X-ray Photon Correlation Spectroscopy of Dynamics in Thermosensitive Gels

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Summary: Temperature-sensitive hydrogels undergo a volume phase transition (VPT) when heated above a critical temperature T_c. For the poly(N-isopropyl acrylamide) (PNIPA)-water system, $T_c = 34$ °C. Below T_c the gels are transparent and highly swollen. On warming above T_c they promptly turn white and start to deswell. The rate of deswelling, however, can be orders of magnitude slower than that of swelling below T_c. The unstable intermediate structure above T_c, can retain the solvent and conserve the sample volume for may days, even with millimetre-sized samples. Light scattering observations of the internal structure of these gels above T_c are precluded by their strong turbidity. Small angle X-ray scattering measurements (SAXS), on the other hand, are less subject to multiple scattering as X-rays penetrate more easily into the bulk material. Conventional (incoherent) SAXS observations reveal intense scattering from smooth internal water-polymer interfaces with an estimated surface area of about 7 m^2/g in the swollen gel. The dynamics in the off-equilibrium high temperature state, investigated by X-ray photon correlation spectroscopy (XPCS), displays a relaxation rate that is linearly proportional to the wavevector q, rather than to q^2 as in diffusion processes. The physical origin of this relaxation is consistent with *jamming*, a phenomenon that is common in other disordered systems.

Keywords: deswelling; jamming; poly(N-isopropyl acrylamide); small angle X-ray scattering

Introduction

Temperature-sensitive hydrogels have for many years been subject to intense scientific scrutiny with a view to their potential applications in biomedical or microfluidic devices. The most studied of these temperature sensitive gels, poly(N-isopropyl acrylamide) (PNIPA), for example, undergoes a phase transition (VPT) when heated above the critical temperature $T_c =$ 34 °C.[1,2] Below T_c the gels are transparent, hydrophilic and highly swollen, the rate of swelling being governed by a collective diffusion coefficient D_c, which at room temperature is about 4×10^{-7} cm^2/s. On warming above T_c they become hydrophobic and promptly turn white, then start to deswell. The rate of deswelling, however, can be many orders of magnitude slower than that of swelling at lower temperature.[3,4] Since such slow deswelling rates may be detrimental in many applications, it is important to understand the underlying process. The object of this study is therefore to determine the structure of the unstable high temperature state and to understand its mechanism of deswelling.

Above T_c, therefore, an unstable intermediate structure develops in the gel that retains the solvent and conserves the

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sample volume. The occurrence of water blisters at the surface of these samples (Figure 1) might suggest that the intermediate state of the bulk gel has a bubble structure in which the water decomposes into droplets, each enclosed in a hydrophobic polymer skin. The strong turbidity, however, precludes light scattering observations of the internal structure of the gels. Small angle X-ray scattering measurements (SAXS), on the other hand, being less subject to multiple scattering, can more easily probe the bulk material.

This paper first reports SAXS measurements using synchrotron radiation as an incoherent source to analyse the structure of these gels. Second, on increasing the spatial coherence of the beam with a small aperture configuration, the dynamics is measured by X-ray photon correlation spectroscopy.

Experimental Part

The experimental observations were conducted at the insertion device line ID10 at the European Synchrotron Radiation Facility in Grenoble. Complementary incoherent measurements were also made at the bending magnet beam line BM2. For the spatially coherent beam, the source was defined by a 12 μm pinhole placed before the sample. Guard slits positioned immediately in front of the sample eliminated unwanted scattering from the pinhole. For the sample-detector distance used, the 22 μm pixel size of the direct illumination CCD detector (Princeton) corresponded to a single coherence area. To reduce radiation damage, a fast shutter exposed the sample to the beam only during the data acquisition duty cycle.

The PNIPA samples were prepared by co-polymerizing N-isopropyl acrylamide with N,N′ methylene bisacrylamide (Waco and Aldrich, respectively) in a molar concentration ratio of 150:1, in presence of ammonium persulphate and N,N,N′,N′ tetramethylene diamine.[4] The 2 mm thick disk-shaped samples were dialyzed in water to remove unreacted chemicals. The polymer volume fraction φ of the swollen gel was 0.03. The samples used in this experiment were measured in the swollen state without further treatment. It was, however, noted that samples that were dried in a desiccator over concentrated sulphuric acid did not always reswell to exactly the same extent, a property that was attributed to additional cross-linking occurring in the deswollen state, probably due

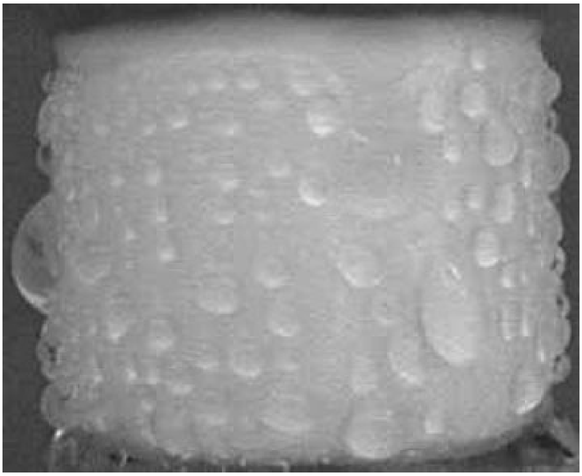

Figure 1.
PNIPA hydrogel above T_c after uniaxial compression, with blister structure at surface.

to residual unreacted groups coming into close contact.

Results and Discussion

Figure 1 shows a PNIPA gel to which an external pressure has been applied above the VPT. In addition to the uniform white colour, corresponding to multiple scattering of visible light, blisters form at the outer surface containing pockets of the liquid escaping under pressure. The intense whiteness of the underlying gel indicates microphase separation with inhomogeneities of size close to the wavelength of visible light, i.e., ca. 1 μm.

Conventional (incoherent) SAXS observations on this system display power law behaviour for the scattering intensity,[4] varying with the wave vector q as q^{-4}. This power law is the signature of scattering from smooth, sharply defined interfaces.[5] In addition, in the range $q > 0.01$ Å^{-1}, a weak extra feature was observed with a characteristic size of about 10 nm, the intensity of which diminished with time.[4] This feature may be interpreted as the thickness a of polymer walls that surround a dense precipitate of water droplets of radius r. In such an ensemble of spherical droplets the polymer volume fraction φ is then related straightforwardly to the volume of the pore walls by

$$\frac{\text{volume of skin}}{\text{volume of bubble}} = \frac{3a}{2r} = \varphi \qquad (1)$$

With $\varphi \approx 0.03$ and $a \approx 10$ nm, Equation 1 yields $r \approx 0.5$ μm, in agreement with the strong multiple scattering exhibited by the gel in visible light.

Figure 2 shows the incoherent SAXS scattering spectrum from the sample at 40 °C, obtained by combining results from ID 10 and BM2. The intensity of this surface scattering is[5]

$$I(q) = 2\pi r_0^2 \Delta\rho^2 \frac{S}{V} q^{-4} \qquad (2)$$

from which the polymer-water interfacial area in the gel, S/V, can be calculated. In Equation 2, r_0 is the classical radius of the electron and $\Delta\rho$ is the difference in electron density between the polymer and the water phase. On the assumption that the polymer phase is 50% hydrated, this yields $\Delta\rho = 1.7\ 10^{22}$ e/cm^3. Hence

$$S/V = 6.9\ \text{m}^2/\text{cm}^3 \qquad (3)$$

For the present model of spherical scattering surfaces, this result corresponds to a radius $r = 0.43$ μm, which is

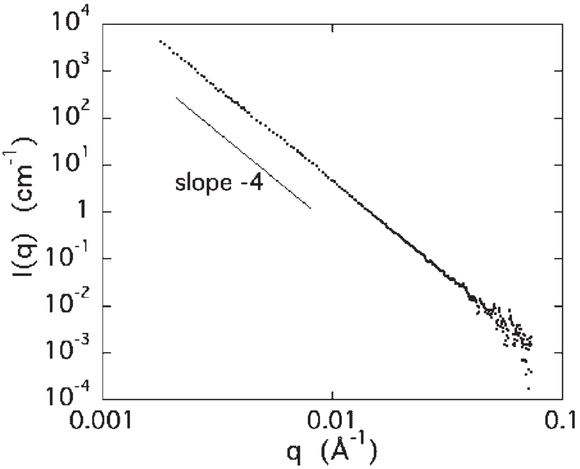

Figure 2.
Incoherent SAXS response of PNIPA gel in the unstable swollen state at 40 °C.

in acceptable agreement with the approximation obtained from Equation 1.

The skin structure, however, cannot be the cause of slow deswelling, since surface blisters occur especially under conditions of fast deswelling. It has been shown, for example, that the rate of deswelling of these gels increases when high cross-link densities are used.[3] Figure 3 shows a video picture of two PNIPA gel samples, the one on the left having been left in a water bath at 50 °C for several hours. The small bubbles surrounding it, exhibiting total internal reflection, are air nucleated in the hot water. The sample on the right, however, was one that had previously been dried in a desiccator. Although it was swollen to the same size as the other, this specimen had been immersed in the hot water for only 5 minutes at the time the image was recorded. Pronounced blisters are apparent on the surface of the fast deswelling gel. The weak contrast and absence of total internal reflection in these blisters confirm that they are filled with water. After a further 5 minutes, the deswelling of this sample was complete. These observations suggest that skin formation is not the cause of slow deswelling, but, on the contrary, a consequence of high deswelling rates. They also indicate that drying can introduce additional inhomogeneities into the swollen gel, which accelerate the deswelling process.[3]

The dynamics in the off-equilibrium high temperature state was investigated by X-ray photon correlation spectroscopy (XPCS). Time correlation functions were constructed for each pixel of the CCD from the sequence of several thousand images and the results were averaged over circular bands on the detector with the same mean scattering vector q, as shown in Figure 4. This procedure generates the ensemble-averaged intensity correlation functions $g(q,t)$, illustrated in Figure 5. The correlation functions were not simple exponentials, and could be approximated by a compressed exponential form

$$g_2(t) - 1 = \beta \exp[-(t/\tau)^\gamma] + \zeta \qquad (4)$$

where $\gamma \approx 1.5$. A single relaxation process, with a time constant τ of the order of 100 s, was found to describe the decay

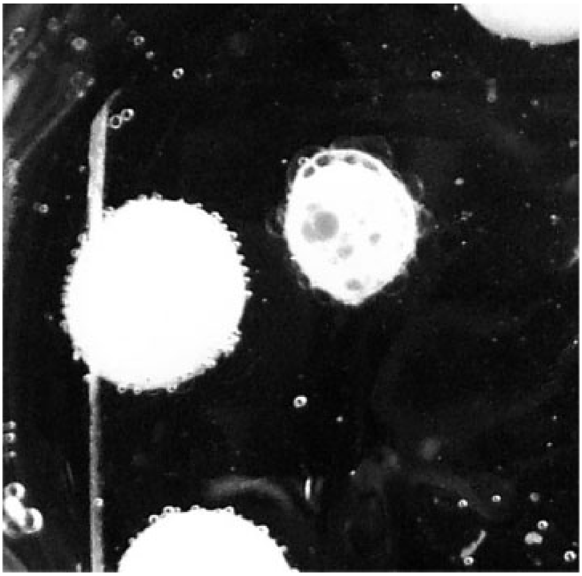

Figure 3.
Two PNIPA gel disks immersed in water at 50 °C. A faint corona of blisters of size about 1 mm can be seen surrounding the disk on the right, which is collapsing rapidly. For comparison, the diameter of the left (slowly deswelling) disk is approximately 7 mm.

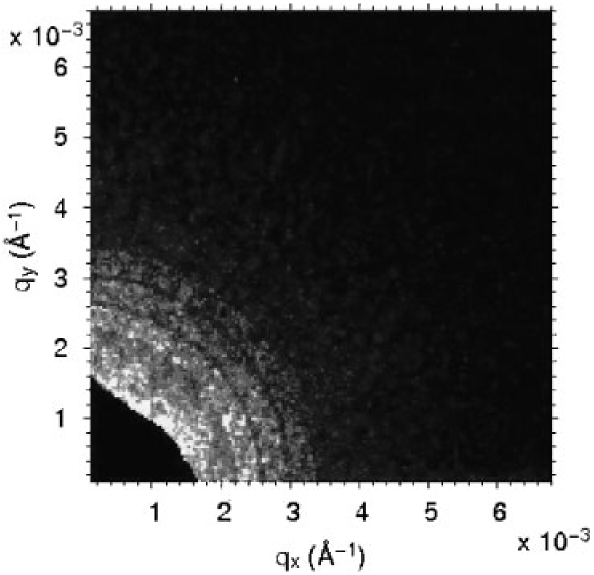

Figure 4.
Instantaneous scattering response recorded on the CCD detector from PNIPA hydrogel at 46 °C (1 s exposure). The dark region at bottom left corner is the beam-stop protecting the detector from the direct beam. Three typical coarse grained circles are highlighted delimiting the range of pixels that contribute to the correlation functions $g_2(q,t)$ at $q = 2.43 \times 10^{-3}$ Å^{-1}, 2.84×10^{-3} Å^{-1} and 3.25×10^{-3} Å^{-1}, respectively.

satisfactorily. The value of the coherence factor β, which remained stable throughout the measurements at approximately 0.15–0.2, albeit appreciably smaller than the $\beta \approx 1$ that is commonly achieved with laser sources, is a token of the high quality of the X-ray optics. The near-zero value of the ensemble averaged baseline, ζ, indicates that static speckles are absent from the scattering pattern and that the signal is

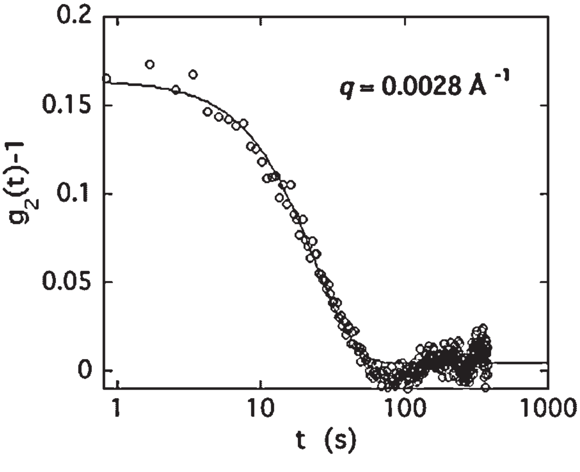

Figure 5.
Intensity correlation function $g_2(t)$-1, measured at $T = 37$ °C for $q = 0.0028$ Å^{-1}. Continuous curve: Equation 4 with fitting parameters: $\beta = 0.16$, $\tau = 23$ s, $\gamma = 1.50$, $\zeta = 0.004$.

therefore free from heterodyning effects.[6] It follows that the gel system behaves like an ergodic fluid, even though it is composed of a cross- linked network.

Since deswelling gels are not at equilibrium the formalism of stationary processes in light scattering is not necessarily the most appropriate. For the present system, which evolves with time, we employ the concept of two-time correlation functions,[7] described by

$$C(q, t_1, t_2) = \langle D(q, t_1) \times D(q, t_2) \rangle \qquad (5)$$

where **q** is the wave vector corresponding to a given pixel and

$$D(q, t) = \{I(q, t) - \langle I(q, t) \rangle\} / \langle I(q, t) \rangle$$

In Figure 6 the two-time function $C(q, t_1, t_2)$ is plotted for the value $q = 0.00243$ Å^{-1}, such that the amplitude is represented by the brightness and $t_1$and t_2 are respectively the horizontal and vertical axes of the figure. At any time t in this representation, the single-time correlation function $g_2(q, t_1 - t_2)$ is found by plotting the amplitude on the line $t_1 = t_2$, perpendicular to the principal diagonal of the figure. It is immediately apparent from Figure 6 that the correlation function becomes increasingly wide with advancing time, or, in other words, the relaxation time τ becomes increasingly long. The decreasing relaxation rate and the compressed exponential form of the correlation function are two of the characteristic traits of *jamming*, in which the elements of a complex system are so crowded that large-scale movement becomes impossible without the application of external forces.[8]

The third criterion by which systems are recognized as being jammed is in the q-dependence of the relaxation time τ. Unlike ergodic systems that obey Fick's equation of diffusion, for which $\tau \propto q^{-2}$, in jammed systems the characteristic relaxation time varies as $\tau \propto q^{-1}$.[9] Figure 7 shows that, within experimental error, the latter

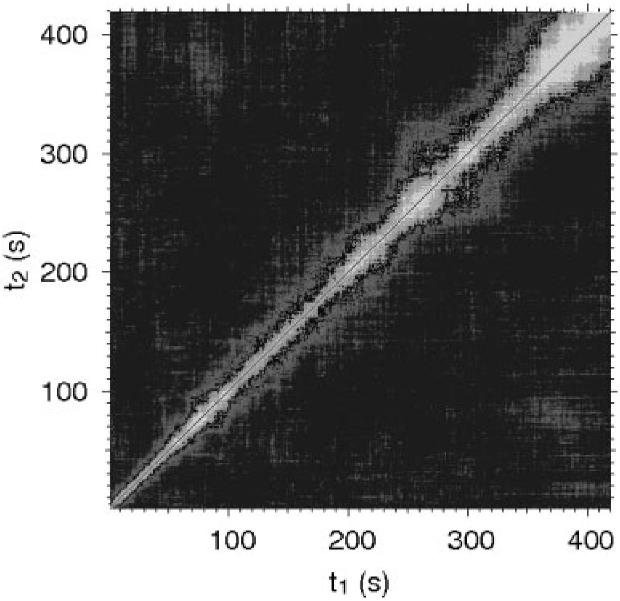

Figure 6.
Two-time correlation function $C(t_1,t_2)$ for $q = 2.43 \times 10^{-3}$ Å^{-1}. The cross-sections $g_2(t_1 - t_2)$, perpendicular to the principal diagonal (fine dotted line), become increasingly broad with advancing time, as the relaxation becomes slower.

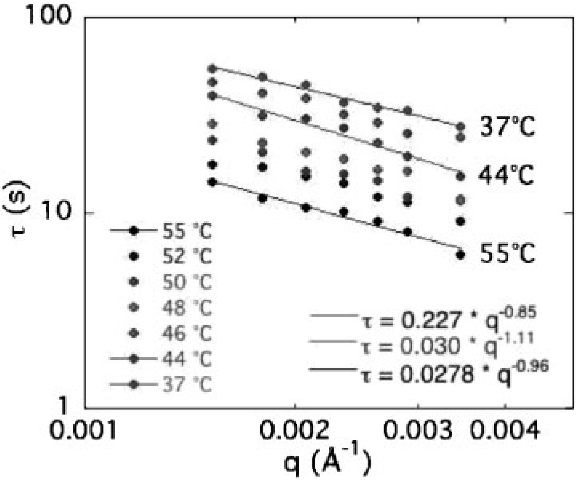

Figure 7.
q-dependence of relaxation time τ at different temperatures.

relationship applies in the present system at all the temperatures studied.

Conclusions

The measurements reported here using X-ray photon correlation spectroscopy support the notion that the ultraslow deswelling rate observed at the volume phase transition in polyNIPA hydrogels is the result of jamming. This phenomenon is intrinsic to the polymer structure and is not attributable to its hydrophobic character in the high temperature regime. It appears that structural inhomogeneities in the gel, such as those associated with cross-links, release the constraints of jamming and facilitate rapid relaxation.

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