

# STRUCTURAL PROPERTIES OF HELICAL SELF-ASSEMBLED POLYMERS WITH HYDROGEN-BONDING.

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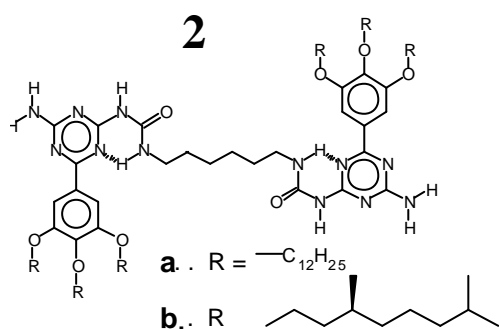
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SANS allows us to establish and follow self-assembly of molecules into polymers of controlled length, shapes and chirality, with chemistry enabling a rich variety of interactions.

First interactions are **hydrogen bonds** : ureidotriazine is the elementary unit which associates via a quadruple hydrogen bond with another ureidotriazine, see sketch below. Molecule (1), **monofunctional** (as far as H-bonds are concerned), selfassociates into **dimers**. Molecule (2), **bifunctional** (two ureidotriazines linked covalently) forms **H-bonded chains**.

A second attraction implies 1 as well as 2, the **stacking of the extended p-p-surfaces** of both molecules. Such solvophobic interaction can induce **columnar order**.

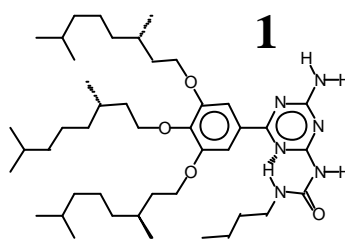
Thirdly, **side molecules** (R = a or b in Figure) gives a third control : they stabilize the self-assembly, and if they possess **chirality** (case b) they can induce it along the chain (for reasons clarified below, we focussed on 1b, 2a and their mixture).



Therefore, all interactions depend on the **type of solvent**. DiMethylFormamide kills both **hydrogen and p-p bonds**. In **chloroform** (deuterated for SANS), **H-bonds take place** : large particle scattering is observed for 2a (**random chain**), but not for the *monofunctional* molecules (1b) which only exist as dimers<sup>3</sup>. In (deuterated) **dodecane** solutions both 1 and 2

display **columnar architecture**. Scattering patterns for 1b have been fitted by the cylindrical-like form factor : the radius, 15 (± 1) Å, is independent on concentration, matching nicely with a column built up of stacked dimerized molecules of 1b. The length of the columns is concentration dependent and increases from 100 Å for a 0.2 wt.% solution to 190 Å for a 1.0 wt.% solution (~ 60 molecules). At **elevated temperatures** (~ 100 °C) the scattered intensity decreases strongly : the molecules only exist as dimers as in chloroform at room temperature, because the  $\pi$ - $\pi$  stacking is overcome (**figure 2**).

The scattering of 2a in dodecane has also been fitted to a cylinder form factor (interpretation at higher concentrations is hampered by inter-columnar gelation). The radius is constant, 17 (± 1) Å, larger than for 1b in agreement with the difference in side-chain length of (a) and (b).



We can also make a **chain-stopper experiment**: monofunctional 1b is mixed with bifunctional 2a in deuterated dodecane, at constant 0.5 wt.% concentration (**figure 1**). The radius of the columns slowly changes from 17 to 15 Å as expected, while the length decreases rapidly after addition of small amounts of 1b, showing the formation of shorter and less stable columns than pure bifunctional 2a. The length of the columns is

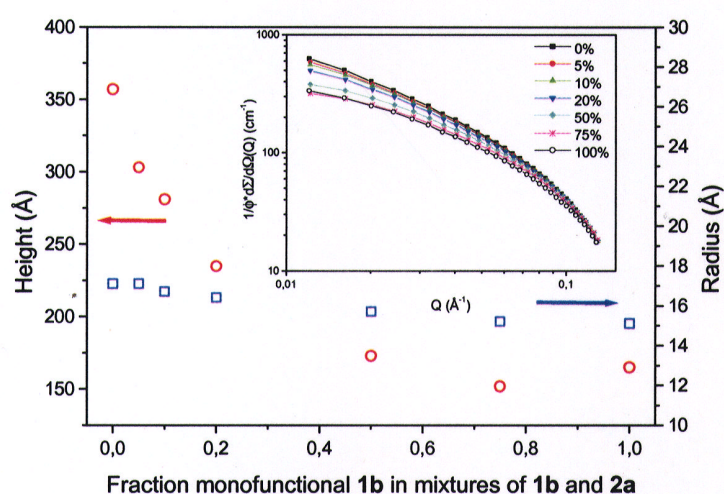
shorter for **1b** due to the absence of the supramolecular polymeric backbone created in **2a** by the covalent links between pairs of H-bonded ureidotriazine units.

This shows how precise can be SANS investigation of these assemblies, in various solvents as soon as they are deuterated ; extensions like contrast variation, partial deuteration, are obvious. From such basis, **most interesting is combination of SANS measure-**

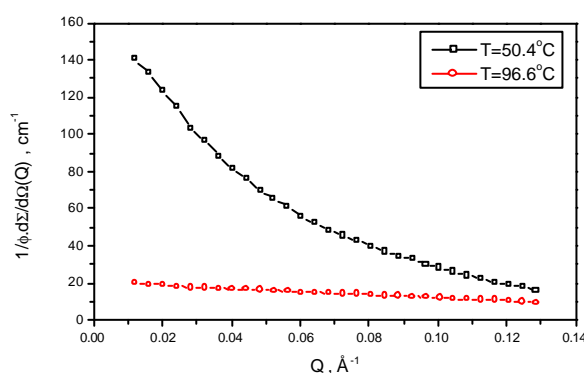
**ments with circular dichroism** : it allows us to see how helicity can be controlled by

the chirality of the R radicals together with strength and shape of the assemblies. E.g., **1b**, in spite of its end position in a **1b/2a** chain, can induce helicity all along the **2a** sequence.

Finally, let us stress that such selfassembly can occur in water, since aromatic regions creates a hydrophobic environment, preventing water to kill H-bonds. One can then fully control such synthetic helices, which can be compared to DNA assemblies in biology.



**Figure 1.** Height (circle) and radius (square) of columns formed by a **2a + 1b** mixture at a constant total weight percentage (0.5 %). Inset : corresponding observed scattering patterns in log-log plots.



**Figure 2.** Temperature effect on SANS from monofunctional (1b) solution in dodecane at 0.96% (v/v) concentration

1. Lehn, J.-M., Makromol. Chem. Makromol. Symp. **1993** 69, 1.
2. Sijbesma, R.P.; Beijer, F.H.; Brunsveld, L; Folmer, B.J.B.; Hirschberg, J.H.K.K.; Lange, R.F.M.; Lowe, J.K.L.; Meijer, E.W. *Science* **1997**, 278, 1601.
3. Hirschberg, J.H.K.K.; Brunsveld, L; Ramzi, A.; Vekemans, J.A.J.M.; Sijbesma, R.P.; Meijer, E.W. *Nature* **2000**, 407, 167.