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Frozen Concentration Fluctuations of Poly(N-isopropyl acrylamide) Gel Decomposed by Neutron Spin Echo

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By employing neutron spin echo (NSE) and small-angle neutron scattering (SANS), we first determined the nano-scale q-behaviors of the frozen concentration fluctuations in a swollen poly (N-isopropyl acrylamide) (NIPA) gel. For a NIPA gel, we observed a crossover from collective diffusion to Zimm single chain dynamics as scattering vector q increases, which is well established for a semidilute polymer solution. We further observed significant retardation of decay of NSE for a NIPA gel at low q, which is attributed to the elastic scattering from the frozen concentration fluctuations. After a careful analysis of two decay curves of a NIPA gel and solution, it is turned out that the elastic scattering, occupying about 40% of the total intensity at $q = 0$, decreases obeying q^{-4} at high q.

KEYWORDS: small-angle neutron scattering, neutron spin echo, polymer gel, frozen concentration fluctuations

§1. Introduction

After pioneering works by T. Tanaka,$^{1)}$ the poly(N-isopropyl acrylamide) (NIPA) gel has been extensively studied from a macroscopic point of view.$^{2)}$ The NIPA gel is a hydrogel, in which partial polymer chains are chemically connected to form a 3-dimensional polymer network in a water matrix. The infinite connectivity of partial chains is crucial to zoom in a microscopic coil-globule transition up to macroscopic length scales, which happens for a NIPA gel at T_v=34.0 °C as a volume phase transition.

From its concentration, a polymer gel can be classified into semi-dilute polymer solution, which normally has large concentration fluctuations. Although the studied NIPA gel is transparent, it might have large concentration fluctuations, as a normal polymer solution. Furthermore, the connectivity prohibits reconfiguration of polymer chains (frozen blob) and relaxation of concentration fluctuations to equilibrium, when its environmental parameters change. Due to the frozen fluctuations thus induced, a polymer gel shows additional small-angle scattering (over scattering), compared to a corresponding polymer solution in equilibrium.$^{2)}$

Small-angle neutron scattering (SANS) observes the concentration fluctuations on a microscopic length scale. The structure factor $S(q)$ obtained by SANS is a snap shot of the concentration fluctuations, where q is scattering vector. Neutron spin echo (NSE), on the other hand, provides the normalized intermediate scattering function of $S(q,t)/S(q)$ within a time domain up to t=10 or 100 ns. If we combine SANS and NSE, we are able to obtain a time-evolving picture of the concentration fluctuations in reciprocal space. In this study, we will report our quantitative analysis of the frozen concentration fluctuations in a swollen gel on nano-length scales, which are intimately connected to the solid-like aspect of a polymer gel.

§2. Experimental

A NIPA monomer, produced by Kohjin Co. Ltd., was purified by recrystallizing its toluene solution in hexane at 4 °C. A the pre-gel solution was prepared by dissolving 7.8 g of the purified NIPA monomer, 0.345 g of N, N′-methylenebisacrylamide (BIS) and 43 mg of ammoniumpersulfate in D_2O of 100 ml. Then an initiator, N, N, N′, N′-tetramethylethylenediamine of 240 ml., was added to the pre-gel solution to initiate polymerization and crosslink. During polymerization for 24 h at 10 °C, the pre-gel solution was poured into a glass plate mold having a gap of 1.5 mm thickness. The NIPA gel thus prepared contains D_2O of 93.0wt% at the reference temperature of 10 °C. We synthesized an uncrosslinked NIPA polymer with the same receipt used for a NIPA gel except for BIS. For SANS measurements, we prepared a polymer solution of the uncrosslinked NIPA of 7.0wt% in D_2O.

Neutron scattering measurements were performed in the Forschungszentrum Jülich. In order to cover a wide q-range of $0.002 < q < 0.2$ Å^{-1} for SANS, we employed a wave length of 7 Å and three detector positions of 2.0, 8.0 and 20.0 m. The scattered neutrons were collected by an area detector of 64.0 x 64.0 cm^2 with a pixel size of 1 cm^2. The 2-dimensional data set thus obtained were corrected for the counting efficiency, the instrumental background and the air scattering on a pixel to pixel basis. After circular-averaging, we converted scattering intensity to the absolute differential cross section per sample volume ($d\Sigma/d\Omega$(q) in unit of cm^{-1}), by using a Lupolen film as secondary standard.$^{3)}$

The incoherent scattering of hydrogen was subtracted as background by using the higher q-region where the

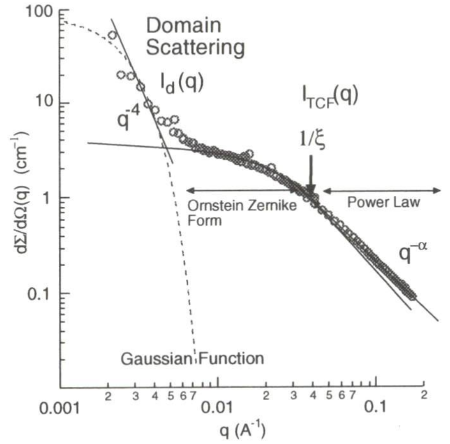

Fig. 1. SANS profile obtained for NIPA gel at 28.0 °C. The broken line indicates a Gaussian scattering function fitted for upturned small-angle scattering at low q.

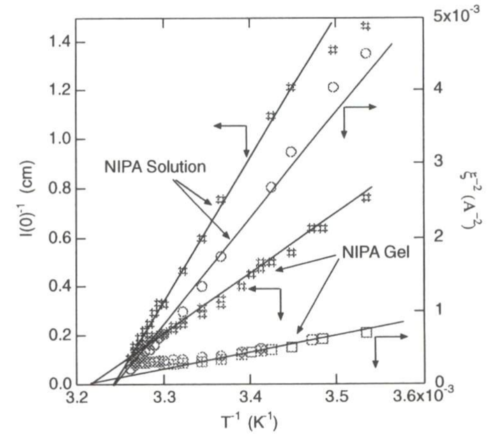

Fig. 2. Temperature dependence of inverse forward scattering intensity $I(q)^{-1}$ and squared inverse correlation length ξ^{-2} for both NIPA gel and solution.

scattering profile becomes q-independent. The details of neutron spin echo spectrometer in Jülich are described in ref.[4]. The sample specimens for both gel and solution were mounted in a Nb-holder, which is temperature controlled. The sample thickness and width are 4.0 mm and 30.0 mm, respectively. For each setting of the nominal scattering angle, the scattered neutrons are detected by a 2-dimensional counter over an area of 28.0 cm diameter, in order to obtain high count rate or interpolation of q-values. The background from a pure D_2O sample was subtracted as background.

§3. Experimental Results

Fig.1 shows the SANS profile for a NIPA gel in a swollen phase at 28.0 °C. At a first glance, the SANS profile from a swollen NIPA gel resembles that from a semi-dilute polymer solution. The semi-dilute polymer solution generally has large thermal concentration fluctuations $< \delta\phi^2 >$, causing small-angle scattering $I_{TCF}(q)$. The apparent discrepancy between a gel andsolution is a strong upturn appearing at low q, which has been often observed for many polymer gels since 1966.[5] According to ref.5, this scattering is attributed to the spatial distribution of chemical crosslinks. If it obeys a Gaussian distribution, we obtain a scattering function of $exp(-\Xi^2 q^2)$ where Ξ is a correlation length. Along this scenario, we evaluated Ξ of the order of 500 Å at 28.0 °C. However after a careful examination on the SANS profiles, we found a long tail of this upturn which decreases with q^{-4}.[6] It seems more reasonable to believe that this upturn originates from domain scattering $I_d(q)$ from polymer-rich domains with sharp interface. This upturn might be related with the micron-scale spatial heterogeneity observed as speckles by light scattering.[7]

$\mathrm{I}_{TCF}(\mathrm{q})$ is sensitive to temperature; for NIPA as the temperature increases, $\mathrm{I}_{TCF}(\mathrm{q})$ increases in its intensity and changes its q-behavior.[8] This is attributed mainly to a change of the osmotic compressibility in a swollen gel. As established for semi-dilute polymer solution, we found two q-regions for $\mathrm{I}_{TCF}(\mathrm{q})$; at intermediate q, we find the Ornstein-Zerinke (OZ)-type scattering, while at high q, we find a power law scattering of $q^{-\alpha}$. The crossover between them appears at $q = 1/\xi$, where ξ is a screening length or a blob size in a swollen gel. We estimated the exponent α from the higher q region of $q\xi > 1$. At 28.0 °C, we obtained the Flory exponent of $\alpha = 1.67$, indicating that polymer chains are swollen well by water.[8] At around 33.0 °C close to T_v, we found $\alpha = 2.0$ indicating a θ-solvent state.[8]

The OZ-type scattering is characterized by two parameters of the forward scattering intensity $I(q = 0)$ and a correlation length ξ. From the intermediate q-region, we estimated the inverse forward scattering intensity $I(q = 0)^{-1}$ and the squared inverse of correlation length ξ^{-2}, by using a so-called OZ plot. Figure 2 shows $I(q = 0)^{-1}$ and ξ^{-2}, which change linearly as a function of inverse temperature $1/T$. Over a wide temperature range from 10 °C to T_v, the forward scattering intensity from a NIPA gel exceeds that from NIPA solution. In our case, the NIPA gel shows stronger scattering even at the reference temperature of 10 °C. The temperature dependence of $I(q = 0)^{-1}$ and ξ^{-2} for a NIPA gel, on the other hand, is much smaller than that for the solution. Finally at T_v, $I(q = 0)$ from a NIPA gel overcomes that from a NIPA solution. It should be denoted that ξ for the NIPA gel becomes temperature-independent at around 30.0 °C, while ξ for NIPA solution changes continuously toward T_v.

The q-positions for NSE measurements ranged from 0.01 to 0.16 Å^{-1}, which corresponds to those for the OZ-type scattering and the power low scattering. Figure 3 shows $S(q,t)/S(q,t = 0)$ obtained for both the NIPA gel and solution. We examined the decay curves carefully from following points of (i) first cumulant, (ii) asymptotic decay behavior for a long time and (iii) Zimm scaling. After these careful examinations, we found a dynamical crossover at around q=0.08 Å^{-1} from the collective diffusion to the Zimm single chain motion as q increases, which is a common feature for both NIPA gel and NIPA solution. It should be denoted that the viscosity of the NIPA gel, determined from a Zimm model, is about 3 times larger than that for pure water (hydrogen interaction effect).

Although the dynamical crossover is common for both NIPA gel and solution, there is significant retardation on decays for the NIPA gel for $0.05 < q < 0.1$ Å^{-1}.

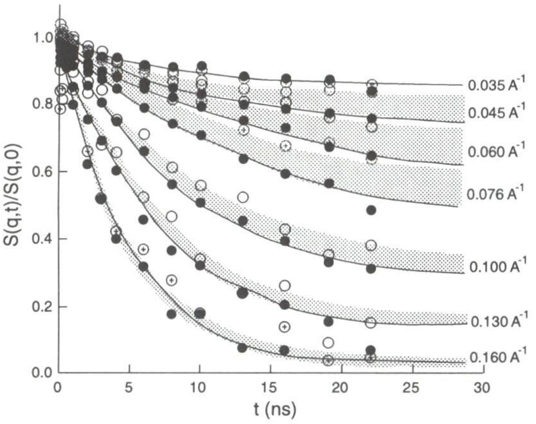

Fig. 3. NSE decay curves obtained for both NIPA gel and solution at 28.0^oC at various q-positions from 0.035 to 0.16 Å^{-1}. The open and filled circles indicate for NIPA gel and solution, respectively. The shadows show difference of decay between NIPA gel and solution at same q-positions. The solid lines are guides for eye.

The shadows in Fig. 3 indicate the difference between NIPA gel and solution at same q-positions. The retardation becomes less obvious and finally at q=0.16 Å^{-1}, the difference between two becomes negligibly small within error bars.

§4. Discussions

The SANS measurements revealed that the concentration fluctuations in a gel is larger than in solution over a wide temperature range up to T_v. Note that the NIPA gel shows over-scattering even at the reference temperature of 10.0 °C. In the course of chemical reactions of polymerization and crosslink, the polymer configuration might be fixed and therefore the concentration fluctuations can not relax to equilibrium. This is a freezing effect during our sample preparation. The frozen blob effect causes further over-scattering at given temperatures. However the concentration fluctuations in NIPA solution grows more rapidly as a function of temperature than those in a NIPA gel. Finally at around T_v, these become comparable. The extrapolation of $I(q = 0)^{-1}$ to zero gives a spinodal temperature T_S. We obtained T_S equal to 38.7 or 35.5 °C for a NIPA gel or solution, respectively. Note that ξ for a NIPA gel becomes temperature-independent about above 30.0 °C.

As denoted above, the chemical crosslinks play an important role to freeze part of the concentration fluctuations in a gel. The total liquid-like concentration fluctuations in a gel $< \delta\phi^2 >$ can be given as a sum of the frozen $< \delta\phi^2 >_f$ and the unfrozen concentration fluctuations $< \delta\phi^2 >_{unf}$. $I_{TCF}(q)$ is also given as a sum of the frozen $I_f(q)$ and unfrozen scattering $I_{unf}(q)$; $I_{TCF}(q) = I_f(q) + I_{unf}(q)$. Note that $I_f(q)$ appears as an elastic scattering component.

In order to explain the retardation which we found by NSE for $0.05 < q < 0.1$ Å^{-1}, we employ a scattering function with an elastic scattering ratio $P(q)$ as follows,

$$S_{gel}(q,t) = S_{gel}(q,t=0)\{P(q)+[1-P(q)]f(t,q)\} \quad (4.1)$$

where $f(q,t)$ is an universal function, satisfying from the collective behavior at low q to the Zimm single chain behavior at high q. As observed at high q, the decay curves for both NIPA gel and solution are identical within error bars, obeying the Zimm model. This means that the segmental motion is simply determined by a hydrodynamic interaction with matrix viscosity. In order to proceed our analysis, we simply assume that the universal function $f(q,t)$ can be replaced with the experimental curves obtained for the NIPA solution; $f(t,q)$=$S_{sol}(q,t)/S_{sol}(q,t = 0)$. As a result of combination between the NSE curves for the NIPA gel and solution, we are able to determine $P(q)$. $P(q)$ thus determined decreases obeying q^{-2} at high q, while at low q, $P(q)$ becomes q-independent. From our analysis based on eq.(4.2), we obtain $P(q)$ of about 0.4 as an elastic level at low q. The elastic scattering component $I_f(q)$ ($\sim S_{gel}(q)P(q)$) is shown in Fig.4. The forward scattering intensity of $I_f(q)$ occupies about 40% of the total. Note that $I_f(q)$ decreases rapidly at high q, following q^{-4}, although there is no sharp interface.

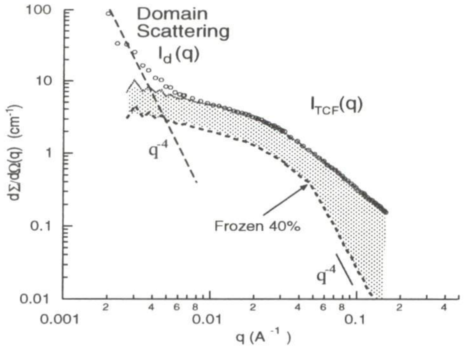

Fig. 4. Elastic scattering from frozen concentration fluctuations in a NIPA gel at 28.0 °C (broken line). The open circles indicate the net SANS profile, which decreases obeying q^{-2} at high q. The shadow indicates small-angle scattering free from a frozen effect.

§5. Conclusions

By using a combined method of NSE and SANS, we sucessfully decomposed the elastic small-angle scattering $I_f(q)$ from the frozen fluctuations in a NIPA gel. The forward scattering intensity of $I_f(q)$ occupies about 40% of the total scattering at 28.0 °C. The asymptotic q-behavior of $I_f(q)$ at high q is q^{-4}, although there is no domain structure with sharp interface. These are new findings on nano-lenght scales, different from the results on micron-lenghth scales reported by the light scattering.[8)]

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