



Experiment title: Slow relaxation in PNIPA gels at volume phase transition

Beamline: ID10	Date of experiment: from: 31 Oct, 10 Nov to: 14 Nov 2005	Date of report:
Shifts: 18	Local contact(s): A. Moussaid, A. Fluerasu	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):

***K. László, Department of Physical Chemistry Budapest University of Technology**

K. Kosik, Department of Physical Chemistry Budapest University of Technology

***E. Geissler, Laboratoire de Spectrométrie Physique, Université J. Fourier de Grenoble**

***C. Rochas, Laboratoire de Spectrométrie Physique, Université J. Fourier de Grenoble**

Report:

In this experiment (SC-1861) X-ray photon correlation spectroscopy measurements were made on the thermosensitive hydrogel poly(N-isopropyl acrylamide) (pNIPA) in the unstable high temperature swollen state. Above 34°C these gels undergo a volume phase transition in which the sample turns white and solvent (water) is expelled from the network. Depending on the cross-link density, deswelling can be either extremely fast or, on the contrary, very slow [1,2]. The questions we wished to investigate are: what is the space filling structure of the gel in the high temperature intermediate state, and what is its dynamics?

The XPCS data were collected using a 12 micron pinhole for the incident beam and a direct illumination CCD. For this experiment the use of a fast shutter was essential to preserve the sample from beam damage. This was controlled by working with an appropriately low duty cycle.

The SAXS properties of this system are dominated by surface scattering (Fig 1), yielding an internal surface area in the swollen gel of about 50 m²/g. The XPCS observations revealed the presence of a "fast" relaxation process with a relaxation rate Γ of the order of 10⁻²-10⁻¹ s⁻¹ [3]. This relaxation is too fast to account for the overall deswelling mechanism. An additional, much slower, relaxation, of the order of 10⁻⁴ s⁻¹, was also observed (Figure 2), but was not reproducible, probably because it is at the limit of detectability in the experimental time window. The autocorrelation function of the fast decay displayed a compressed exponential form, $\exp(-(\Gamma t)^n)$, where $n \approx 1.5$. Γ is approximately proportional to q , suggesting that the unstable high temperature state of the gel is a jammed system (Figure 3).

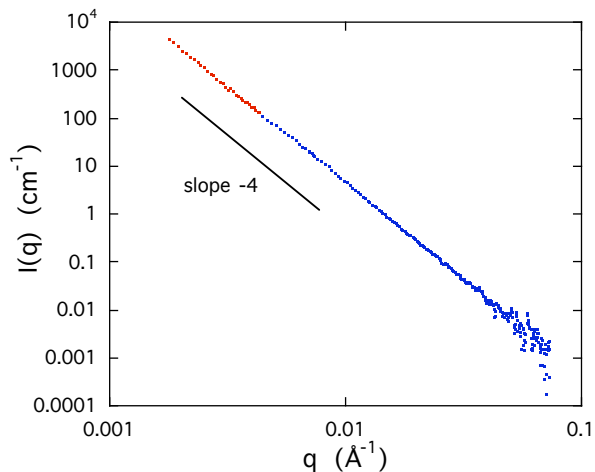


Figure 1. Integrated scattering from pNIPA (data from BM2 and ID10).

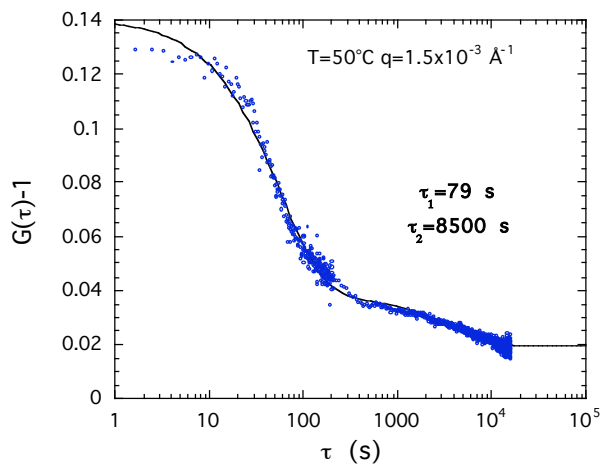


Figure 2. Intensity correlation function showing fast and slow relaxation at $q=1.5 \cdot 10^{-3} \text{ \AA}^{-1}$. Continuous line is fit to a 2-exponential decay.

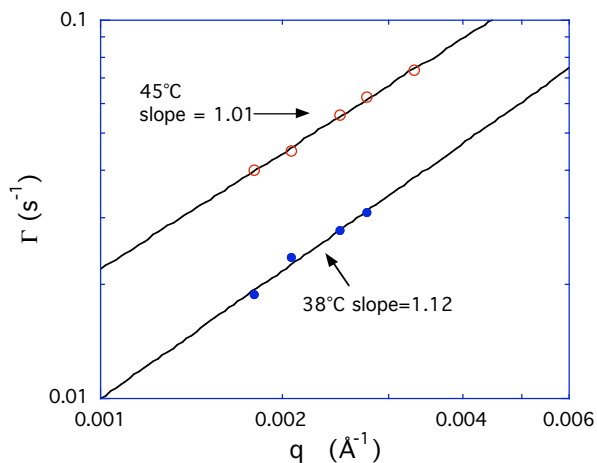


Figure 3. q -dependence of fast relaxation rate Γ

These results were reported in an invited lecture at the ESRF Workshop on soft matter in February 2006 [3].

References

1. Kinetics Of Volume Phase Transition In Poly(N-Isopropylacrylamide) Gels.
T. Okajima, I. Harada, K. Nishio, S. Hirotsu *J. Chem. Phys.* **116**, 9069 (2002).
2. High-sensitivity isothermal and scanning microcalorimetry in PNIPA hydrogels around the volume phase transition
K. László, K. Kosik, E. Geissler *Macromolecules* **37**, 10067-10072 (2004)
- 3 DLS and XPCS in Thermosensitive Gels
E.Geissler, A.Fluerasu, A.Moussaïd, K.Kosik, K.László, *Workshop on Dynamical Phenomena in Soft Matter* ESRF February 2006.