Pressure Effects on the Inhomogeneities of Environmentally Sensitive Polymer Gels

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Summary: The effects of pressure at gel preparation on the inhomogeneities were investigated by small-angle neutron scattering. Poly(N-isopropylacrylamide) (PNIPA) gels, known as thermosensitive polymer gels undergoing volume transition, were prepared at various pressures ranging from 0.1 to 300 MPa. The scattering intensity increased with increasing P_{prep}, up to 200 MPa, then decreased by further increase in P_{prep}. The degree of inhomogeneities evaluated by the ratio of the static and dynamic correlators exhibited a similar behavior to that of the ensemble average light scattered intensity, $\langle I \rangle_E$. The physical meaning of the gel inhomogeneities is discussed from the viewpoint of swelling thermodynamics. It will be shown that the increase in the swelling degree is due not to an increase in the miscibility of PNIPA with water but to the increase in inhomogeneities.

Introduction

Poly (*N*-isopropylacrylamide) (PNIPA) hydrogels are known to be temperature-sensitive gels.[1,2] Upon a slight increase in temperature above the transition temperature, T_C ($\approx$ 34 °C),[3,4] PNIPA gels undergo a shrinking transition. The environment sensitivity is mainly ascribed to the nature of strong hydrophobicity of the *N*-isopropyl group located on the side chain. Hydrophobicity is related to ordering of water molecules surrounding hydrophobic groups. That is, water molecules around an *N*-isopropyl group are ordered and form an iceberg structure[5] in order to minimize the number of contacts with the hydrophobic group. However, this ordered structure is broken by thermal motion of water molecules when temperature is increased above the so-called volume phase transition temperature T_C. This leads to demixing between PNIPA and water. This volume transition is induced by pressure as well.

Since the iceberg formation involves positive change in volume, pressurizing is expected to decrease the LCST (the lower critical solution temperature), resulting in a shrinking transition. However, contrary to this speculation, a swelling transition is commonly observed.[6-8] According to Kato, the Flory interaction parameter is a

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quadratic function of pressure, which results in a reentrant swelling-shrinking transition as pressure is increased.[8] Zhong et al. reported that the pressure sensitivity of PNIPA gels is a consequence of their temperature sensitivity and is a result of the increase in its LCST with temperature.[7] We reported that the structure and dynamics of PNIPA gels are more or less frozen during the preparation process of the gel.[9] For example, when a PNIPA gel is prepared at a high pressure, P_{prep}, it keeps a memory of the circumstance of gel preparation even after releasing the pressure.[10] In this paper, we discuss the P_{prep} dependence on the microscopic structure of PNIPA gels on the basis of small-angle neutron scattering (SANS) data. It will be shown that there is a critical pressure at which inhomogeneities diverge.

Experimental Section

A series of poly(*N*-isopropylacrylamide) (PNIPA) gels were prepared by redox polymerization. Prescribed amounts of NIPA monomer (purchased from ACROS, U.S.A.) and *N,N'*-methylenebisacrylamide (BIS; cross-linker, Wako Chemicals) were dissolved in distilled water (total volume 50 ml), whose concentrations were 700 and 8.63 mM, respectively. By adding 1.7 mM of ammonium persulfate (initiator; Wako Chemicals) and 3.0 mM of *N,N,N',N'*-tetramethylenediamine (accelerator; Wako Chemicals) to the solution, polymerization was initiated. The polymerization was carried out in a 10 mm test tube at room temperature (20 ±1°C) under several pressures which were applied by a wet-bag type cold isostatic pressing equipment (Dr. CIP®; KOBE STEEL LTD) for 24 h. The preparation pressure, P_{prep}, was varied from 0.1 to 300 MPa.

The SANS experiments were carried out on the research reactor, SANS, at The Institute of Solid State Physics, The University of Tokyo. A flux of cold neutrons with a wavelength of 7.0 Å irradiated the sample, and the scattering intensity profile was collected with an area detector of 128 x 128 pixels (0.5 mm/pixel). The sample-to-detector distance was set to be 4 m, which covered the accessible q range being 0.01 to 0.078 Å^{-1}. Here, q is the scattering vector. The sample was placed in a brass chamber with quartz windows and the chamber was thermo-regulated within an error of ± 0.1 °C at the sample position with a NESLAB 110 water-circulating bath. The sample thickness was 4 mm. The scattering intensities were circularly averaged by taking account of the detector inhomogeneities, corrected for cell scattering, fast neutrons, transmission, and incoherent scattering, and then calibrated to the absolute intensities with a polyethylene standard sample (Lupolen).

Results and Discussion

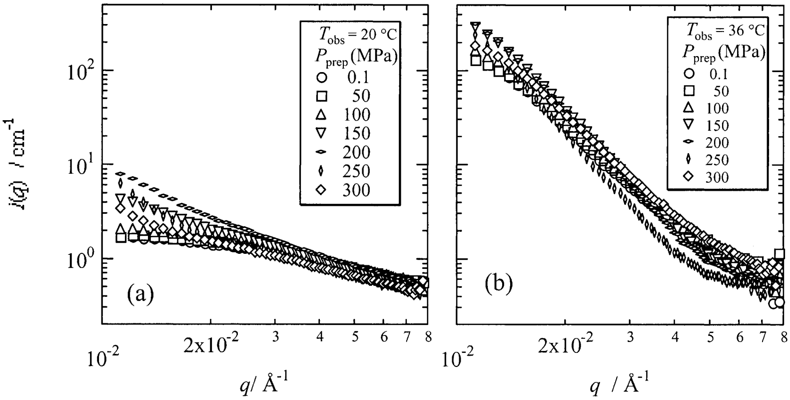

Figure 1. SANS scattering function, $I(q)$, of PNIPA gels prepared at various pressures, P_{prep}. The observation temperatures were (a) T_{obs} = 20 and (b) 36 °C.

Figure 1 shows the SANS intensity profiles, $I(q)$, of PNIPA gels prepared at various pressures, P_{prep}'s, where q is the momentum transfer. The observation temperatures, T_{obs}, were (a) 20 and (b) 36 °C. Fig. 1a shows that $I(q)$ depends on P_{prep}, at low q regions, while no P_{prep} dependence is resolved at high q regions (q ≥0.04 Å^{-1}). When the observation temperature was increased to T_{obs} = 36 °C, $I(q)$ increased markedly at all q regions and the P_{prep} dependence becomes less significant (Fig. 1b). This figure indicates that the temperature effect is much larger than the pressure effect. Note that $I(q)$ at T_{obs} = 20 °C became strongest at P_{prep} ≈200 MPa.

Figure 2 shows the P_{prep} dependence of $I(q$ = 0.011 Å$^{-1})$ observed at various T_{obs}'s. This shows two important features of PNIPA gels. One is that $I(q)$ increases with increasing T_{obs}, and the other is that $I(q)$ has an maximum (or $I(q)$ is divergent) at P_{prep} ≈200 MPa, irrespective of T_{obs}. The PNIPA gels underwent phase separation at P_{prep} ≥200 MPa.

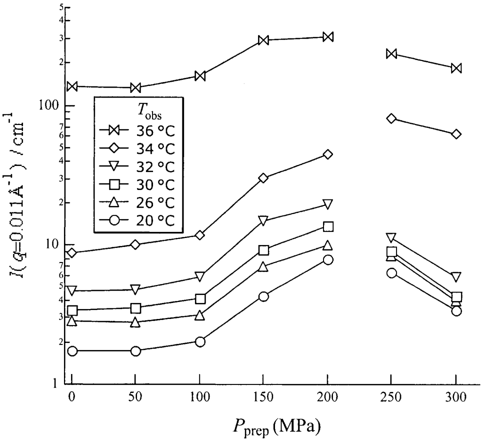

Figure 2. P_{prep} dependence of $I(q = 0.011\ \text{Å}^{-1})$ of PNIPA gels observed at various observation temperatures, T_{obs}.

Figure 3a shows the P_{prep} dependence of ensemble-average light scattering intensity, $<I>_E$.[10] $<I>_E$ was obtained by measuring scattering intensity at 100 different sampling points in a gel. Here, similarly to $I(q)$ observed by SANS, a divergence in $<I>_E$ is observed. Shrinking kinetics experiments on this series of gels indicate that the PNIPA gels underwent phase separation for $P_{prep} > 170$ MPa and the shrinking rate is increased by a factor of 10^3.[10] The SANS results obtained here are in good accordance with these results. The inset of Fig. 3a shows a $1/<I>_E$ vs. P_{prep} plot, in which $<I>_E$ diverges at $P_{prep} = 168$ MPa.

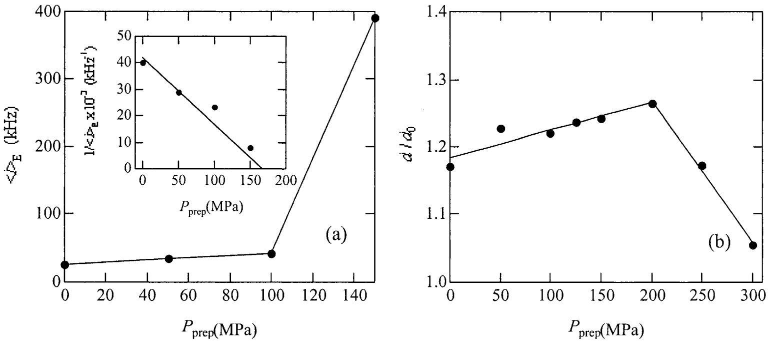

Figure 3. P_{prep} dependence of (a) ensemble average scattering intensity, $<I>_E$, and (b) equilibrium swelling ratio, d/d_0.

Figure 3b shows the equilibrium swelling ratio, d/d_0, of the PNIPA gels prepared at various P_{prep}'s, where d and d_0 are the diameters of the gel at observation and preparation, respectively. Interestingly, d/d_0 increases with P_{prep} and has a maximum around $P_{\mathrm{prep}} \approx 170$ MPa. The increase in d/d_0 means that the gel becomes more inhomogeneous with increasing P_{prep} and the effective number of cross-links is greatly reduced by formation of polymer-rich domains. The subsequent decrease in d/d_0 results from phase separation of the gel, resulting in a lack of domain-connecting chains responsible for swelling. This speculation is supported by the experimental evidence for the preparation temperature dependence of the equilibrium swelling.[11]

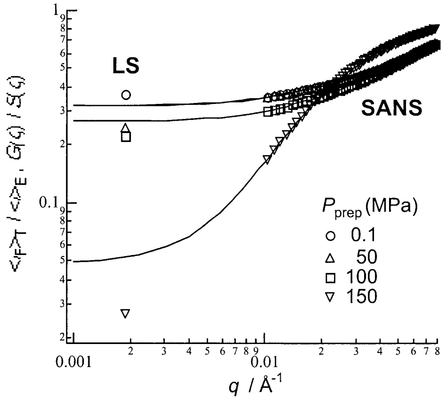

Figure 4. q dependence of the degree of inhomogeneities, $G(q)/S(q)$ and $<I_F>_T/<I>_E$ evaluated by SANS and LS, respectively. The solid lines are the theoretical functions calculated with the Panyukov-Rabin theory.

Figure 4 shows the q dependence of the static inhomogeneities. The q range is converted from the SANS to LS regimes. The solid lines are the fit with Panyukov-Rabin theory[12] on the structure factor of polymer gels, which theoretically takes account of static inhomogeneities. Hence, the total scattering intensity is written by,

$$I(q) = KS(q) = K\left[G(q) + C(q)\right] \qquad (1)$$

where K, $S(q)$, $G(q)$, and $C(q)$, are the proportionality constant, the structure factor, the thermal correlator, and the static correlator, respectively. The ratio, $G(q)/S(q)$, is a measure of the degree of inhomogeneities, taking smaller values with larger inhomogeneities. Though the details of the theory are described elsewhere,[12,13] the extraporation of $G(q)/S(q)$ fits well to $<I_F>_T/<I>_E$ for $P_{\mathrm{prep}} \leq 150$ MPa.

The divergence of light scattering intensity of PNIPA in water was first reported by Otake et al. for PNIPA aqueous solutions.[14] Our LS results show that $<I>_E$ increases steeply for $P_{prep} > 100$ MPa. As shown in the inset of Fig. 3a, the plot of $1/<I>_E$ vs P_{prep} indicates a linear relationship between $1/<I>_E$ vs P_{prep} and $<I>_E$ diverges at $P_{prep} = P_{prep,C} = 168$ MPa. Although, the reason for the presence of such a critical pressure has not been elucidated at all, it may be related to the unique properties of water molecule itself, as pointed out by Tanaka,[15] who proposed a two state model for liquid water, i.e., the presence of two competing orderings in water. One is density ordering and the other is bond ordering. This model features a crossover pressure ($\approx$200 MPa). It is not clear that this crossover pressure is related to the critical pressure disclosed in this work. A further investigation to clarify this issue is now in progress.

Conclusion

The microscopic structure of PNIPA gels have been investigated with small-angle neutron scattering as a function of gel preparation pressure, P_{prep}. The scattering intensity, $I(q)$, was found to be P_{prep} dependent, particularly in the low q region. $I(q)$ increased with increasing temperature. $I(q)$ exhibited a strong P_{prep} dependence and was largest for the gel prepared at $P_{prep} = 200$ MPa. The degree of imhomogeneities was found to be a smooth function of q in the scattering regions of SANS and LS, and the inhomogeneities increase with lowering q.

Acknowledgment

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