PRAMANA
— journal of
physics

Vol. 75, No. 6
December 2010
pp. 1209–1214

Quasi-elastic laser light scattering study of polyacrylamide hydrogel immersed in water and salt solutions

M SIVANANTHAM and B V R TATA*
Condensed Matter Physics Division, Indira Gandhi Centre for Atomic Research, Kalpakkam 603 102, India
*Corresponding author. E-mail: tata@igcar.gov.in

Abstract. Polyacrylamide (PAAm) hydrogels immersed in water and aqueous NaCl solutions were investigated for their structure and dynamics using static and quasi-elastic laser light scattering (QELS) techniques. Ensemble-averaged electric field correlation function $f(q,t)$ obtained from the non-ergodic analysis of intensity-autocorrelation function for PAAm gel immersed in water and in 5 M NaCl showed an exponential decay to a plateau with an initial decay followed by saturation at long times. The value of the plateau was found to depend on NaCl concentration and was higher than that of water. Collective diffusion coefficient, D, of the polymer network of the hydrogel immersed in water and in different concentrations of NaCl was determined by analysing $f(q,t)$. The measured diffusion coefficient showed linear decrease with increase in concentration of NaCl. The characteristic network parameters were obtained by analyzing $f(q,t)$ with harmonically bound Brownian particle model and from static light scattering studies.

Keywords. Polyacrylamide hydrogel; salt solution; diffusion coefficient; light scattering; inhomogeneities.

PACS Nos 61.25.hp; 78.35.+c; 36.20.-r

1. Introduction

Hydrogels consist of hydrophilic network of polymer strands that are cross-linked by chemical or physical bonding and are insoluble in any solvent [1]. Their swelling and shrinking ability can be controlled by tuning the interaction between the polymeric network and the solvent. There are several factors such as ionic strength, temperature, electric field and pH that affect the swelling/shrinking of hydrogels. These hydrogels have several industrial and high-tech applications (for example, in pharmaceutical and food industry and for making tunable photonic crystals), which simulated experimental work on the thermodynamic properties of hydrogels in aqueous and salt solutions. Though there are several studies on swelling/shrinking of ionic copolymer gels [2], the studies on non-ionic polymer hydrogel such as polyacrylamide (PAAm) hydrogel in salt solutions are limited. Quasi-elastic laser light

scattering (QELS) (also known as dynamic light scattering (DLS)) and static light scattering (SLS), respectively are appropriate techniques to probe the dynamics and length scales of the gel network. Unlike in polymer solutions, the motion of polymer segments in a gel is restricted to particular regions of the sample due to the cross-linking of chains, hence span only restricted region of phase space. Hence, gel may be regarded as a non-ergodic system, as a time-average measurement on a particular portion of the sample will not be equivalent to an ensemble-average measurement. Thus gels provide an interesting opportunity to study the differences between the time and ensemble averages using QELS technique. Here we show that, QELS and SLS techniques provide valuable information in probing the dynamics and the structure of PAAm hydrogels as well as in studying the influence of salt concentration on the polymer hydrogel network.

2. Experimental methods

2.1 *Synthesis*

PAAm hydrogels were prepared by photopolymerization using the monomer solution containing 10% w/w acrylamide (AAm) (99%, Merck) and 0.5% w/w N,N'-methylene bisacrylamide (MBA) (99%, Ottokemi). 1 μl of the photoinitiator 2,2′-diethoxyacetophenone (DEAP) (98%, Acros Organics) was added for every 1 ml of the deionized monomer solution. This mixture was filtered (filtering was done by 0.1 μm Millipore syringe filter) and injected into a cylindrical quartz cell of 8 mm diameter. Then it was exposed to 360 nm soft UV rays from 300 W UV/Vis lamp for half an hour. After polymerization, hydrogel was kept in water for a week to reach equilibrium and then light scattering measurements were done on water-swollen gel (WSG). Later it was allowed to equilibrate in various concentrations of NaCl (1, 2, 3, 4 and 5 M) and then light scattering measurements were carried out on salt-swollen gel (SSG).

2.2 *Dynamic and static light scattering measurements*

SLS and QELS experiments were carried out on WSG and SSG samples using a Malvern 4700 (Malvern Instruments, UK) light scattering set-up equipped with a goniometer, a multi-tau correlator and a 250 mW diode-pumped solid-state laser operating at 532 nm. Incident laser beam was vertically polarized and the scattered intensity was collected using a vertically aligned Glan-Thomson prism placed in front of the photomultiplier tube (PMT). The time-averaged intensity–intensity autocorrelation function (ICF), $g_{\mathrm{T}}^{(2)}(q,t)$, was accumulated for 30 min at a scattering angle (θ) of 60° using a multi-tau correlator at a given scattering wave vector $q = (4\pi n/\lambda)\sin(\theta/2)$, where n is the refractive index of water and λ is the wavelength of incident laser beam. Time-average intensity $\langle I(q)\rangle_{\mathrm{T}}$ and ensemble-average intensity $\langle I(q)\rangle_{\mathrm{E}}$ were collected for 10 min. $\langle I(q)\rangle_{\mathrm{E}}$ is measured by rotating the sample at a speed of 2 rpm using a computer-controlled stepper motor. SLS

measurements as function of scattering angle were carried out by rotating the sample at 2 rpm with 500 μm aperture in front of the PMT and collecting the scattered intensity for 10 min at each θ.

2.3 *Data analysis by non-ergodic method*

QELS data were analysed using Pusey and van Megen method [3]. The time-averaged ICF, $g_{\mathrm{T}}^{(2)}(q,t)$, obtained from QELS measurement can be written as

$$g_{\mathrm{T}}^{(2)}(q,t) = \frac{\langle I(q,0)I(q,t)\rangle_{\mathrm{T}}}{\langle I(q,0)\rangle_{\mathrm{T}}^2}. \tag{1}$$

For a non-ergodic system, the ensemble-averaged $f(q,t)$ can be obtained from the time-averaged ICF using the relation

$$f(q,t) = \frac{Y-1}{Y} + \frac{(g_{\mathrm{T}}^{(2)}(q,t) - \sigma_{\mathrm{I}}^2)^{1/2}}{Y}, \tag{2}$$

where σ_{I}^2, the mean-square intensity fluctuation is defined as

$$\sigma_{\mathrm{I}}^2 = \frac{\langle I^2(q)\rangle_{\mathrm{T}}}{\langle I(q)\rangle_{\mathrm{T}}^2} - 1 \tag{3}$$

and the non-ergodic parameter $Y = \langle I(q)\rangle_{\mathrm{E}}/\langle I(q)\rangle_{\mathrm{T}}$. By measuring $g_{\mathrm{T}}^{(2)}(q,t), \sigma_{\mathrm{I}}^2$ and Y, one gets the dynamic structure factor $f(q,t)$ using eq. (2). We follow the harmonically bound Brownian particle model (HBBP) [4,5] for interpreting the $f(q,t)$ which is given by

$$f(q,t) = \exp[-q^2\delta^2[1 - \exp(-(t/\tau))]], \tag{4}$$

where δ^2 is the mean squared displacement (MSD) of the scatterer that is trapped in the gel network and cannot diffuse infinitely far, τ is the decay time of the network and is related to the diffusion coefficient D by $\tau = 1/Dq^2$. The parameters δ^2 and τ are obtained by non-linear least-squares fitting the experimental $f(q,t)$ to eq. (4).

3. Results and discussion

3.1 *Dynamic light scattering*

Dynamic structure factors of WSG and SSG (5 M NaCl) with 0.5% MBA are shown in figure 1.

Notice that both exhibit an initial decay followed by a plateau. The value of the plateau is higher for SSG than that for WSG. The fits to eq. (4) are shown as continuous lines. The decay time τ and MSD δ^2 obtained from the fit are

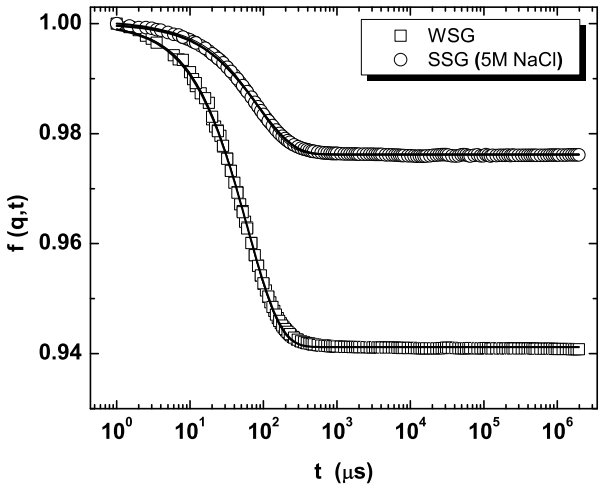

Figure 1. Dynamic structure factor, $f(q,t)$, of WSG and SSG (5 M NaCl) with 0.5% MBA gel at $\theta = 60°$. Solid lines are fits to eq. (4).

respectively 61.7 μs, 246.1 nm^2 for WSG and 83.9 μs, 97.6 nm^2, for SSG (5 M NaCl). Further, we also observed that when WSG is immersed in 5 M NaCl, it undergoes swelling. Swelling is responsible for the increase in τ and decrease in δ^2. Gel is viewed as a network of microgel clusters; the increase in cluster size is responsible for reduction in MSD in NaCl. As result of this swelling, the dynamics is hindered even further (i.e. increase in decay time). The collective diffusion coefficients of the gel network obtained from decay time τ for different concentrations of NaCl are shown in figure 2. The linear decrease in D with increase in NaCl is due to the systematic swelling of the gel network in NaCl.

3.2 *Static light scattering*

The ensemble-averaged scattered intensity $\langle I(q)\rangle_{\mathrm{E}}$ of WSG and SSG (5 M NaCl) with 0.5% MBA is shown in figure 3. The scattered intensity at low q-region is more compared to high q-region for both WSG and SSG (5 M NaCl) because of the presence of inhomogeneities in the gel. The scattering profile was fitted with the combination of Gaussian and Lorentzian functions given as [6]

$$I(q) = I_{\mathrm{G}}(0)\exp(-\Xi^2 q^2/2) + I_{\mathrm{L}}(0)/(1+\xi^2 q^2), \tag{5}$$

where $I_{\mathrm{G}}(0)$ and $I_{\mathrm{L}}(0)$ are coefficients of Gaussian and Lorentzian terms, Ξ is the size of the inhomogeneities in the gel network and ξ is the correlation length. The increase in scattered intensity of SSG (5 M NaCl) over WSG implies the increase in the size of the inhomogeneities.

The size of the inhomogeneities as well the mesh size estimated by fitting the experimental data to eq. (5) revealed that size of the inhomogeneities increases from 296 to 337 nm when the PAAm gel is transferred from water to 5 M NaCl whereas the correlation length decreases slightly from 40 to 37 nm.

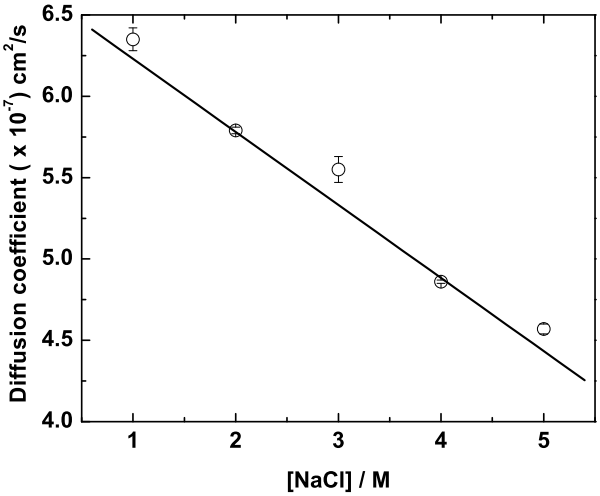

Figure 2. Collective diffusion coefficient D as a function of [NaCl]. Solid line is a guide to the eye.

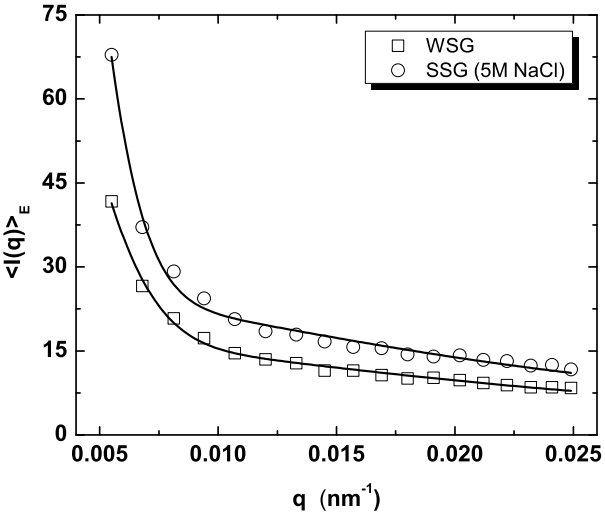

Figure 3. Ensemble-averaged scattered intensity $\langle I(q)\rangle_{\mathrm{E}}$ of WSG and SSG (5 M NaCl) with 0.5% MBA. Solid lines are fits to eq. (5).

4. Conclusions

We have prepared PAAm hydrogel and investigated their swelling in water and different concentrations of NaCl. By employing QELS technique we have shown that PAAm gel exhibits non-ergodicity and the gel dynamics obeys HBBP model. The characteristic parameters of the gel network has been obtained by analysing $f(q,t)$. The analysis of SLS measurements has revealed the existence of static

inhomogeneities in PAAm gel. These inhomogeneties are also found to swell along with gel network when immersed in NaCl.

References

[1] T Tanaka, *Sci. Am.* **244**, 110 (1981)
[2] J P Baker, H W Blanch and J M Prausnitz, *Polymer* **36**, 1061 (1995)
[3] P N Pusey and W V Megen, *Physica* **A157**, 705 (1989)
[4] K P V Sabareesh, S Jena and B V R Tata, *AIP Proceedings* **832**, 307 (2005)
[5] J Z Xue, D J Pine, S T Milner, X L Wu and P M Chaikin, *Phys. Rev.* **A46**, 6550 (1992)
[6] S Mallam, F Horkay, A M Hecht, A R Renie and E Geissler, *Macromolecules* **24**, 543 (1991)