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Phase Separation Induced Mechanical Transition of Poly(*N*-isopropylacrylamide)/Water Isochore Gels

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ABSTRACT: Poly(*N*-isopropylacrylamide) (NIPAAm) gels immersed in water (isobar gels) are known to undergo a volume phase transition at $T_c \cong 34$ °C. This transition, due to the release of hydrophobic hydration, leads to dramatic changes in physical properties, such as mechanical, optical, and thermal properties. We dealt with NIPAAm isochore gels, where the gels were isolated from water to keep the gel concentration, and investigated the mechanical and thermal properties of the gels as functions of temperature, cross-link density, and polymer concentration. The dynamic storage modulus, E', increased suddenly at T_c by a factor of 10 or more and became frequency dependent with increasing temperature. The enthalpy change related to the dissociation of the hydrophobic hydration was obtained as a function of the gel concentration. It was found that about 13 water molecules were released to dehydrate one NIPAAm molecule. Attenuated total reflection (ATR) infrared absorption spectroscopy was also conducted to elucidate the local environment of the NIPAAm gel network.

Introduction

Since the discovery of the volume phase transition of polymer gels,[1] the transition phenomenon has been studied extensively from both academic and application points of view.[2,3] Many physical properties, such as mechanical, thermal, and optical properties, change dramatically at the phase transition temperature, T_c. Tanaka et al. observed divergence of the light scattered from the polyacrylamide gel at T_c.[4] Li and Tanaka studied the volume phase transition by calorimetry and observed critical phenomena in the heat content and the order parameter at T_c.[5] They found that the critical exponents for the poly(*N*-isopropylacrylamide) (PNIPAAm) gel are the same as those predicted for three-dimensional Ising models. Shibayama et al. observed a critical behavior of the scattered intensity and the correlation length for PNIPAAm gels with the small-angle neutron scattering technique and obtained the critical exponents which were again in good agreement with the Ising model.[6]

Theories of volume phase transition were initiated by Dusek and Patterson for stretched gels.[7] Tanaka observed a discrete volume phase transition for a partially ionized polyacrylamide gel in acetone/water and proposed a theory for a discrete volume phase transition by incorporating the effects of ionic comonomers.[1] Although several other theories[8–12] have been proposed so as to refine the treatment by Dusek et al.[7] and Tanaka,[1] the essential features remain in the context of the Flory–Rehener theory[13–15] for the swelling of network polymers.

Mechanical properties of polymer gels undergoing a volume phase transition have recently been studied by Hirotsu,[16,17] who found a dissipation of the elongational modulus and the Poisson ratio at T_c. This was the case of an isobar gel where the abrupt change in the mechanical properties could be ascribed to the volume transition at T_c. In this study, however, we investigated the mechanical properties of isochore gels, i.e., the gel concentration being fixed, and found a remarkable increase in the dynamic moduli at T_c. Isochore gels are superior to isobar gels in the rate of response. Isochore gels can reach a new equilibrium state much faster than isobar gels upon a change of temperature.[6] This is due to the fact that the equilibration does not accompany any adjustment of their volume. Since the volume change in isobar gels is governed by mutual diffusion of the network and the solvent, the rate of equilibration is inversely proportional to the square of the gel size. On the other hand, the rate of equilibration of isochore gels seems to be simply dependent on the rate of heat transfer. This nature of isochore gels is also important from the viewpoint of applications, such as temperature sensitive rubber and/or shock absorbent.

Table 1. Description of Gel Samples

sample code	NIPPAm (mol/L)	BIS (10^{-3} mol/L)	APS (10^{-3} mol/L)	TEMED (10^{-3} mol/L)	BIS ratio (%)
NB04	0.69	8.62	1.75	8.0	38.5
NB06		12.9			57.7
NB10		22.4			100
NB14		31.4			140
NB20		44.8			200

We thus discuss the origin of the change of the mechanical properties at the transition temperature by studying viscoelastic properties of the gel. The variation of the local environment of PNIPAAm gels, the main contributor to the volume phase transition, is studied by Fourier transform infrared absorption spectroscopy and differential scanning calorimetry.

Experimental Section

Samples. *N*-Isopropylacrylamide (NIPAAm) monomer, kindly supplied by Kohjin Chemical Co. Ltd., was purified by recrystallization. The details of the procedure are described elsewhere.[6] Thus purified NIPAAm was mixed with prescribed amounts of *N,N'*-methylenebis(acrylamide) (BIS), and ammonium persulfate (APS) in distilled water. After degassing, *N,N,N',N'*-tetramethylethylenediamine (TEMED) was added to initiate redox polymerization in a glass mold. The polymerization was conducted for 16 h at 20 °C. Thus poly-NIPAAm (PNIPAAm) slab-shaped gels having several cross-link concentrations were prepared. The gels were washed in distilled water for more than 3 days. Table 1 shows the description as well as the sample codes. The sample code was given by the ratio of the BIS ratio, i.e., the BIS concentration ratio with respect to that of NB10. NB10 is a gel for the critical composition at which the swelling–shrinking curve becomes discrete.[5]

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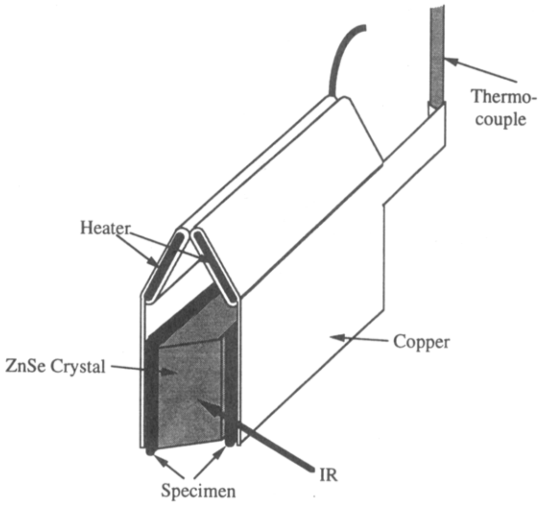

Figure 1. Illustration of the temperature controllable ATR sample holder.

Samples for dynamic mechanical measurements and thermal measurements were prepared by punching out a piece of gel slab of about 7 mm thick and 20 mm in diameter, followed by gradual shrinking at a temperature slightly above the transition temperature, T_c. For the infrared absorption study, about 1-mm-thick slab gels in the swollen state were used.

Dynamic Mechanical Measurements. Dynamic mechanical measurements were conducted on a Rheospectoler DVE-V4, Rheology, Co., Ltd. A synthesized wave strain composed with 2^n-Hz sine waves, n being 0 to 7, was loaded to the gel. The relative strain was kept less than 1% of the sample thickness, i.e., 20–40 μm. The static load was in the range between 0.1 and 0.39 N. The compressive complex modulus, $E^* = E' + iE''$, was obtained as a function of temperature, where E' and E'' are the storage and loss moduli, respectively. The heating rate was 0.5 °C/min and it took about 100 min to complete a temperature scan. Water-absorbed absorbent cotton was placed near the sample so as to reduce water evaporation from the sample. Although a small amount of weight loss due to water evaporation was detected, it did not seriously affect the analysis of the mechanical data, as will be shown in Figure 7.

Infrared Absorption Spectroscopy. Infrared absorption spectra for the gel samples and the corresponding polymer films were obtained with a Firis 100 Fourier transform infrared absorption spectrometer, Fuji Electric Co., Ltd., a model equivalent to a Matheson Firis 100. Because PNIPAAm gels became opaque at temperatures above T_c, the attenuated total reflection (ATR) method was employed for gels. The temperature of the gel film attached to the internal reflecting element (IRE), a ZnSe crystal cut to 60°, was controlled with a laboratory made temperature controllable sample holder, as shown in Figure 1. An isochore gel film was sandwiched between a copper plate and the IRE for both sides of the IRE. The temperature was regulated with a set of a heater and a thermocouple. This setup allowed us to obtain FTIR spectra as a function of temperature. The temperature was regulated within the error of ±0.2 °C. The resolution was 4 cm^{-1}, and spectra of 256 scans were accumulated.

Differential Scanning Calorimetry (DSC). DSC thermograms were obtained with a DSC3100, Mac Science Co., Ltd. Gel samples of 15–30 mg were sealed in seal-type aluminum pans, and DSC thermograms were recorded with the heating rate of 1 °C/min. No noticeable weight loss of the gel sample was detected during DSC runs in the temperature range between 20 and 60 °C. The gel concentration was determined by weighing the wet and dried gels.

Results and Discussion

1. Swelling Behaviors. Figure 2 shows the swelling behavior of the gels used in this study. D/D_0 is the linear swelling ratio, where D is the size of the gel at a given temperature and D_0 is that of the as-prepared gel. All the gels were in equilibrium with the surrounding water. According to Li and Tanaka,[5] we designed the cross-link density so that NB04 and NB06 gels had a discontinuous transition around 34.5 °C, whereas NB14 and NB20 showed a continuous volume transition at the same temperature and NB10 was on the border of the two types of transitions. However, the cross-link density dependence of the continuity of the transition was not clearly observed due to a poor accuracy of the gel size measurement.

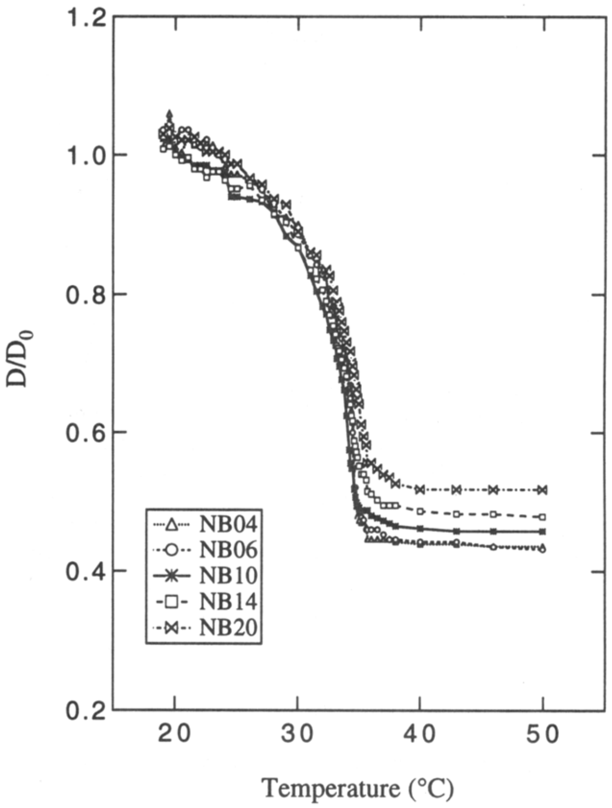

Figure 2. Swelling curve of NIPAAm gels in water. D/D_0 denotes the linear swelling ratio.

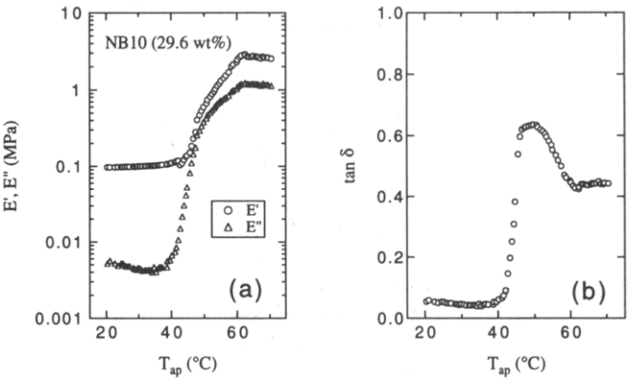

Figure 3. Apparent temperature, T_{ap}, dependencies of (a) the dynamic storage modulus, E', and loss modulus, E'', and (b) the loss tangent, tan δ, as a function of temperature for NB10 (29.6 wt %).

2. Mechanical Properties. Figure 3 shows the result of uniaxial compression for NB10 at 29.6 wt %. The frequency was 8 Hz. The apparent temperature, T_{ap}, dependencies of (a) the storage (E') and loss moduli (E'') and (b) the loss tangent, tan δ, are plotted. Note that this gel is in an isochore condition, i.e., isolated from the water reservoir. Both E' and E'' show steep upturns beginning around $T_{ap} = 40$ °C. Tan δ has a peak at the corresponding temperature. The temperature at which the upturn was detected was about 6 deg higher than T_c. This is simply due to the fact that the instrument has a temperature gap between the sample and the detecting positions because of a large heat capacity of the gel sample compared with conventional samples, e.g., thin plastic films. We checked that the upturn temperature corresponded to the phase separation temperature of the gel by visual observation. It should also be noted here that the gel is very elastic at $T < T_c$ since $\tan \delta$ is close to zero. This supports the validity of the treatment by Tanaka et al.,[18] where they regarded a gel as an elastic matter and discussed the cooperative diffusion of gels in terms of the theory of elasticity. However the gel becomes viscoelastic at $T > T_c$.

This kind of abrupt increase in the modulus was also observed by Hirotsu for the static modulus NIPAAm gels at 33.6° C.[16,17] However, his gel was an isobar gel. The change of the static modulus observed by Hirotsu was mainly due to the volume phase transition and was interpreted with the Flory-type mean-field theory.[12,13] However, in the case of an isochore gel, e.g., NB10, no volume change is allowed across T_c. Young's modulus (i.e., the elongational modulus), E, is related to the bulk modulus, K, by the following equation:

$$K = \frac{E}{3(1 - 2\sigma)} \tag{1}$$

where σ is the Poisson ratio. According to Hirotsu,[17] $\sigma \cong 0.3$ for $T < T_c$ and $\sigma \cong 0.48$ for $T > T_c$. Thus K is expected to be on the same order as or 1 order of magnitude larger than E.

The modulus of the gel is usually discussed with the bulk modulus, K. The bulk modulus for isobar gels is given by[1,6,10,19]

$$K = \frac{k_B T}{a^3}\left\{\frac{\phi^2}{1 - \phi} - 2\chi\phi^2 + \frac{\phi_0}{N_x}\left[\frac{1}{2}\left(\frac{\phi}{\phi_0}\right) - \frac{1}{3}\left(\frac{\phi}{\phi_0}\right)^{1/3}\right]\right\} \tag{2}$$

where $k_B T$ is the Boltzmann energy, a is the segment length, and N_x is the degree of polymerization between neighboring cross-links. ϕ and ϕ_0 are the volume fraction of the polymer in the gel at a given condition and that at the reference state. ϕ is simply estimated from the swelling ratio by assuming no volume change on mixing. ϕ_0 was taken to be the volume fraction of the polymer in the as-prepared gel. χ is the Flory interaction parameter given by

$$\chi = \frac{\Delta h - T\Delta s}{k_B T} \tag{3}$$

Δh and Δs are the enthalpy and entropy parameters. The value of Δh for PNIPAAm gels in aqueous solutions is reported to be between -5.5×10^{-21} and -7.5×10^{-21} J by Otake et al.[20] For theoretical calculations, we employed an average of these values, i.e., -6.5×10^{-21} J. On the other hand, Δs can be easily estimated if the Flory's Θ temperature is known, i.e., $\chi = 1/2$ at $T = \Theta$. By approximating $\Theta = T_c$, one gets $\Delta s = -2.8 \times 10^{-23}$ J/K. N_x in eq 2 cannot be estimated from the stoichiometric relation between NIPAAm and BIS monomers since the possibility of cyclization during polymerization of NIPAAm is rather high.[21] If one uses the calculated value of N_x obtained by the stoichiometric relation, the contribution of the entropy elasticity to the bulk modulus (the last term in the brace of the right hand side of eq 2) is underestimated. However, the contribution was negligible compared to the mixing free energy terms (the first and second terms) for deswollen gels. Thus we approximate eq 2 as

$$K \cong \frac{k_B T}{a^3}\left\{\frac{\phi^2}{1 - \phi} - 2\chi\phi^2\right\} \tag{2a}$$

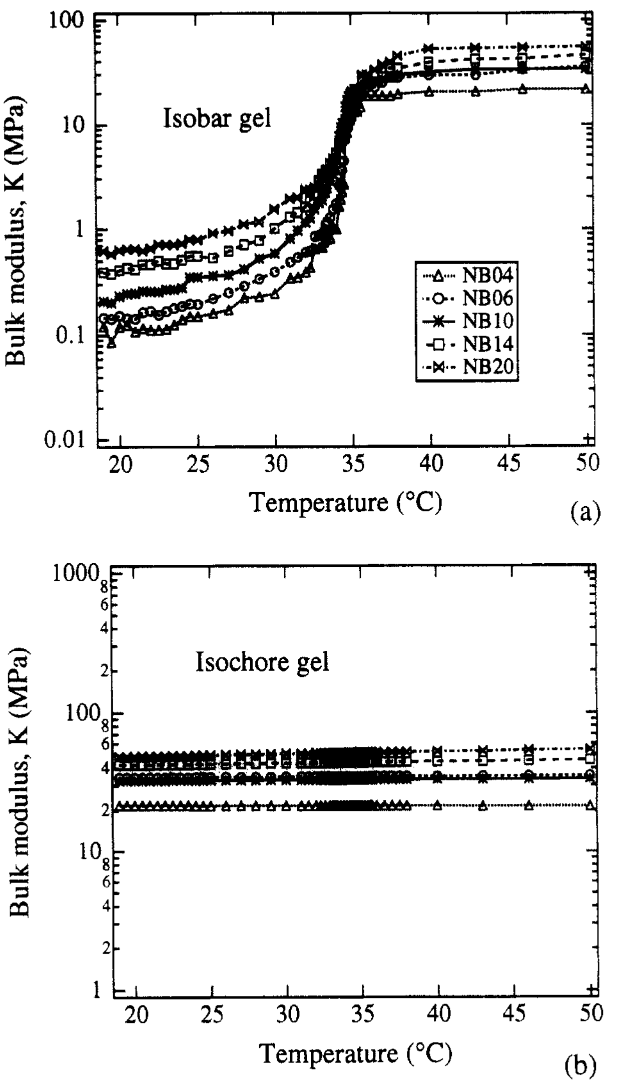

Figure 4. Predicted bulk moduli, K, for (a) an isobar gel and (b) an isochore gel based on eq 2a and the data in Figure 2.

Equation 2a allows us to avoid the uncertainty of N_x and ϕ_0. Figure 4 shows the comparison of the predicted bulk modulus, K, for (a) isobar and (b) isochore gels calculated with eq 2a, a = 6 Å, and the data in Figure 2. As shown in the figure, an abrupt increase in K is expected for the isobar gel, but not for the isochore gel. In the case of the isobar gel, K does increase suddenly at T_c, as was observed by Hirotsu.[16,17] However, the calculations for isochore gels do not predict any noticeable change in K at T_c although a stepwise increase in E' and E'' was observed experimentally, as shown in Figure 3. A similar phenomenon was observed by Hrouz and Ilavsky for poly(*N*,*N'*-diethylacrylamide) gel and its copolymer gels with sodium methacrylate. They observed an abrupt increase in the shear modulus upon a stepwise increase in temperature.[22]

Now let us discuss the origin of the abrupt increase in E' and E'' above T_c. Since the volume phase transition of gels is a phenomenon originated from a phase separation between polymer rich and poor domains, a phase separation occurs at $T = T_c$. As a matter of fact, the presence of a two phase structure of NIPAAm isochore gels above

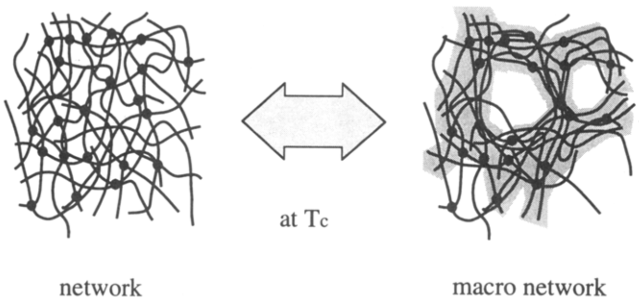

Figure 5. Schematic illustration of the macro network.

T_c was reported elsewhere.[6] The mechanical transition observed must be due to the phase separation because no volume change is involved in the isochore gels. Since the polymer chains are connected to each other via chemical bonds, a macroscopic phase separation is forbidden and a local densification of polymer subchains takes place to form a "macro network". This macro network consists of bundles of polymer chains (polymer rich domain) surrounded by a polymer poor matrix, as depicted in Figure 5. This is a bicontinuous structure since the bundles of polymer chains are interconnected to each other and form an infinite network immersed in an interconnected solvent rich phase. In a shrunken state, a gel is composed of this kind of macro network immersed in a highly swollen network of PNIPAAm chains. We guess that the increase in the modulus is mainly due to the formation of this macro network.

On the basis of this macro network model, let us discuss the modulus, E. Suppose a scaling rule applies to the relation between E and the polymer concentration C as follows:[23]

$$E \sim \frac{k_B T C}{N_x} = kC^{\alpha} \tag{4}$$

where k and α are a proportional constant and an exponent, respectively. According to the scaling rules for swollen gels in equilibrium with its solvent, α is given to be 2.25 and 3, respectively, for a good solvent and Θ solvent. For $T > T_c$, the gel is phase separated into a two phase structure consisting of a polymer rich phase (bundles of polymer chains) and a solvent rich phase having the volume fraction ϕ_p and $(1 - \phi_p)$, respectively. When the additivity of the modulus is assumed, E for such a two phase structure is given by

$$E = \phi_p E_p + (1 - \phi_p) E_s \tag{5}$$

where E_p and E_s are the moduli for the polymer rich phase and the solvent rich phase, respectively. Equation 5 is obtained by the so-called parallel model for composites.[24] Since the macro network forms an infinite network, the parallel model is more reasonable than the series model. The modulus in a homogeneous state ($T < T_c$), E_0, is given by

$$E_0 = kC_0^{\ \alpha} \tag{6}$$

where C_0 is the gel concentration in the homogeneous state. With increasing temperature above T_c, the gel phase separates into two phases having polymer concentrations of C_p and C_s, respectively, for the polymer rich and solvent rich phases. The volume fractions of these phases are simply given by the level rule as follows:

$$\phi_p = \frac{C_0 - C_s}{C_p - C_s} \qquad \phi_s = \frac{C_p - C_0}{C_p - C_s} \tag{7}$$

where ϕ_p and ϕ_s are the volume fractions of the polymer rich and solvent rich phases, respectively. By substituting eq 7 into 5 and assuming $C_p = mC_0$ and $C_s = 0$, we get

$$E \cong \frac{1}{m} k (mC_0)^{\alpha} = E_0 m^{\alpha - 1} \tag{8}$$

where m is the ratio of the polymer concentrations in the polymer rich phase with respect to that of the one phase state. In eq 8, we assumed $C_s = 0$ for simplicity. Equation 8 means that the modulus for the phase separated gel is $m^{\alpha-1}$ times larger than the homogeneous gel having the concentration C_0. Thus E is larger than E_0 provided $m > 1$ and $\alpha > 1$. We show here a simple example, e.g., $C_0 \cong 20$ wt %, $C_p \cong 100$ wt %, and $\alpha = 2.5$. This gives $E/E_0 \cong 11$. Thus a 1 order of magnitude increase in E is simply predicted. Although this calculation may be an exaggeration, this type of discussion is valid as long as the concentration dependence of the modulus is much stronger than that of the volume fraction.

Figure 6 shows the temperature dependence of E' of NB10 at (a) 20.0, (b) 29.6, and (c) 39.4 wt %. A synthesized strain of a 2^n-Hz sine wave strain was applied to a slab gel. Steep increases in E' are observed in all the samples. It should be noted that E' does not have any frequency dependence at $T < T_c$ but a significant frequency dependence appears for $T > T_c$. This is due to the change of the nature of the gel from an elastic matter to a viscoelastic matter with increasing T. Furthermore, the value of E' has the concentration dependence: the higher the concentration, the higher E'. This kind of concentration dependence was observed for all samples having different cross-link densities. It is also noteworthy that Hirotsu observed a dissipation of the modulus as well as the Poisson ratio at T_c, which was explained as the divergence of the osmotic compressibility. Such a dissipation was not observed here, which may be due to the fast rate of the temperature scanning in the measurement of E'. However, Figure 6 shows a symptom of the dissipation of E' for the low frequency components, e.g., the 1-Hz component. The dissipation of the bulk modulus at T_c was also observed by small-angle neutron scattering.[6]

Figure 7 shows time dependence of E' for NB04 after a temperature jump from 23 °C to (a) 43 °C followed by another jump to (b) 50 °C. When the sample temperature was raised, E' decreased slightly due to an instability of the temperature jump followed by a stepwise increase. After the increase in E', E' became time independent, which was also observed in the second jump (b). This clearly indicates that the stepwise increase in E' and E'' shown in Figures 3 and 6 is not due to the time course of temperature scanning but due to the temperature dependence of E' and E''.

We now discuss the molecular interaction between the NIPAAm segment and water molecules on the basis of the results of FTIR absorption spectroscopy so as to elucidate the change of the local environment of the network chains below and above T_c.

3. Infrared Absorption Spectroscopy. Molecular interactions between polymer chains and solvent molecules in a gel can be studied with several kinds of spectroscopic methods, such as NMR,[25] fluorescence,[26-29] and FTIR absorption spectroscopies. We employed here attenuated total reflection (ATR) FTIR spectroscopy.

Figure 8 shows survey spectra for the NB10 gel film obtained at 24, 34, 40, and 60 °C. The absorption peak

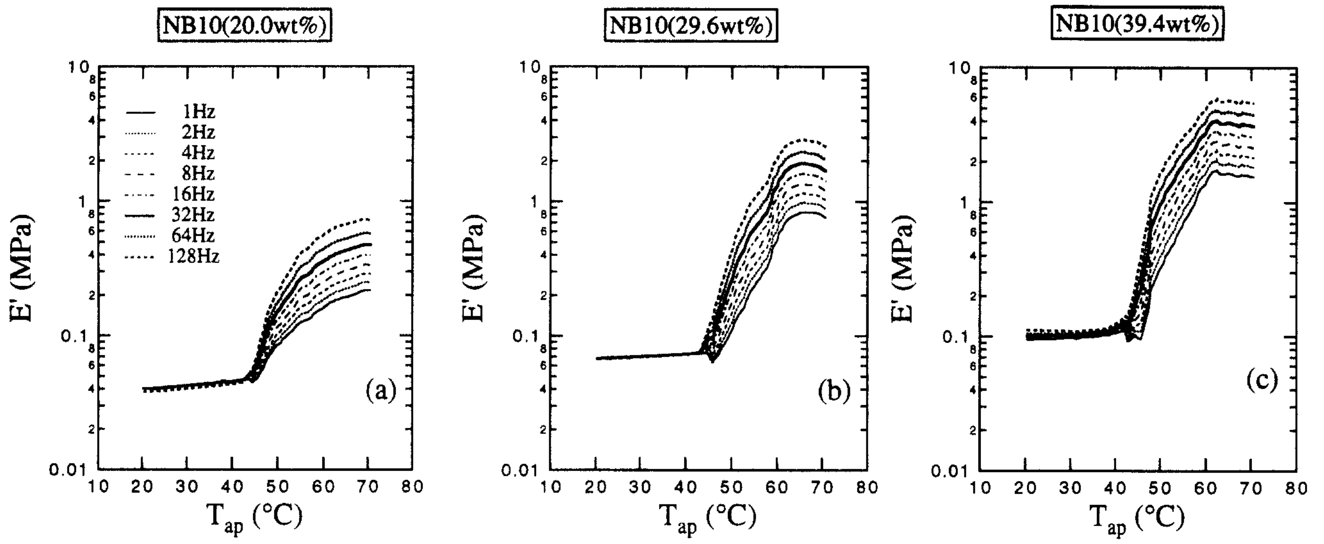

Figure 6. Apparent temperature, T_{ap}, dependence of the storage modulus, E', for NB10 at different concentrations: (a) 20.0 wt %, (b) 29.6 wt %, and (c) 39.4 wt %.

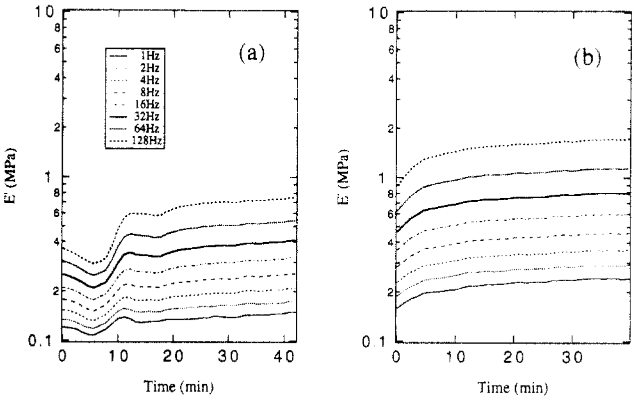

Figure 7. Time dependence of E' after a temperature jump (a) from 20 to 43 °C and (b) from 43 to 50 °C.

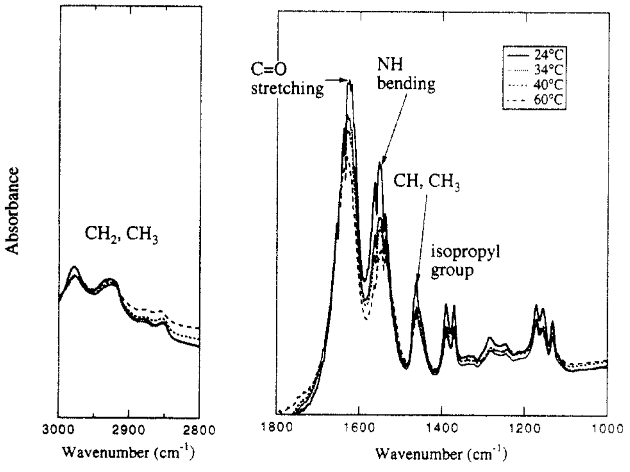

Figure 8. ATR-FTIR survey spectra for NB10 measured at several temperatures.

bands located at 1370–1400 cm^{-1} correspond to the vibration of the isopropyl group. The absorption bands at 1440–1490 cm^{-1} are the coupled band of the antisymmetric vibration of C—H and the symmetric vibration of CH_3. The bands around 1550 and 1640 cm^{-1} are related to the amide NH bending and C═O stretching vibrations, *respectively*. The absorption region between 2840 and 3000 cm^{-1} corresponds to C—H stretching vibrations of the methyl and methylene groups. This assignment was carried out by comparing the ATR spectra with those obtained by the transmission absorption method since the latter were more clearly resolved and were well established in the literature, particularly for polyurethane having amide groups.[30,31] Absorptions above 3000 cm^{-1}, where the O—H vibration band is seen, were not analyzed here because information related to the hydrogen bond between NIPAAm groups and/or that with water molecules is buried due to the presence of a large amount of water.

By employing a peak resolving technique,[32] we extracted the information about the C═O stretching (1640 cm^{-1}), N—H bending (1550 cm^{-1}), and C—H stretching vibration (2840–3000 cm^{-1}) peaks. Here we only discuss the result of the variation of the peak position of the CH_3 and CH_2 absorption bands. Further discussions are reported elsewhere.[33] Figure 9 shows changes of peak positions of CH_2 and CH_3 bands. Both the CH_2 and CH_3 bands for gel NB10 shift to a lower frequency above T_c, indicating an increase in constraints of the C—H stretching vibrations of CH_2 and CH_3 groups, whereas no abrupt change is detected for the polymer film (dried). Tokuhiro et al.[25] studied changes of NMR spectra for the PNIPAAm gel with temperature. They detected an appearance of a broad peak above $T > T_c$, indicating formation of solidlike aggregates. In addition, their measurement of the spin-lattice relaxation showed a decrease in mobility of the CH_3 group above T_c. This observation agrees well with our ATR-FTIR results and supports the validity of the model of the macro network formation.

4. **Differential Scanning Calorimetry (DSC).** The enthalpy change of dissociation of the hydrophobic solvation of the PNIPAAm gel, ΔH, was studied with DSC as a function of the gel concentration. Figure 10 shows DSC thermograms of NB06 measured with (a) a sealed pan and (b) an open pan. The open pan was prepared by making a pinhole in the sealed pan. In the case of a sealed pan, no endotherm due to water evaporation was detected, as shown in Figure 10a. In the case of the open pan, on the other hand, a huge endotherm was detected, having a peak at around 90 °C in addition to the small dissociation endotherm at T_c. This figure, therefore, indicates the endotherm obtained with a sealed pan is purely due to the dissociation of the hydrophobic solvation.

Figure 11 shows the DSC thermograms for NB06 gels having different gel concentrations. All of the thermograms show distinct endotherms, from which the transition temperature, T_c, and the enthalpy of dissociation, ΔH, were evaluated from the onset position and from the area of the endotherm, respectively. Figure 12 shows the

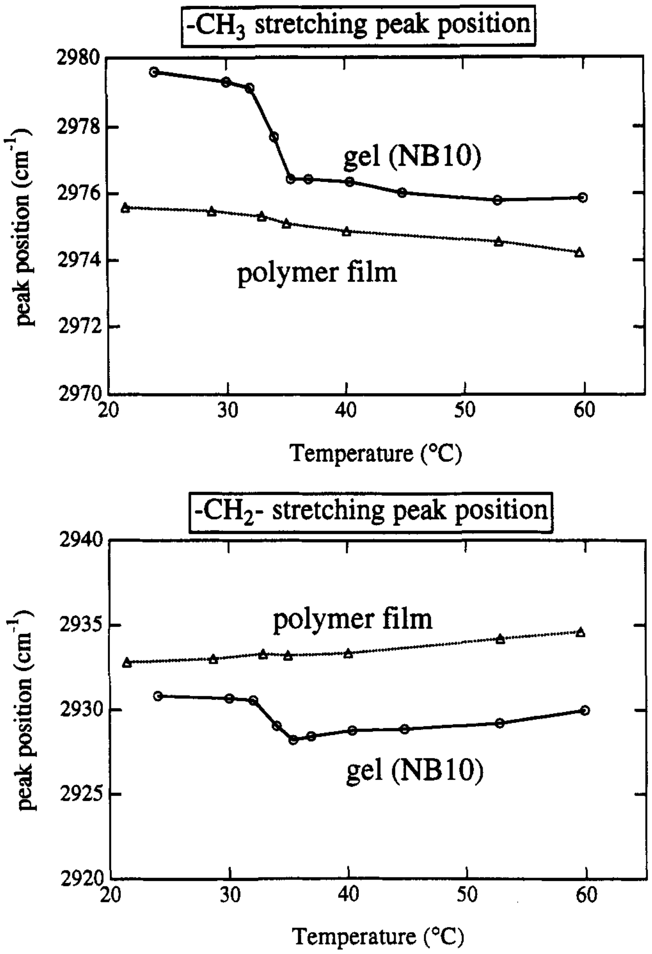

Figure 9. Temperature dependence of the peak positions of the CH_3 and CH_2 stretching bands measured for the gel NB10 and the corresponding linear polymer film.

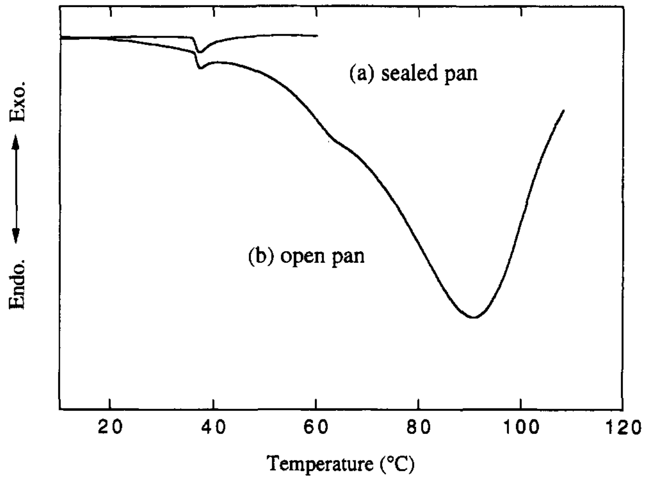

Figure 10. DSC thermograms of NIPAAm gels measured with a sealed pan and an open pan.

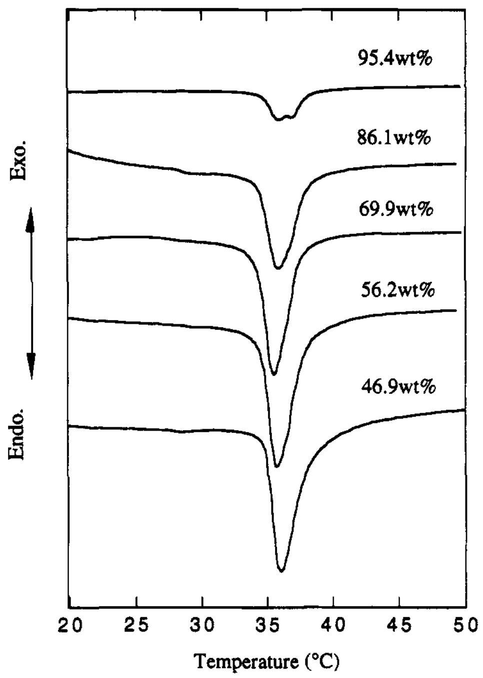

Figure 11. DSC thermograms of NIPAAm gels having different gel concentrations.

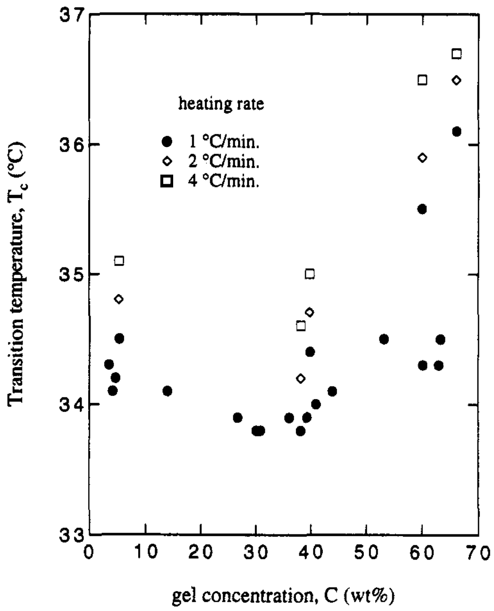

Figure 12. Gel concentration dependence of the transition temperature, T_c.

variation of T_c with gel concentration. The heating rate dependence of T_c is also given. It was surprising that T_c depends on the gel concentration. This tendency was seen irrespective of the heating rate, as shown in the figure. The gel concentration at which T_c has a minimum is roughly identical to the equilibrium gel concentration in the shrunken state.

If there exists a stoichiometric relation between the NIPPAm monomer unit and water molecules to form hydrophobic solvation, the relation can be examined on the basis of simple algebra. Suppose x mol of NIPAAm monomer units accompany y ($=nx$) mol of water molecules to create 1 mol of hydrophobic solvated structure with the solvation enthalpy ΔH, one gets

$$(\Delta H)_{\mathrm{gel}} \equiv \frac{\Delta H}{x+y} = \begin{cases} \dfrac{\Delta H_{\mathrm{N}}}{n} Y & 0 < Y \le Y_{\mathrm{m}} \\ \Delta H_{\mathrm{N}}(1-Y) & Y_{\mathrm{m}} < Y \le 1 \end{cases} \tag{9}$$

where Y and Y_m are the mole fraction of water and that at the stoichiometric relation, which are given as follows:

$$Y = \frac{y}{x+y} \qquad Y_{\mathrm{m}} = \frac{nx}{x+nx} \tag{10}$$

$(\Delta H)_{\mathrm{gel}}$ and ΔH_{N} are the enthalpy of dissociation per mole of gel sample and of NIPAAm monomer unit, respectively. A similar analysis was conducted by Guenet and McKenna for isotactic polystyrene in several organic solvents.[34]

Figure 13 shows the water mole fraction, Y, dependence of the enthalpy of dissociation per mole of gel, $(\Delta H)_{\mathrm{gel}}$. As

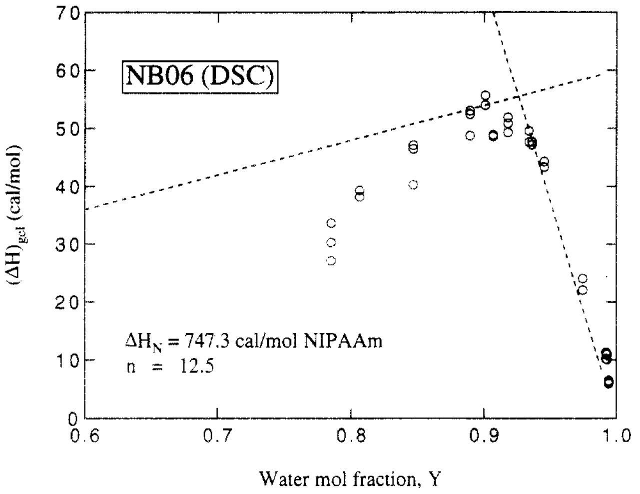

Figure 13. Water mole fraction dependence of $(\Delta H)_{gel}$. The dashed lines are drawn according to eq 9.

expected from eq 9, the data points are fitted with a triangle-shape function, from which the stoichiometric ratio, n, and the enthalpy of dissociation per mole of NIPAAm monomer unit, ΔH_N, were estimated to be 12.5 and 0.747 kcal/mol (3.12 kJ/mol of NIPAAm), respectively. The value of ΔH_N is in good accordance with the result of Otake et al., i.e., 1.5 J/g of NIPAAm solution for 45.8×10^{-5} mol of NIPAAm/g of solution, equivalent to 3.28 kJ/mol of NIPAAm.[20] The order of the hydrophobic interaction of NIPAAm with water is 1 order smaller than that of typical hydrogen bonding. The estimated n, the mole ratio of the NIPAAm monomer units to water molecules, indicates that about 13 water molecules are released from a NIPAAm monomer unit when hydrophobic solvation is dissociated. This value corresponds to the NIPAAm concentration of 33.4 wt %. It should be noted here that the NIPAAm concentration in the shrunken state (obtained at $T > T_c$) is roughly 35 wt %, irrespective of the initial NIPAAm and BIS (cross-linker) concentrations.[6] This problem was also discussed by Grosberg[12] with the concept of a crumpled globule state. We propose here a different model for the shrunken state. It is reasonable to deduce that a NIPAAm gel accompanies about 13 water molecules per NIPAAm monomer unit to form the hydrophobic solvated structure. In other words, we can state that excess water molecules in a gel with a lower gel concentration are physically trapped by the polymer network and these water molecules do not contribute to the hydrophobic solvation. Although the bound water molecules are dissociated at $T > T_c$, the molecules are located near the NIPAAm macro network without escaping from the gel and keep the macroscopic size of the gel in the shrunken state, as shown in Figure 5. This may be the reason why NIPAAm gels have a shrunken state with a fixed concentration.

Concluding Remarks

Changes in the mechanical and thermal properties of NIPAAm gels above and below the phase separation temperature, T_c, were investigated. It was found that an abrupt increase in the dynamic storage, E', and loss moduli, E'', at T_c was observed for NIPAAm isochore gels. Since the gel concentration was kept constant across T_c, this change in the moduli was interpreted to be due to a formation of phase separated structure above T_c, i.e., the formation of a macro network in the presence of a solvent rich matrix. Although the volume fraction of the polymer rich phase is small, it dominantly contributes to the mechanical properties of the gel in the phase separated state. In this state, the frequency dependence of the moduli was also observed. On the contrary, in the homogeneous state at $T < T_c$, no significant frequency dependence was detected, indicating the gel is essentially a matter of elasticity.

ATR-FTIR spectroscopy disclosed significant changes in the local environments of CH_3 (on the side chain group of the NIPAAm gel) and CH_2 groups (on the backbone chain of the NIPAAm gel) at $T = T_c$.

It was also found that about 13 water molecules were dissociated from a NIPAAm monomer unit upon the phase separation at $T = T_c$. The enthalpy of the dissociation is estimated to be 3.1 kJ/mol of NIPAAm. The estimated stoichiometric relation well explains the NIPAAm gel concentration in the shrunken state.

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