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A study on dynamics of water in crosslinked poly (*N*-isopropylacrylamide) gel by n.m.r. spectroscopy

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The dynamics of crosslinked poly (*N*-isopropylacrylamide) gel have been studied by means of pulsed-gradient spin-echo (PGSE) ^{1}H nuclear magnetic resonance (n.m.r.), pulse ^{1}H n.m.r. and ^{1}H n.m.r. imaging. The self-diffusion coefficients of HDO (D_{HDO}) in D_2O (containing a small amount of HDO) in the gels with various degree of swellings were determined by the PGSE ^{1}H n.m.r. method. From these experimental results, it was found that the D_{HDO} is decreased as the degree of swelling is decreased, and D_{HDO} in the gels with a constant degree of swelling in going from 20 to 45°C is transitionally decreased at about 32°C, which corresponds to the phase transition temperature. From the detailed analysis of proton spin–spin relaxation time T_2 determined by the pulse ^{1}H n.m.r. method, the process of the volume phase transition of the gel has been elucidated. Furthermore, spatial information about the molecular motion of water in the gel sample was obtained by T_2 enhanced ^{1}H n.m.r. imaging.

(Keywords: crosslinked poly(*N*-isopropylacrylamide) gel; n.m.r. spectroscopy)

INTRODUCTION

It has been demonstrated that nuclear magnetic resonance (n.m.r.) methods such as pulse ^{1}H n.m.r., pulsed-gradient spin-echo (PGSE) ^{1}H n.m.r., ^{1}H n.m.r. imaging and solid-state high-resolution ^{13}C n.m.r. provides useful information about the molecular motion and structure of polymer gels[1–12]. In the poly(*N*-isopropylacrylamide) (PNIPAM) system considered here, we have elucidated the dynamical and structural features of poly(*N*-isopropylacrylamide) in aqueous solution as a function of temperature through the observations of proton (^{1}H) spin–lattice relaxation times (T_1) and spin–spin relaxation times (T_2) by pulse ^{1}H n.m.r.[1], and of ^{13}C chemical shifts by solid-state high-resolution ^{13}C n.m.r.[2]. From these experimental results, it was clarified that the molecular motion and structure of water and PNIPAM in this system transitionally change at around 32°C, at which PNIPAM in water is well known to show phase transition from sol to gel[13,14].

As a continuation of these research works on PNIPAM system, we aim to elucidate dynamics of water in a crosslinked PNIPAM gel systems as a function of temperature microscopically and macroscopically by means of PGSE ^{1}H n.m.r., pulse ^{1}H n.m.r. and ^{1}H n.m.r. imaging methods.

EXPERIMENTAL SECTION

Materials

N-isopropylacrylamide (NIPAM) (Tokyo Kasei Kogyo) was recrystallized from hexane solution. *N,N'*-Methylene-bisacrylamide (MBAA) (Wako Pure Industries) used as a crosslinking monomer was recrystallized from ethanol solution. $K_2S_2O_8$ (Wako Pure Chemical Industries) used as the polymerization initiator was recrystallized from aqueous solution. *N,N,N',N'*-Tetramethylethylenediamine (Tokyo Kasei Kogyo) was used as the polymerization accelerator without purification.

PNIPAM gel was prepared by redox polymerization of NIPAM and MBAA in aqueous solution at 273 K for 24 h in a glass tube with various diameters. By varying the amount of MBAA, PNIPAM gels were obtained with different degrees of swelling.

The degree of swelling of PNIPAM gel (Q) is defined as the ratio of the mass of swollen polymer gel ($M_{swollen}$) to that of dried polymer (M_{dry}) as follows

$$Q = M_{swollen}/M_{dry}$$

Measurements

The diffusion-coefficient measurements on water in PNIPAM gel were carried out by PGSE method by means of a JEOL GSX-270 n.m.r. spectrometer operating at 270.1 MHz for ^{1}H with a home-made pulsed-gradient generator at various temperatures. In the PGSE ^{1}H n.m.r. method the ($\pi/2$-τ-π) pules sequence and two gradient-field pulses are used as shown in *Figure 1*, where τ is the pulse interval[15,16]. The relationship between echo signal intensity and pulse field gradient parameters is given by

$$\ln[A(\delta)/A(0)] = -2\tau/T_2 - \gamma^2 g^2 D^2 \delta^2 (\Delta - \delta/3)$$

where $A(\delta)$ and $A(0)$ are echo signal intensities at $t = 2\tau$ with and without the magnetic field gradient pulse length δ, respectively. γ is the gyromagnetic ratio of the proton, g is the field gradient strength, D is the self-diffusion coefficient and Δ is the gradient pulse interval. To obtain the D value, the $A(\delta)$ values are measured with changing δ and $\ln[A(\delta/A(0)]$ are plotted against $\gamma^2 g^2 D^2 \delta^2 (\Delta - \delta/3)$. The D value

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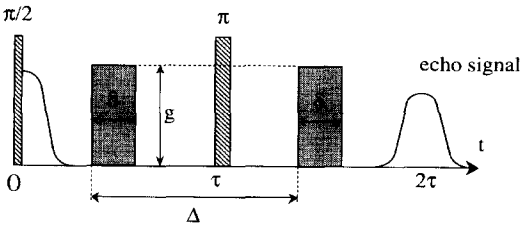

Figure 1 Pulsed field gradient pulse sequence for measuring diffusion coefficient

was determined from the slope of a plotted line. Spectral width and data points were 4.0 kHz, 4096, respectively. The field-gradient strength was 5.88 T m^{-1}. The gradient pulse interval and the field gradient pulse length were 30 ms and 0.06–2.0 ms, respectively.

^1H pulse n.m.r. measurements were carried out with a Brucker minispec PC-20 spectrometer operating at 20 MHz, varying the temperature. The Carr–Purcell–Meiboom–Gill (CPMG) method for the measurements of T_2 was used[16,17]. Analysis of the T_2 signal was carried out using the nonlinear least squares method by an NEC PC9801 microcomputer.

^1H n.m.r. imaging measurements were carried out by means of a JEOL GSX-270 n.m.r. spectrometer operating at 270.1 MHz with a JEOL NM-GIM270IT10 imaging system at temperatures from 296 to 313 K. In these experiments the ^1H spin density and the ^1H T_2 images of water molecules in the gel were observed. As reported previously[8,9], this imaging pulse sequence is based on the spin-echo pulse sequence of Hahn. The data processing for two-dimensional images was performed by the Fourier imaging method. In the ^1H n.m.r. imaging experiments, the gradient strengths used for the slice selection was 0.22 T m^{-1} and the slice thickness was 0.2 mm. The number of data points and accumulations were 256 and 2, respectively, to obtain ^1H n.m.r. image signals with a reasonable signal-to-noise ratio.

During the n.m.r. experiments, the heating and cooling rates are *ca.* 1 min °C^{-1}. The n.m.r. experiments were carried out after enough elapsed time to reach a given temperature.

RESULTS AND DISCUSSION

Self-diffusion of water in PNIPAM gel as a function of the degree of crosslinking

The swelling curves of PNIPAM gel in water is shown as a function of temperature in *Figure 2*. As seen from this figure, the degree of swelling (Q) of the gel is decreased with an increase in temperature from 20 to about 30°C, and is transitionally decreased around 33–34°C.

The D values of HDO (D_{HDO}) in a PNIPAM gel swollen with deuterated water (D_2O), in which a small amount of HDO is contained, have been determined under the state of equilibrium swelling at 23°C as a function of Q (*Figure 3*). The D_{HDO} value in the gel is increased with an increase in Q and asymptotically approaches the D_{HDO} in neat D_2O at $Q > 40$.

The molecular motion of solvent during the volume phase transition is revealed through the observation of D_{HDO}. The D_{HDO} values for water in a PNIPAM gel ($Q = 66$ at 20°C) and neat water are plotted against temperature in *Figure 4*. The D_{HDO} of HDO in neat D_2O is linearly increased with an increase in temperature. During the n.m.r. experiments on the gel, water is exuded and wiped away. The D_{HDO} value

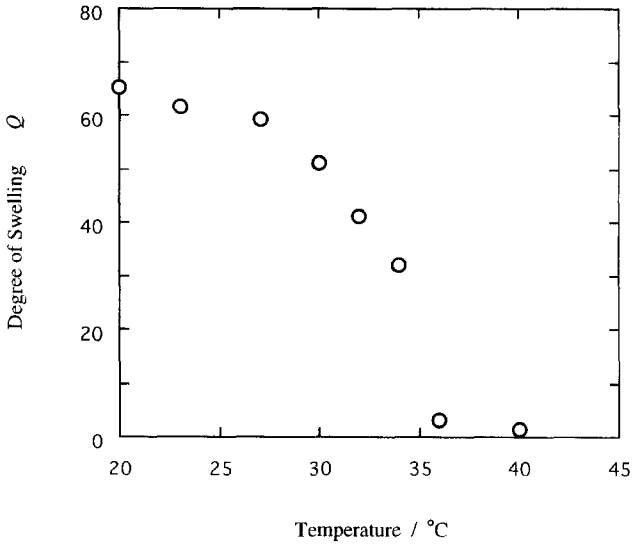

Figure 2 The temperature dependence of the degree of swelling Q under state of equilibrium for a PNIPAM gel

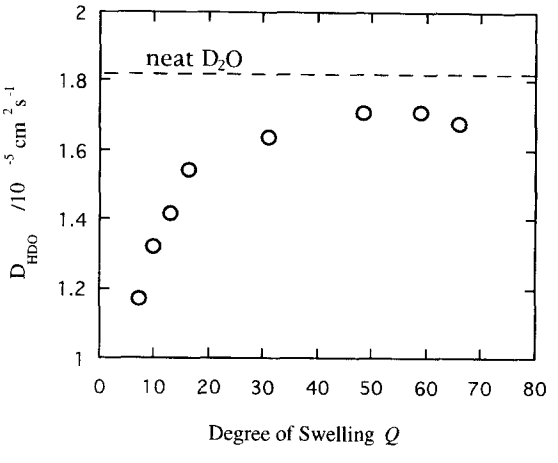

Figure 3 The dependence of diffusion coefficient for HDO, D_{HDO} on the degree of swelling (Q) in a PNIPAM gel. The dashed line indicates the diffusion coefficient of a small amount for HDO contained in neat D_2O

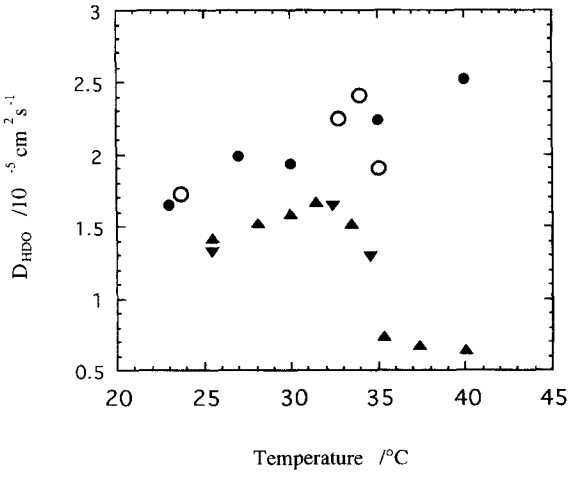

Figure 4 The temperature dependence of the diffusion coefficient for water molecule (D_{HDO}) in PNIPAM gel with equilibrated volumes (○), in NIPAM gel with a constant volume ($Q = 4$; heating (▲) and cooling (▼)) and in neat D_2O (●)

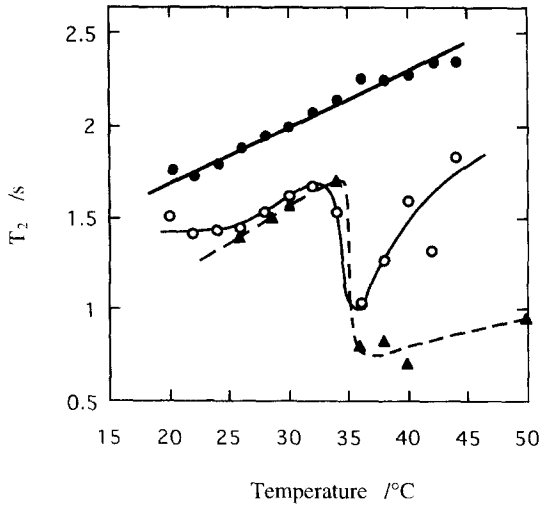

Figure 5 The temperature dependence of $^1HT_2$ for H_2O in neat water (●), in a PNIPAM gel (○), and in a PNIPAM gel with a constant volume (▲)

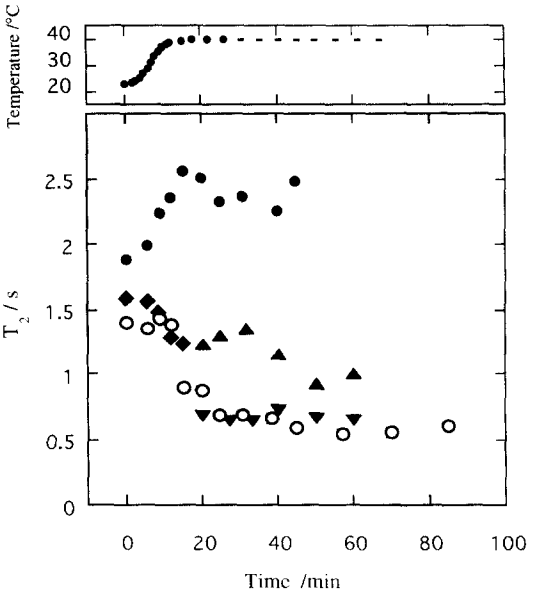

Figure 6 Time courses of $^1HT_2$ for water in neat water (●),in sample Gel-A (◆), and in sample Gel-B (○). After elevation of temperature, Gel-A shows two components of T_2; (▲) and (▼)

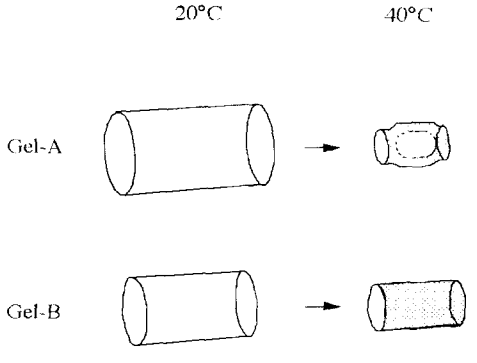

Figure 7 Diagrammatic illustration of shape change for samples Gel-A and Gel-B by varying temperature

increases as the temperature is increased up to 34°C, and at the volume phase transition temperature (T_{VPT}; 34°C), the D_{HDO} value transitionally decreases. This means that the mobility of water in the gel is increased with an increase in temperature up to 34°C in spite of the decrease in Q from 66 to 30 (as shown in *Figure 2*), and is transitionally decreased at 34°C due to the large decrease of the Q value. After the T_{VPT}, PGSE ^1H n.m.r. signal becomes very broad due to a large decrease in molecular motion by shrinkage of the gel.

The molecular motion of water in the gel at a constant value of Q has been studied. A PNIPAM gel in the shrunk state is put in an n.m.r. sample tube to determine D_{HDO} at various temperatures by heating and cooling, as shown in *Figure 4*. The D_{HDO} value is decreased around the T_{VPT}. Such a decrease of D_{HDO} is caused by decrease of the mobility of water caught by polymer networks which are formed by physical crosslinking at the T_{VPT}. This process is reversible for heating and cooling as seen from *Figure 4*.

Phase transition of a PNIPAM gel viewed from $^1HT_2$

Figure 5 shows the plots of the $^1HT_2$ values of H_2O in neat water (●) and in the PNIPAM gel (○) against temperature at atmospheric pressure. The T_{2i} value of neat water increases as the temperature is linearly increased, and this shows that the mobility of water is monotonically increased within an increase in temperature within the measurement temperature range. The T_2 value of HDO in the PNIPAM gel increases as the temperature is increased up to 33°C. At T_{VPT} (34°C), the T_2 value is transitionally decreased. As the temperature is further increased, the T_2 value is increased again. Such behaviour is very similar to that in aqueous PNIPAM solutions as reported by us previously [1]. During the n.m.r. measurements, the gel shrinks with an increase in temperature and exuded water is wiped away. This implies that the mobility of water in the gel increases with an increase in temperature up to 33°C, in spite of a much smaller change of the Q value compared with the mobility of neat water, decreases transitionally at 33°C due to a large decrease in the Q value, and increases again with a further increase in temperature during which the Q value does not change.

In *Figure 5*, the $^1HT_2$ values of H_2O in a PNIPAM gel with $Q = 4$ (▲) are plotted against temperature from 20 to 45°C, where the degree of swelling is kept a constant. The T_2 value increases as the temperature is increased up to 34°C, and at the volume phase transition temperature, the T_2 value transitionally decreases again in spite of a constant Q value. Such behaviour can be understood by assuming that intermolecular interaction between the networks polymer chains above the transition temperature form, and so the mobility of water molecules is more restricted by the polymer networks than that below the transition temperature.

Shrinkage process of a PNIPAM gel viewed from $^1HT_2$ and ^1H n.m.r. imaging

In the shrinkage process of a PNIPAM gel induced by elevating temperature over T_{VPT}, the PNIPAM gel often forms the skin structure, in which the unshrunk inner layer is surrounded by the shrunk outer layer, and so it takes long time to complete the shrinkage process. (As seen from *Figures 4 and 5*, the change of D_{HDO} and T_2 is not so sharp and therefore the shrinkage process may arise from lower temperature than 32°C). *Figure 6* shows the time dependence of the $^1HT_2$ values for sample Gel-A with $Q = 13$ obtained by temperature change from 20 to 40°C and for sample Gel-B with $Q = 30$ at 20°C, as diagrammatically illustrated in *Figure 7*. In sample Gel-A, it was found from

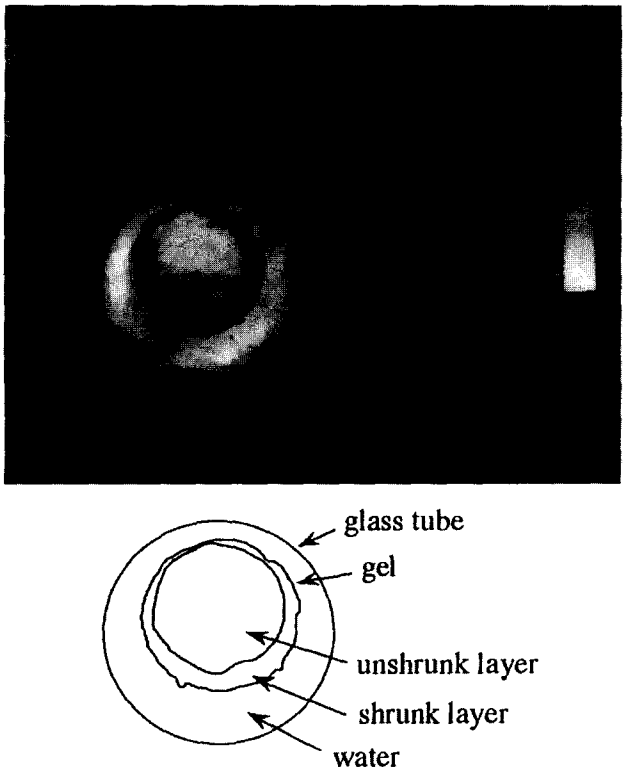

Figure 8 Observed $^1HT_2$ enhanced image of a PNIPAM gel ($Q = 40$) after rapid temperature change from 20 to 40°C

the T_2 curve that the two components with different $^1HT_2$ occur after the temperature was raised, in which the short T_2 component comes from the shrunk hard outer layer and the long T_2 component from the unshrunk soft inner layer. The T_2 value in the long T_2 component decreases slowly with the elapse time after 20 min, while that in the short T_2 component is independent of the elapsed time. This shows that the Q value of the unshrunk inner layer decreases after the formation of skin structure.

In order to know spatial information about the molecular mobility of the gel with skin structure during the shrinkage process, the ^1H n.m.r. imaging was observed. *Figure 8* shows a T_2 enhanced image for the gel ($Q = 44$ at 20°C) in water after elevating temperature. The magnitude of ^1H spin density is differentiated by 256 steps, and then the observed ^1H spin density image is represented by colours from white, representing the highest density, to dark red representing the lowest density. The region with red, lower density, is observed in the outer layer of the gel. This is the skin structure. The outer of the gel, indicated by white colour, is squeezed water. The unshrunk inner layer is indicated by the blue-coloured region. It is clear that the inner layer with the unshrunk regions is surrounded by the shrunk outer layer. The structure of such a layer will be changed by heating rate, etc.

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