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Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

http://193.49.43.2:8080/smis/servlet/UserUtils?start

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title: Study of the Growth of Supramolecular Polymers Based on Hydrogen-Bonding in solution.**	**Experiment number**: SC-931
Beamline: BM02	**Date of experiment**: from: 29 August 2001 to: 31 August 2001	**Date of report**: 01 March 2001
Shifts: 3	**Local contact(s)**: Dr Cyrille ROCHAS	*Received at ESRF:*

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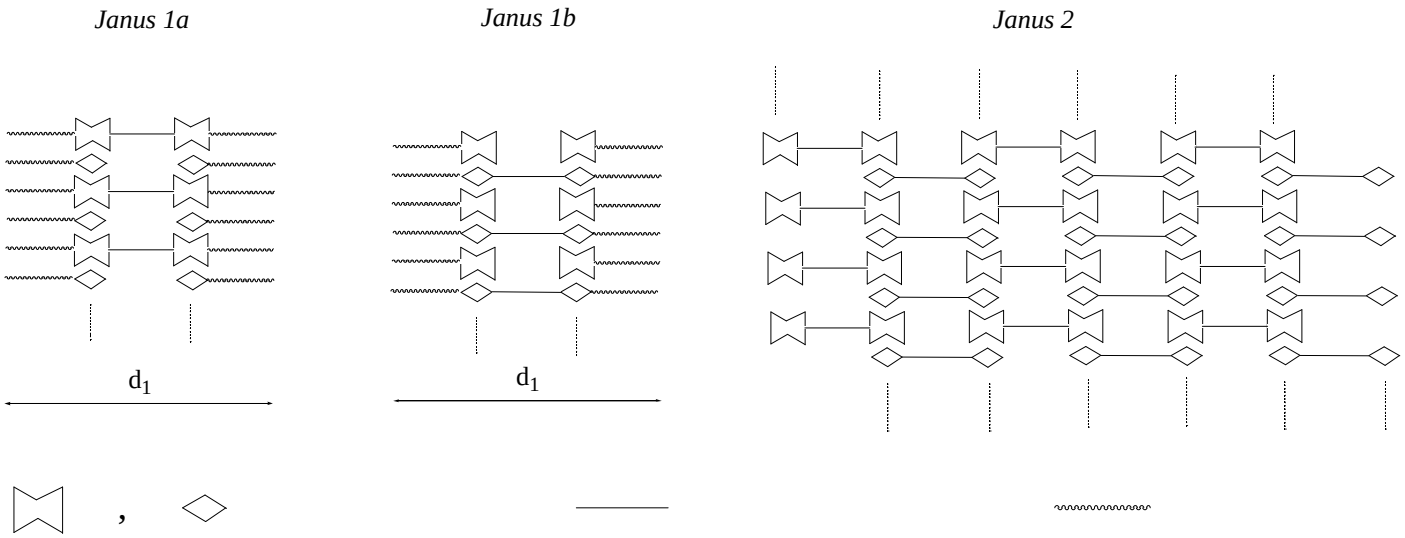
Report:

In the course of our studies on supramolecular polymers based on hydrogen-bonding, we introduced Janus-type recognition sites (Scheme 1), capable of reversible binding into predicted ribbon-like (*Janus 1a* and *1b*) and sheet-like (*Janus 2*) "primary" structures.



Scheme 1

Recent static laser light scattering experiments combined with Transmission Electron Microscopy showed that huge aggregate form in toluene, chloroform and THF dilute solutions with unexpected distinct behaviours of *Janus 1a* and *1b*.

ESRF X-Ray Scattering on concentrated samples proved to be a valuable tool in comparing the structural and dynamic behaviours of these systems in different solvents.

¤ In toluene, *Janus 1a*, *1b* and *2* show identical $\Delta Iq^2/c = f(q)$ profiles (where $\Delta I = I_{obs} - I_{solv}$, and c is the concentration of the polymer g/L), consistent with rod like structure, very little influenced by temperature. Indeed, in such a non polar solvent, the hydrogen bonds, which are responsible for polymer formation and growth, are expected to be rather robust. Nevertheless, the size of the assembly seems to depend strongly on concentration, as illustrated by Fig.1

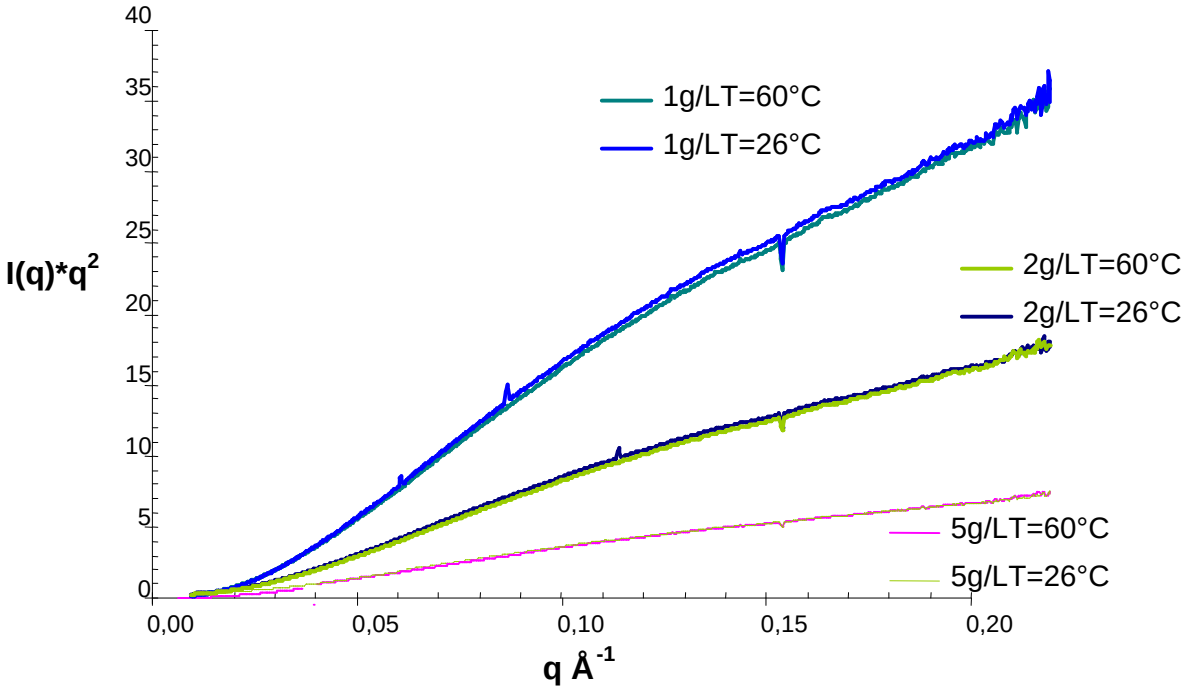
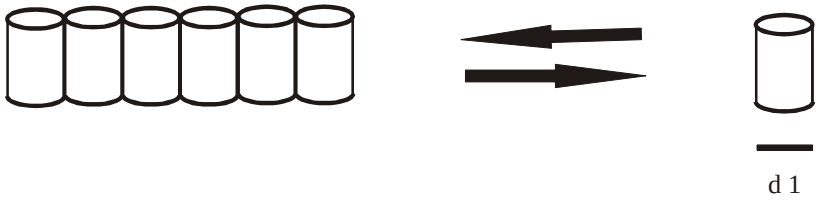


Figure 1 : *Janus 1b* in toluene; temperature / concentration dependance

¤ In THF, *Janus 1b* shows nearly the same high stability and concentration dependence, with profiles in agreement with a rod-like structures, whatever temperature and concentration, indicating relatively strong association in THF.

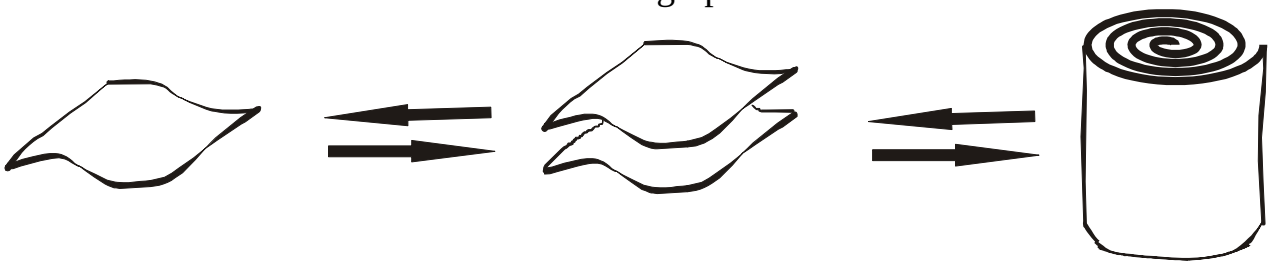
On the contrary, *Janus 1a* and *Janus 2* are more sensitive to heating, all the more so as they are dilute.

In particular, heating a 0.5 % solution of *Janus 1a* from 23°C to 60°C gives rise to a transition between a population composed mainly of rod-like species to a population of smaller cylinder-like assemblies (cf scheme 2), the diameter of which corresponds to the width of a single ribbon (d_1 in scheme 1). Interestingly, the high temperature state can be retained by fast cooling of the cells, indicating slow re-equilibration under the experimental conditions.



Scheme 2 : Proposed mode of self-association of *Janus 1a* in THF

Structural changes seem to occur to *Janus 2* according to concentration. In dilute solutions (0.4 g/L), rod-like species predominate, with a Bragg signal that can be assigned to the overlay of sheets (*assembled sheets* in scheme 3). When concentrated, the same compounds contains a large proportion of cylindrical species (*"cigar-like" cylinder*, scheme 3), such as those observed on the electron micrographs.



sheet *assembled sheets* *"cigar-like" cylinder*

Scheme 3 : Proposed mode of self-association of *Janus 2* in THF

Thus temperature and concentration dependent RX scattering at the ESRF confirmed tendencies observed using static laser light scattering and transmission electron microscopy, and largely contributed to the elucidation of the hierarchical mode of self-assembly of those supramolecular polymers.

Further studies are on going in order to validate the proposed models.