

Detailed description of sample preparation and XPCS experiments

The gel precursor solutions contained N-isopropyl acrylamide (NIPA) with (N,N'-methylenebisacrylamide) (BIS) as cross-linker with monomer mass ratio NIPA/BIS=150 and total monomer concentration 9% w/w [S1]. After polymerization, the samples were washed in water to remove unreacted monomers and allowed to swell to equilibrium. Sample A was used without further treatment, while sample B was dried over concentrated sulphuric acid for several weeks before being re-swollen in water at room temperature. Sample C was a PNIPA gel co-polymerized with a crown ether, which acts as a bulky spacer in the network structure [S2]. In the direct measurements of the gel deswelling in Figure 3, least squares fits for the values of v are A : 3.1×10^{-7} cm/s, B : 5.5×10^{-4} cm/s, and C : 1.8×10^{-3} cm/s.

The intense multiple scattering of visible light by PNIPA gels above T_{VPT} is a major impediment for studying this system by dynamic light scattering. For this reason, XPCS, owing to the relatively weak scattering of X-rays by hydrogenous materials, was used for dynamic observations. The XPCS measurements were made on beam line ID10A at the European Synchrotron Radiation Facility, Grenoble, France, at wavelength $\lambda=1.5$ Å and resolution $\Delta\lambda/\lambda=3 \times 10^{-4}$. The photon flux through the 8 μm defining pinhole was approximately 3×10^9 photons/s. Unwanted scattering from the pinhole was removed by guard slits placed approximately 25 cm downstream. Intensity correlation functions $g_2(t)-1$ were collected from the direct illumination CCD detector by taking spatial averages of the correlation functions from a large number of pixels forming a ring having the same value of q . The temperature dependence of the relaxation rate $\Gamma=vt$ can be described by an activation energy $E=74 \pm 11$ kJ/mol, in consistency with the findings of Zhao et al. [S3].

As stated in the text, when the sample moves uniformly with a centre of mass velocity u with respect to the beam, the decay of the intensity correlation function in photon correlation experiments is affected in two ways. Firstly, the region of the sample exposed to the beam is renewed after a time R/u , where R is the radius of the incident beam at the sample. The resulting decay is modulated by a factor $(1- ut/R)$, the analytical form of which depends on the cross-sectional geometry of the beam. Secondly, when the incident beam is divergent, the whole scattering pattern shifts in the same direction as the sample. In the present case where the beam is defined by a pinhole of radius R_0 , the angular divergence of the emerging X-ray beam is

approximately λ/R_0 , and the rate of loss of coherence at the detector is u/R_0 . When integrated over a ring of detector pixels having the same value of q , an additional factor $(1-ut/2R_0)$ applies to the decay of the intensity correlation function. Neither of these contributions depends on q , and their effect in the present measurements was too small to be observed.

Supplementary References

- [S1] K. László, K. Kosik, E. Geissler, *Macromolecules* **37**, 10067-10072 (2004).
[S2] K. Kosik, E. Wilk, E. Geissler, K. László, *J. Phys. Chem. B* **112**, 1065-1070 (2008).
[S3] Z.X. Zhao, Z. Li, Q.B. Xia, E. Bajalis, H.X. Xi, Y.S. Lin *Chem.Eng. J.* **142**, 263–270 (2008).