{J_1(Qr \sin\theta)}{Qr \sin\theta} \sin\theta d\theta \right|^2 \quad (1)$$

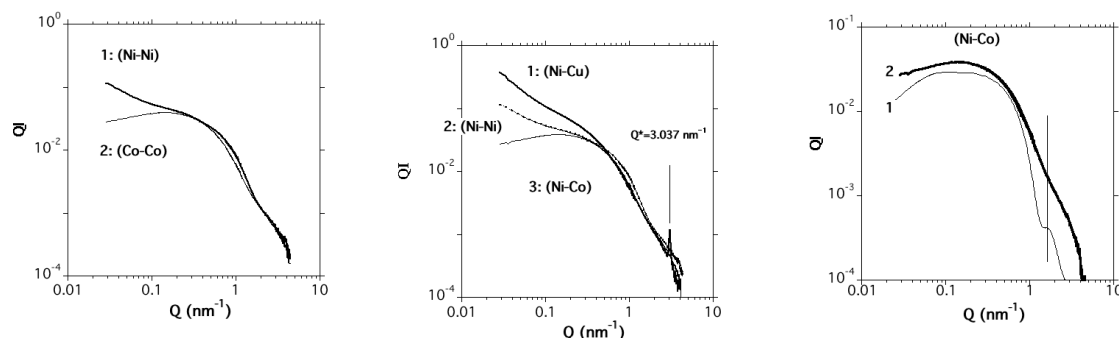
When all the sites are not occupied, it is reasonable to expect a significant fraction of short rods in the solutions or viscoelastic solutions. The molecular weight of the supramolecular polymers is in thermal equilibrium and the associated length is expected to be very polydisperse. Expression 1 is to be convoluted with a distribution function such as the Flory-Schulz's one.

$$\langle I(Q, L, l_p) \rangle_z = \frac{\int N(L) L^2 I(Q, L, l_p) dL}{\int N(L) L^2 dL} \quad (2)$$

Figure 1, left illustrates the effect of the metal type (between Ni and Co) on the corresponding scattering curves. The Holzer representation is used to facilitate the identification of a Q -domain where a plateau is associated to the existence of long fibers (Ni) and a broad bump to the existence of rods (Co). A broad bump is seen at $Q \sim 2.2 \text{ nm}^{-1}$ indicating that the fibers have a rather polydisperse cross-section (diameter $\sim 5.0 \text{ nm}$). At very low- Q ($Q < 0.1 \text{ nm}^{-1}$), an extra-scattering (with respect to the plateau reference) is observed with NiNi that is assumed to account for the entanglement zones of the gel network.

Figure 1-center, shows that the proportion of rods in the system is dependent on the sequence of metallic cations inserted in the coordination sites. All of them form fibrillar structures of comparable diameters (see large- Q decay and loose oscillation). Interestingly, in the case of the copper complex (Ni-Cu sequence), a very well-resolved diffraction peak is observed at $Q = 3.0728 \text{ nm}^{-1}$ ($\langle d \rangle \sim 2.05 \text{ nm}$) the origin of which is still a debating issue (lateral packing of fibers in the entanglements zones?).

Figure 1-right, shows an example of the modeling for short rods (non-convoluted with a FS distribution) and showing the qualitative agreement of the approach.



Figures 1:

Left: Comparison between NiNi and CoCo supramolecular polymers in DMF at $C \sim 0.5 \%$ (counter-ion is Cl-): QI versus Q scattering curves. Center: Hetero metallo polymers: role of the metallic sequence on the proportion of short rods. Right: thin curve 1, example of a theoretical modeling of the scattering by short (monodisperse in length) and polydisperse in diameter ($\Delta r/r \sim 0.22$, $r_0 = 2.7 \text{ nm}$, $L/2r_0 = 5$) ; bold curve 2, experimental data for a Ni-Co complex.

At this stage, the SAXS technique has been successfully applied to this class of multiresponsive metallosupramolecular polymers. The non-aggregated state is characterized by the absence of coherent scattering in a purely liquid system (for the appropriate choice of Redox conditions-the electrolytic set-up was transported on the ESRF site- or metallic stoichiometry). The aggregated state was characterized by the presence of a scattering that can be interpreted as a network of entangled long fibers (gels) or a suspension of short rods (viscous solutions or loose gels) depending on the type of metallic cations and stoichiometry and following expression 1.