Magnetic field control of structure and function of poly(N-isopropylacrylamide) gels

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Abstract

The swelling and elastic behavior, hydration energy, and molecular diffusion of poly(N-isopropylacrylamide) gels (NIPA gels) prepared under magnetic fields (mag-gels) were investigated. The diameter of gels in swollen state at 298 K increased steeply with increasing magnetic field to become 40% larger at 28 T than at zero-field. The magnetic field effect on volume change depended strongly on the intensity and direction of the field. The change in length was larger in the direction perpendicular than parallel to the applied magnetic field, suggesting that polymer chains in the network should be aligned, despite very low chain density, to show structural and magnetic anisotropy. This structural anisotropy caused a difference in diffusivity of iodine in mag-gels. Mag-gels showed a more significant discontinuity in the volume phase transition than zero-field gels. Magnetic fields induced the volume phase transition over a critical magnetic field $H_c$ even in high cross-link conditions for the preparation of continuous volume change gels. Mag-gels had a small density of cross-link, e.g. the effective degree of cross-link of less than 1/2 at 10 T, and increase in the heat of volume phase transition or hydration energy. The magnetic-field induced volume phase transition relates to significant decrease in cross-link.

Keywords: Gel; Magnetic field; Volume phase transition; Magneto-orientation; Cross-link density; Hydration

1. Introduction

High magnetic fields are now available in the laboratory because of the development of superconducting technology. Many kinds of magnetic field effects have been investigated, such as radical pair reactions, molecular ordering, and crystallite growth, etc. However, it is still difficult to handle molecules and low density materials by magnetic fields, because magnetic energy is much less than thermal energy.

Hydrogels have been investigated from the viewpoint of not only their scientific interest but also their technological uses such as drug delivery systems and actuators. Thus, it is very important to develop the methodology for control of structures and properties of gels.

The magnetic energy $E_r$ of diamagnetic hydrocarbon chains is given by the following equation [1].

$$ E_r = -\frac{H^2}{2}(\chi_\perp + \Delta \chi \cos^2 \phi)Nv $$

where $H$ is the magnetic field intensity, $\chi_\perp$ the magnetic susceptibility perpendicular to the molecular axis, $\Delta \chi$ the magnetic anisotropy, $\phi$ the angle between magnetic field and molecular axis, $v$ the volume of a chain and $N$ the number of chains. Although $E_r$ of a non-magnetic monomer or polymer chain is not enough to orient under magnetic fields, a polymer chain network produced in the polymerization process may orient cooperatively in a magnetic field. Therefore, magnetic fields may be a useful method for structural control of gels.

Gel properties depend on distribution of the polymer chains, densities of both chains and cross-links, and hydration in gels. If these factors can be controlled by magnetic fields, novel gels could be produced. Chemically-cross-linked poly(N-isopropylacrylamide) gels (NIPA gels) in water undergo a discontinuous volume change or volume phase transition with increasing temperature at about 307 K [2–5]. This environmental sensitivity is mainly ascribed to strong hydrophobicity of the $N$-isopropyl group located on the side chain. At low temperature, water molecules around an isopropyl group are highly ordered and form an iceberg structure in order to minimize the number of contacts with hydrophobic groups [6]. This water structure is broken by thermodynamic perturbations such as temperature rise to lead to the volume phase transition.
When a gel is prepared under magnetic fields, it ‘remembers’ how it was made because cross-links fix its initial structure. In this work, samples of a typical thermo-responsive gel, NIPA gel, were prepared under high steady magnetic fields and their physical properties were examined.

2. Experimental section

NIPA gels were prepared by radical polymerization of \(N\)-isopropylacrylamide (kindly supplied from KOHJIN Co., Ltd) as a monomer, \(N,N'\)-methylenebisacrylamide (BIS) as a cross-linker, potassium peroxodisulfate (KPS) as an initiator, and \(N,N',N'\)-tetramethyl-ethylene diamine (TEMED) as an accelerator [7–9]. The monomer concentration was fixed at 700 mM, and BIS concentration of 4.3–34.4 mM, usually 8.6 mM, were used to investigate the effect of cross-link density. An 8 ml aqueous mixed solution of the monomer and BIS was kept at 278 K and 2 ml aqueous KPS solution (150 mM), then 60 μl TEMED were added. The polymerization was allowed to proceed for 1 h at 278 K in a glass capillary of 0.4 mm inner diameter to make a cylindrical gel. Magnetic fields were applied perpendicular (\(H_t\)) and parallel (\(H_s\)) to capillaries for 1 h using a superconducting magnet (Sumitomo Heavy Industries Ltd; \(H \leq 10\) T) and a hybrid magnet (National Institute for Materials Science; \(H \leq 30\) T). Then, the capillaries remained quiescent under zero field at 278 K for 24 h. The cylindrical gel samples were taken out of the capillaries, washed repeatedly by temperature swing in large amounts of distilled water to remove residual chemicals, and then dried gently at room temperature in air. These gels will be referred as a zero-field gel and mag-gel (\(H_t^-\) and \(H_s^-\)-gels).

The dried gels were cut into 20 mm long rods and immersed in distilled water for 24 h to reach swelling equilibrium. The swelling behavior of gels was observed by an optical microscope coupled with a CCD camera as temperature was increased from 278 to 318 K under zero field. Equilibrium time was 2 h at each temperature.

The molecular diffusion of \(I_2\) in gels was examined at 298 K using \(H_t^-\) and \(H_s^-\) gels and a zero-field gel prepared in 2.0 mm (i.d.) glass capillaries. The gels containing 1% starch were partially immersed vertically their edge in an aqueous KI/\(I_2\) solution at 298 K and the velocity of color changing front was observed at zero-field.

Differential scanning calorimetry (DSC) experiments were carried out with a Rigaku DSC8230 calorimeter from 298 to 333 K at the heating rate of 0.1 K/min, referring to a pure water [8]. The melting point of indium was used to calibrate the temperature. The dried NIPA gels were immersed into distilled water for 24 h and then cut into 1 mm pieces. The swollen gels were sealed in aluminum pans.

3. Results and discussion

Fig. 1 shows the volume phase transition of NIPA gels prepared under a 10 T magnetic field parallel (\(H_t\)) and perpendicular (\(H_s\)) to the axis of a glass capillary. The zero-field gel shrank discontinuously from a swollen state with increase in temperature at 306.8 K [10,11]. The swelling diameter of both mag-gels prepared under a 10 T magnetic field became larger than that of a zero-field gel, although an \(H_t^-\)-gel was much thicker than a \(H_s^-\)-gel. As magnetic fields made gels thinner at shrunken state, the volume phase transition of the mag-gels was very significant, especially when magnetic fields were applied in parallel to the direction of change in length, in this case, to the radial direction of a gel (\(H_s\)). This means that an \(H_t^-\) gel can swell much more in the radial direction than in the length direction, which was confirmed using a cylindrical gel containing carbon black for positioning, indicating that magnetic fields induced structural anisotropy. The temperature of the volume phase transition of NIPA gels was independent of magnetic field.

The diameter in the swollen state at 298 K increased markedly with increase in magnetic field, and the degree of diameter increment reached about 40% at 28 T (\(H_s\)) compared to that of a zero-field gel [12], as shown in Fig. 2. The diameter
change due to magnetic fields was larger in an $H_t$-gel than an $H_s$-gel, e.g. 25% for $H_t$ against 10% for $H_s$ at 10 T. In the shrunk state (308 K), the diameter decreased less than 10%. In lower magnetic field less than 10 T ($H_t$) or 15 T ($H_s$), the volume changes depended more strongly on magnetic field intensity, followed by gradual increase in volume up to 30 T. Similar behavior was observed for other chemically-cross-linked gels such as poly-acrylamide and poly-($N,N$-diethylacrylamide) gels (not shown). Magnetic fields should align NIPA polymers formed in polymerization process of NIPA monomers. The hydrocarbon backbone and amide groups in NIPA gel tend to orient in perpendicular and presumably parallel, respectively, to a magnetic field, as schematically shown in Fig. 3. In other words, polymer chains in $H_\perp$ cylindrical gels should be parallel to the cylinder axis. The structural anisotropy of a dry $H_\perp$ gel was detected as magnetic anisotropy ($|\Delta \chi| = 3.0 \times 10^{-8} \text{ emu/g}$) with a SQUID magnetometer.

The structural anisotropy of mag-gels was also detected as difference in molecular diffusion in gels. Fig. 4 shows that the rate of iodine diffusion in NIPA gels containing starch increased in the order $H_\perp$, zero-field, and $H_\parallel$ gels. The diffusion constant of I$_2$ in $H_\perp$ (10 T)- and $H_\parallel$ (10 T)-gels was about 10% larger and 20% less, respectively, than that in a zero-field gel. This trend seems to be consistent with the magnetic orientation of polymer chains, suggested above. Such molecular diffusion control due to magnetic field suggests the potential of magnetic fields for material separation.

The molecular diffusion in mag-gels is understandable from the viewpoint of chain orientation, but the swelling behavior of mag-gels or the increase in diameter of both $H_\perp$- and $H_\parallel$-gels seems not to be because mechanical extension of a gel network in one-dimension should be accompanied by shrinkage in another. Therefore, magnetic orientation of chains in polymerization must be different from mechanical chain orientation and relate to chemical processes. A simple model for the swelling mag-gel is a polymer network comprising magnetically-ordered chains connected by similarly-oriented cross-link chains, in which hydrocarbon backbone are folded along a glass capillary (Fig. 3). Taking the folded network out of the capillary, the gel may swell in all directions. As described below, the experiments suggest that other factors such as dangling chains and hydration as well as magnetic chain-ordering should be responsible for swelling of mag-gels.

It is well known that decrease of BIS concentration at constant monomer concentration in preparation, $q^{\text{pre}}$, promotes the swelling of NIPA gels. Since magnetic fields also promoted swelling at a swollen state, as shown in Fig. 2, it is presumed that magnetic fields would lead to reduction of the effective cross-link density, $q^{\text{eff}}$, in polymer network. Then, we can estimate $q^{\text{eff}}$ by comparison of the diameter of mag-gels and gels prepared at different $q^{\text{pre}}$. Fig. 5 demonstrates the estimation process. For example, the diameter of a 10 T gel, 0.50 mm, corresponds to the diameter for $q^{\text{pre}} = 0.006$, as indicated by the dashed line. The $q^{\text{pre}}$ value may be referred to the effective cross-link density, $q^{\text{eff}}$. The $q^{\text{eff}}$ value at 10 T was 1/2 of a zero-field gel or the initial degree of cross-linkage, $q^{\text{pre}} = 0.0123$, indicating that a 10 T gel was very soft. For a 28 T gel, $q^{\text{eff}} = 0.003$, which was only 1/3. The $q^{\text{eff}}$ values

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Fig. 3. A plausible network structure of a cylindrical gel under an $H_\perp$ magnetic field. $\parallel$ expresses the point at which the backbone chain extends to direction out-of-the-paper. $\bullet$, dangling chains; $\ast$, end groups of dangling chains; (i-Pr), iso-propyl groups.

Fig. 4. Diffusion distance of I$_2$ in NIPA gels at 298 K (open, $H_t$-gel; closed, $H_s$-gel) as a function of time. Magnetic field, $H/T$: circle, 0; triangle, 5; diamond, 10.
estimated in such manner are plotted as a function of magnetic field in Fig. 6. All data were obtained from gels prepared at \( q_{\text{pre}} = 0.0123 \). \( q_{\text{eff}} \) decreased markedly with increasing magnetic field, demonstrating that gels were very much softened by magnetic fields. The Young’s modulus of mag-gels supported the softness, e.g. the Young’s modulus of a 10 T gel was about 1/3 of a zero-field gel. Considering that no change in an average \( q_{\text{eff}} \) value, estimated from C/N ratios of gels obtained by elemental analysis, with magnetic field was detected, a dangling chain, one of whose edges is not cross-linked, would be formed by magnetic fields. The increase of dangling chain with magnetic fields was confirmed by the results that the elastic relaxation time of mag-gels was much longer than that of a zero-field gel. This is considered that the formation of cross-link points should be inhibited because of magneto-orientation of polymer chains. Also, the average number of monomer residue between cross-linking points increased with increasing magnetic field, which was estimated by the equation given by Flory [13]. These demonstrate reduction of cross-link density in mag-gels.

When magnetic fields were applied to reactant solutions that normally would give rise to gels that show no volume phase transition, the volume phase transition of NIPA gels was able to be induced. A NIPA gel having high degree of cross-link, \( q_{\text{pre}} = 0.0492 \), showed continuous volume change at around 307 K, but after a 28 T magnetic field was applied to the same reactant solution, a significant discontinuous volume change appeared at 306.8 K, as shown in Fig. 7. The discontinuity was enhanced with increasing magnetic field and not saturated even at 30 T. Fig. 8 shows the variation of diameter of NIPA gels of swollen and shrunken states at the volume phase transition

Fig. 5. Variation of diameter of swollen NIPA gels (\( q_{\text{pre}} = 0.0123 \)) at 298 K as a function of magnetic field intensity \( H \) (●) and initial degree of cross-link \( q_{\text{eff}} \) (≡ \( C_{\text{NIPA}}/C_{\text{BIS}} \) in preparation, \( C_{\text{NIPA}} = 700 \) mM; □). Dashed line demonstrates how to estimate the effective degree of cross-link \( q_{\text{eff}} \) at 10 T. Arrow indicates the \( q_{\text{eff}} \) value at 10 T.

Fig. 6. Variation of the effective degree of cross-link as a function of magnetic field intensity. Broken line is an average \( q_{\text{eff}} \) value estimated from the elemental analysis of C and N.

Fig. 7. Volume changes of NIPA gels prepared at \( q_{\text{pre}} = 0.0492 \) at zero-field (●) and 28 T (▲) with temperature.

Fig. 8. Variation of diameter of NIPA gels of swollen (closed) and shrunken states (open) at the volume phase transition temperature (306.8 K) as a function of magnetic field in gel preparation. \( q_{\text{pre}} \): circle, 0.0123; square, 0.0492.
temperature (306.8 K) as a function of the magnetic field strength used in gel preparation. A usual NIPA gel prepared at $q_{\text{pre}} = 0.0123$ showed a typical volume phase transition. Applying magnetic fields to reactant solutions for the gel, the diameter difference between swollen and shrunken states at 306.8 K became much larger with increasing magnetic field. In the case of a gel showing no volume phase transition in the absence of a magnetic field, the volume phase transition occurred over a critical magnetic field $H_c$; e.g. 10 T for gels prepared at $q_{\text{pre}} = 0.0492$. The volume phase transition will be subject to diffusion of polymer network in medium [14], which depends on polymer concentration and cross-link density. Since magnetic fields produced dangling chains to reduce seriously cross-links, the volume phase transition may occur as in low $q_{\text{pre}}$ gels. However, the induced volume phase transition due to magnetic fields is not explained completely by a reduction of the degree of cross-link or $q_{\text{eff}}$, suggesting that the induced volume phase transition would be subject to other factors than the network density, such as dangling chain concentration and hydration around chains.

The thermal behavior of NIPA gels prepared under magnetic fields is depicted in Fig. 9. The transition temperature was again unchanged by magnetic fields. On the other hand, endothermic peak areas of mag-gels were larger than that of a zero-field gel. The heat of volume phase transition of NIPA gels, $J/(\text{mol residue})$, increased with increase in magnetic field. This suggests that the amount of hydrated water around the polymer chains increased by gel formation under magnetic fields.

4. Conclusion

Strong magnetic fields used in preparing NIPA gels significantly affected the volume and swelling behavior of the gels via magnetic orientation of the polymer chains, dangling chain formation, and hydration enhancement to make gels soft. Structural and magnetic anisotropies of NIPA gels were induced by magnetic fields, which led to anisotropic diffusion of $I_2$ in the gels. Moreover, magnetic fields induced volume phase transition over a critical magnetic field $H_c$. New insight, demonstrating the potential of magnetic fields, was obtained, but the mechanism is still unclear, and the results raise many questions, such as; how the very low density polymer chains in the network orient cooperatively by magnetic fields, what is the interaction between hydration shell and magnetic field, does the magnetic field affect the polymerization reaction, what is the formation process and role of dangling chains, etc.

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