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ESRF

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:** Multiscale Caracterizations Of Cryogels For Biomedical Applications	**Experiment number**: 02 01 702
Beamline:	**Date of experiment**: from: June the 15th 2006 to: June the 19th 2006	**Date of report**:
Shifts:	**Local contact(s)**: Dr. Françoise Bley	*Received at ESRF:*

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Report:

Cryogels are highly interconnected porous gels that are synthesised upon cryogenic treatment of systems potentially capable of forming a gel. Cryotropic gel formation proceeds in a non-frozen microphase existing in the macroscopically frozen sample. **Interconnected** systems of **macropores** and sponge-like morphology are typical for cryogels. Structural and mechanical properties of these materials are controlled by the temperature of cryogelation, monomers and crosslinker concentration, the time the sample is kept in a frozen state, the freezing/thawing rates, the nature of the solvent, and the use of soluble and insoluble additives, between others. The unique macroporous morphology of cryogels, the facility of the process technology, in combination with osmotic, chemical and mechanical stability, make them very attractive matrices for tissue scaffolding and separation media for biological fluids (protein aggregates, membrane fragments, viruses, cell organelles and even whole cells) [1].

The aim of this project was the systematic characterization of new efficient macroporous biomaterials (monolithic cryogels) for biomedical applications. Different families of cryogels based on acrylic acid (AA) and 2-hydroxyethyl methacrylate (HEMA), *N*-isopropylacrylamide (NIPA) or chitosan (CHI) were studied. The influence of several parameters (temperature of polymerization, monomer concentration, crosslinker concentration…) on the structure of these materials was evaluated. To this end small-angle scattering (SAXS) measurements were performed over a broad range of wave vector q.

Two different experimental set-ups were used. The incident energy was set to 15.193 keV ($\lambda = 0.77$ Å) and the sample-to-detector distances were 206.4 and 35 . 1 cm. These configurations provided data in the range $\sim 4\times10^{-3}$ Å$^{-1} \le q \le 1$Å^{-1}, the beam-stop was a small pillar 2 mm diameter lead wire. An indirect illumination CCD detector (Princeton Instruments), cooled by a Peltier effect device, with pixel size d=50μM was used.

In order to show an example of the type of information that is obtained from this series of experiments, we analyse here the SAXS curves obtained for samples derived from cryogels based on NIPA and crosslinked with a new pseudopeptide crosslinker. NIPA monomer gives rise to temperature-sensitive polymers when

polymerized in the right proportion. These materials undergo a volume phase transition (shrink) when heated above their *lower critical solution temperature* (LCST).

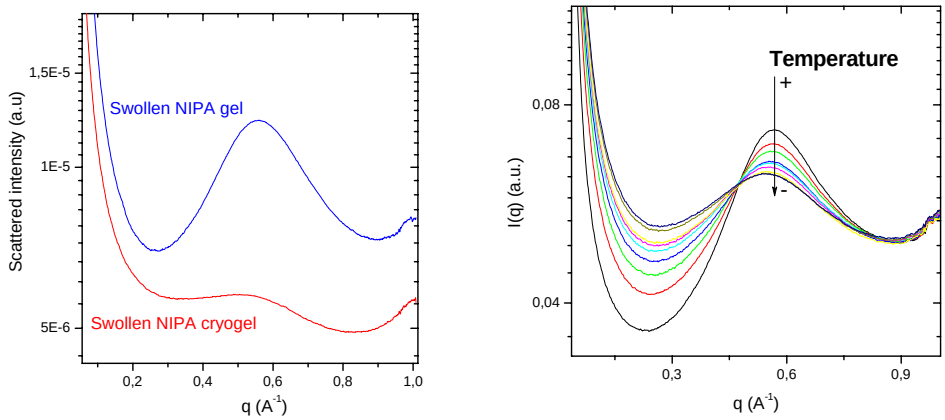
Structure of NIPA conventional gels (synthesised at 50ºC) and cryogels (synthesised at -12ºC) in the dried and swollen state were compared using SAXS. Both materials presented a clear peak at 0.55 $Å^{-1}$ when dehydrated that decreased in the swollen gels and almost vanished in the swollen cryogels (Figure 1). This features indicated the existence of a well-defined structure in the studied gels [2], as clusters with different glass transition temperatures dispersed in the gel. Intensity of the peak increased with the concentration of the crosslinker, which pointed out that it facilitates cluster formation.

Swollen cryoNIPA was heated at 60ºC and let it cool down inside the apparatus. When swollen cryogels were heated and cooled above and bellow the LCST, the peak at 0.55 $Å^{-1}$ increased and decreased reversibly indicating that the sample recovers its original structure after several heating-cooling cycles. The peak is slightly shifted to lower *q*. This feature indicates a swelling of the sample due to the change from hydrophobic to hydrophilic character of NIPA above and bellows it's LCST. Figure 2 shows the evolution of the SAXS during the cooling process (the black curve was obtained at temperature above the LCST of the polymer).

From this series of experiments it may be concluded that:

- SAXS is good technique for the characterization of cryogels, and particularly of smart-cryogels
- The structure of conventional gels (obtained at 50ºC) and the structure of cryogels (obtained at sub-zero temperatures) are different in the swollen state as cryogels almost loosed their well-defined organization (peak at 0.55 $Å^{-1}$).
- Cryogels recovered their structure reversibly during heating and cooling cycles
- Additional SAXS measurements would be necessary to understand the arrangement of the polymeric chains in the cryogel walls, which is probably responsible of the remarkable properties (fast T-response, shape memory, better mechanical and chemical stability…) of these materials

Analysis of the data for the other series of materials is currently in progress.



References

[1] Polymeric cryogels as promising materials of biotechnological interest. V. I. Lozinsky, I. Yu. Galaev, F. M. Plieva, I. N. Savina, H. Jungvid, B. Mattiasson, *Trends in Biotechnology* (2003) 21 (10), 445.

[2] Microphase separation in dehydrated N-isopropylacrylamide/sodium acrylate gel. M.Sugiyama, S. Kawajima, Y. Soejima, A. Nakamura, N. Hiramatsu, T. Kikukawa, A.Suzuki, K. Hara, *Jpn. J. Appl. Phys. 38* (1999) L1360-L1362