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In summary, our result shows that by avoiding preaveraging approximations numerical solutions give a better agreement with the measured data than Kirkwood and Zimm's theory for polymer chains. This result also is close to Zimm's Monte Carlo study based on 50 segments. These agreements confirm that the numerical method that sums up two-particle interactions (Oseen tensor) to calculate the hydrodynamic frictions gives a good prediction; thus the scheme used here can serve as a good method to calculate hydrodynamic properties of other more complicated aggregates such as various fractal clusters where the measurement is still lacking.[17]

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Thermal Analysis of the Volume Phase Transition with *N*-Isopropylacrylamide Gels

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ABSTRACT: Experimental work was done to study the thermoshrinking-type volume phase transition of *N*-isopropylacrylamide (NIPA) gel in aqueous solutions. The experiments principally consisted of the application of thermal analysis with a differential scanning calorimeter (DSC) to NIPA gels and to aqueous solutions of linear NIPA polymer (PNIPA) and poly(vinyl methyl ether) (PVME), whose gel is characteristic of the thermoshrinking type. The transition temperatures of NIPA gel obtained from DSC analysis were compared with those usually obtained from standard swelling experiments. This comparison clarified the efficiency of DSC for the determination of the transition temperature. For the linear polymer solutions, the transition temperatures obtained from DSC were satisfactorily consistent with their cloud points. Both the transition temperature and heat of the collapse of the NIPA gel showed similar values to those of the PNIPA solutions, which permitted the inference that the volume phase transition is controlled primarily by the same factors as the coil–globule transition of the linear polymer. The transition heat of collapse of the gel was endothermic and its absolute value was larger than those reported for nonpolar organic solution systems. Similar results were obtained with the linear polymer solutions. The experimental results were interpreted by using the concept of hydrophobic interaction. The addition of low molecular weight substances changed the transition temperature. This can be explained through the viscosity *B* coefficient.

I. Introduction

The volume phase transition of hydrogels[1] has been attracting much attention because of its technological and scientific importance. A gel can change in volume discontinuously as much as 1000-fold when surrounding conditions such as solvent composition,[2–4] salt concentration,[5] pH,[6] and temperature[1,3] vary continuously. With respect to temperature dependence, three types of phase transitions have been reported. The first is the thermoswelling type, or expansion with temperature;[1] the second is the thermoshrinking type, or collapse with temperature;[3] and the third is the "convexo" type, a mixture of the two types described above.[4]

It has been reported that the type of transition depends largely on the affinity of the monomers for water.[7] Therefore, for an explanation of temperature dependence, it would be important to consider the molecular structure of monomer units in a gel. Thermoswelling hydrogels mostly contain hydrophilic monomers such as acrylamide, acrylic acid, and methacrylic acid, and their transition can be explained by Tanaka's thermal mixing model.[1,3,4] On the other hand, the main examples of thermoshrinking hydrogels are composed of monomers like *N*-methylacrylamide, *N*,*N*-diethylacrylamide, and *N*-isopropylacrylamide (NIPA), whose hydrophobic substituents make them less hydrophilic. Transition in their cases cannot be precisely depicted by the Tanaka model.

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Accordingly, both hydrophilicity and hydrophobicity should be born in mind when volume phase transition, especially the thermoshrinking type, is considered.

When hydrophobic solutes are introduced into water, two phenomena are simultaneously observed.[8-13] One is hydrophobic hydration, in which the water molecules form cagelike structures around the hydrophobic solutes. As a result of this hydration, nonpolar molecules become soluble in water. The other is hydrophobic interaction, or the association of hydrophobic solutes. In general, an increase in temperature results in a reduction of the total number of water molecules structured around the hydrophobic solutes, which promotes hydrophobic interaction. Consequently, a rise in temperature strengthens the hydrophobic interaction. This is quite contrary to other interactions such as dipole–dipole, van der Waals, and electrostatic forces.

Recently Hirotsu[14] investigated the phase behavior of NIPA gel/water/alcohol systems and explained thermoshrinking by the destruction of hydrogen bonds between water molecules and NH or C=O of NIPA. However, our above discussion seems to suggest that the hydrophobic interaction contributes to the volume phase transition of thermoshrinking polymers. Ulbrich and Kopeček[15] also pointed out the importance of hydrophobic interactions in their studies on the mechanical properties of N-substituted acrylamide gels at room temperature.

Before the volume phase transition was empirically demonstrated in synthesized gels, its existence was theoretically predicted by Dušek and Patterson.[16] They suggested that the volume phase transition of gels is similar to the coil–globule transition of polymer chains in poor solvents and can be regarded as a first-order phase transition. Therefore, transition heat should be detectable during the volume phase transition. Further, thermoshrinking phase transition should be an endothermic process involving a greater transition heat than phase transition with no hydrophobic interaction.[17] Accordingly, thermal analysis appears to be a useful method to clarify the relation between volume phase transition and hydrophobic interraction and may offer a key to the understanding of the transition phenomena of gels.

The present work is focused on the thermoshrinking-type volume phase transition of NIPA gel. Thermal analyses with a differential scanning calorimeter (DSC) were performed for the gel and the aqueous solutions of the linear NIPA polymer (PNIPA) to clarify the contribution of the hydrophobic interaction in the phase transition. We also measured the swelling ratio of the gels and the cloud point of the polymer solutions. For comparison, similar experiment were conducted with *N*-acryloylpyrrolidine (NAPy) gels in pure water, linear polystyrenes (PSt) in cyclohexane, and aqueous poly(vinyl methyl ether) (PVME) solutions. The reasons these samples were used are as follows: the NAPy gel has been reported to undergo a continuous thermoshrinking volume change;[18] high molecular weight PSt in cyclohexane has been reported to undergo a coil-to-globule transition with a decrease in temperature;[19,20] and PVME is also reported to undergo a thermoshrinking volume change in the gel form.[21]

II. Experimental Section

1. **Preparation of Samples.** The solvents used in the experiments were water, cyclohexane, and aqueous solutions of methanol (MeOH), ethanol (EtOH), 2-propanol (iPrOH), 1-propanol (nPrOH), 1-butanol (nBuOH), and dimethyl sulfoxide (DMSO). The alcohols and the cyclohexane were all special grade (Wako Pure Chemicals Co., Ltd.) and used without further purification. The DMSO was purified by dehydration with potassium hydride (Wako Pure Chemicals Co., Ltd.) and successive vacuum distillation. The water was distilled, deionized, and degassed. For the low molecular weight additive, urea and glycerol were used. They were all special grade (Wako Pure Chemicals Co., Ltd.) and used as received.

Table I
Samples for the Thermal Analyses

sample	name	molec wt,[a] × 10^{-4}	molec wt distrib[a]	note
1	PNIPA	210	48.0	method 1
2	PNIPA	230	6.7	method 1
3	PNIPA	5.9	2.8	method 2
4	PNIPA	3.3	3.4	method 2
5	PNIPA	11.6	2.9	method 2
6	PNIPA	20.3	3.4	method 2
7	PNIPA	7.6	2.4	method 2
8	PNIPA	3.5	2.0	method 2
9	PNIPA	1.1	2.0	method 2
10	PVME	1.5	3.6	
11	PVME	5.7	61.0	
12	PSt	10.7	1.01	
13	PSt	123	1.02	
14	NIPA gel			
15	NIPA gel			BIS × 3/4
16	NIPA gel			BIS × 1/2
17	NIPA gel			BIS × 1/4
18	NAPy gel			

[a] The molecular weight and its distribution were measured by GPC calibrated with poly(oxy ethylene).

The NIPA gels were prepared by free radical polymerization in water at 0 °C. The reagents used were, main-chain monomer, NIPA; cross-linking reagent, *N,N'*-methylenebis(acrylamide) (BIS); initiator, potassium persulfate (KPS); and accelerator, *N,N,N',N'*-tetramethylethylenediamine (TEMED). The reagents, BIS, KPS, and TEMED, were all special grade (Tokyo Kasei Kogyo Co., Ltd.) and used without further purification. The NIPA monomer, provided by Eastman Kodak Co., Ltd., was recrystallized from a benzene/*n*-hexane mixture and dried in vacuo for 1 day. Polymerization was conducted according to the following procedure. Seventy millimoles of NIPA and 0.7 mM BIS were dissolved in 50 mL of water, while 0.3 mM KPS was dissolved in another 50 mL of water. The two solutions were then both cooled to 0 °C. They were then mixed, and 0.2 mL of TEMED was added to the mixture. Cylindrical gel samples (1.6-mm diameter and 20-mm length) were prepared according to the method reported by Amiya et al.[22] The gel rods were immersed in 3 wt % iPrOH aqueous solution for 1 day to stop polymerization and to wash away any residual chemicals. Subsequently, the gel rods were taken from the solution and immersed in an excess amount of pure water until equilibrium was attained.

The PNIPA samples were prepared by two different methods. The first one was the same as employed for the gel samples without the addition of the cross-linking reagent (method 1). The other was a synthetic method reported by Fujishige (method 2).[23] The main difference between the polymers of both methods was their molecular weight. The NAPy gel submillimeter beads, supplied by Mitsui Toatsu Co., Ltd., were immersed in pure water for 1 week before being used in the experiments. The PSt used were standard samples of different molecular weights supplied by Tosoh Co., Ltd., and were used as received. Two PVME samples of different average molecular weight were provided by Tokyo Kasei Kogyo Co., Ltd., and used without further treatment.

2. **Thermal Analysis.** Thermal analyses were carried out with a differential scanning calorimeter (Seiko I Inc., Model SSC-5000 DSC-100). Polymers and gels used in the thermal analyses are listed in Table I. Experimental conditions and results are tabulated in Table II. In the table, concentrations of the aqueous solutions are expressed in two ways. One is the mole percentage of the nonaqueous component in the total solvent, and the other is the mole number of the nonaqueous solvent in the unit weight of solution (mole/gram of solution). During

Table II
Experimental Conditions and Results

run	sample	solvent	additive concn, mol/g of soln	monomer unit concn × 10^5, mol/g of soln	cloud point, °C	transitn point, °C	transitn heat	
							J/g of soln	kJ/mol
1	14 (NIPA gel)	water	0	45.8[a]		34.0	1.5	3.3
2	14 (NIPA gel)	water	0	38.3[a]		34.0	1.5	3.9
3	15 (NIPA gel)	water	0	30.3[a]		34.0	1.3	4.3
4	16 (NIPA gel)	water	0	29.3[a]		34.1	1.3	4.4
5	17 (NIPA gel)	water	0	20.1[a]		34.0	0.9	4.5
6	14	water/DMSO (3)		42.4[a]		33.2	1.2	2.8
7	14	water/DMSO (5)		46.5[a]		31.3	1.1	2.4
8	14	water/DMSO (7)		56.7[a]		27.7	1.0	1.7
9	18 (NAPy gel)	water	0	48.3[b]		cannot be detected		
10	5 (PNIPA)	water	0	12.4	31.5	31.2	0.7	5.6
11	6 (PNIPA)	water	0	12.3		31.3	0.7	5.7
12	7 (PNIPA)	water	0	12.4		31.2	0.7	5.6
13	8 (PNIPA)	water	0	12.3		31.2	0.6	5.7
14	9 (PNIPA)	water	0	12.4		31.3	0.7	4.8
15	1 (PNIPA)	water	0	65.4		31.0 (30.7)[c]	3.4 (−3.4)[c]	5.2
16	1 (PNIPA)	water	0	52.3	30.9 (31.0)[c]	31.7 (31.7)[c]	2.9 (−2.7)[c]	5.5
17	1 (PNIPA)	water	0	39.2	32.3 (31.6)[c]	32.3 (32.2)[c]	2.1 (−2.1)[c]	5.4
18	1 (PNIPA)	water	0	26.1	33.0 (32.0)[c]	33.0 (32.3)[c]	1.4 (−1.3)[c]	5.4
19	1 (PNIPA)	water	0	13.1	33.8 (32.8)[c]	33.5 (32.7)[c]	0.7 (−0.7)[c]	5.3
20	1 (PNIPA)	water	0	6.5	34.3 (32.8)[c]	33.7 (32.9)[c]	0.4 (−0.3)[c]	6.1
21	1 (PNIPA)	water	0	3.3	35.2 (32.0)[c]	33.9 (33.1)[c]	0.2 (−0.2)[c]	6.1
22	1 (PNIPA)	water/DMSO (3)	1.41×10^{-3}	58.6	29.5	30.1	2.0	3.4
23	1 (PNIPA)	water/DMSO (5)	2.23×10^{-3}	54.6	27.6	28.2	2.2	4.0
24	1 (PNIPA)	water/DMSO (7)	2.97×10^{-3}	51.1	23.8	26.0	1.9	3.7
25	2 (PNIPA)	water/MeOH (0.9)	4.94×10^{-4}	12.3	33.6	33.2	0.8	6.5
26	2 (PNIPA)	water/MeOH (1.8)	9.74×10^{-4}	12.5	33.0	33.0	0.8	6.4
27	2 (PNIPA)	water/MeOH (3.7)	1.99×10^{-3}	12.3	31.6	31.8	0.7	5.7
28	2 (PNIPA)	water/EtOH (0.9)	4.92×10^{-4}	12.6	33.0	32.9	0.8	6.3
29	2 (PNIPA)	water/EtOH (1.9)	9.96×10^{-4}	12.3	31.8	31.7	0.8	6.5
30	2 (PNIPA)	water/EtOH (5.1)	2.60×10^{-3}	12.5	25.8	25.9	0.7	5.6
31	2 (PNIPA)	water/nPrOH (0.9)	4.90×10^{-4}	12.5	29.7	29.8	0.8	6.4
32	2 (PNIPA)	water/nPrOH (2.2)	1.13×10^{-3}	12.4	23.1	23.4	0.9	7.3
33	2 (PNIPA)	water/nBuOH (0.2)	1.13×10^{-4}	12.4	31.1	31.2	0.8	6.5
34	2 (PNIPA)	water/nBuOH (0.9)	4.92×10^{-4}	12.4	19.2	21.1	1.0	8.1
35	2 (PNIPA)	water/urea	3.33×10^{-4}	12.4	33.8	33.3	0.8	6.5
36	2 (PNIPA)	water/urea	1.00×10^{-3}	12.4	33.1	32.6	0.7	5.7
37	2 (PNIPA)	water/urea	3.33×10^{-3}	12.4	32.0	31.8	0.7	5.6
38	2 (PNIPA)	water/glycerol	5.38×10^{-4}	12.4	32.4	32.1	0.8	6.5
39	2 (PNIPA)	water/glycerol	1.09×10^{-3}	12.4	30.8	30.5	0.7	5.6
40	2 (PNIPA)	water/glycerol	1.63×10^{-3}	12.4	28.8	28.3	0.6	4.8
41	10 (PVME)	water	0	520		35.6 (35.0)[d]	19.2	3.8
42	10 (PVME)	water	0	105	32.4	35.9 (32.5)[d]	4.5	4.3
43	10 (PVME)	water	0	51.7	32.0	35.9 (35.9)[d]	2.3	4.4
44	10 (PVME)	water/DMSO (1)	5.01×10^{-4}	103	32.8	34.4 (32.5)[d]	3.9	3.8
45	10 (PVME)	water/MeOH (1)	5.17	107	33.7	36.4 (33.4)[d]	4.0	3.7
46	11 (PVME)	water	0	520	33.9	35.6 (35.1)[d]	20.4	3.9
47	11 (PVME)	water	0	103	32.3	36.0 (32.5)[d]	4.7	4.6
48	11 (PVME)	water	0	64.5	32.3	36.0 (32.3)[d]	2.8	4.3
49	11 (PVME)	water/EtOH	5.14×10^{-4}	103	34.9	36.9 (34.4)[d]	4.2	4.1
50	11 (PVME)	water/iPrOH	5.10	104	34.2	36.8 (33.7)[d]	3.2	3.1
51	12 (PSt)	cyclohexane	0	48.9		cannot be detected		
52	13 (PSt)	cyclohexane	0	49.3		cannot be detected		

[a] Determined from the swelling ratio. [b] Determined from the ratio of dried weight to wet weight at 25 °C. [c] Data in the blankets were obtained on cooling. [d] Data in the blankets were obtained from the beginning of the shoulder.

the thermal analyses, solvents that had no polymer were used as reference.

3. Swelling Ratio and Cloud Point Measurements. The swelling volume of NIPA gels was measured by calibrated scale photography. The swelling ratio was determined according to Tanaka et al.[2] Temperature was controlled within ±0.1 °C.

The swelling ratio of NAPy gel particles was also measured in water by using a phase-contrast microscope (Olympus Co., Ltd., Model BHS) with a calibrated scale.

The cloud point of the linear polymer samples was measured visually. The applicability of the common visual method was checked by a light scattering photometer (Otsuka Denshi Co., Model LS-601) equipped with a 488-nm Ar ion laser source and a thermoregulated xylene bath. The accuracy of the temperature regulation was within ±0.05 °C.

III. Results

Figure 1 shows the temperature dependence of the equilibrium swelling ratio of the NIPA gel at different DMSO concentrations. The addition of small amounts of DMSO lowered the transition temperature and increased the magnitude of the volume change. On the other hand, at high DMSO concentrations, only minute swelling with temperature was detected. Figure 2 shows the swelling curve of NAPy gels in pure water as a function of temperature. This hydrogel underwent a continuous thermoshrinking volume change. From the DSC measurements, it was impossible to determine whether or not the NAPy gel underwent a phase transition (run 9 of Table II).

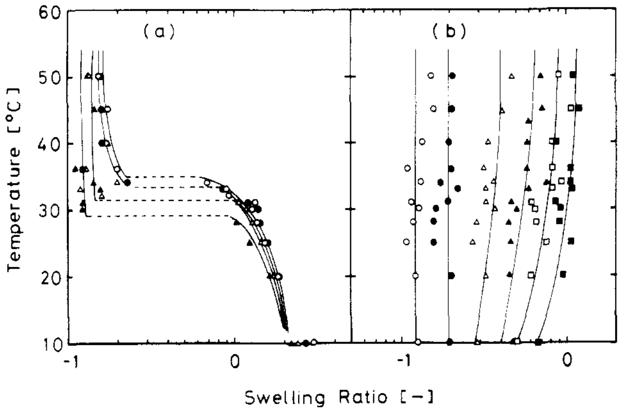

Figure 1. Equilibrium swelling curves of NIPA gel in a DMSO/water mixture plotted as a function of temperature. Lines are guides for the eye. The concentrations of DMSO are (a) ○, 0%; ●, 3%; △, 5%; ▲, 7%; and (b) ○, 20%; ●, 50%; △, 70%; ▲, 80%; □, 90%; ■, 100%.

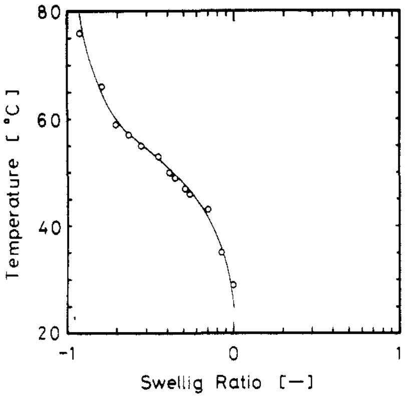

Figure 2. Equilibrium swelling curves of a NAPy gel in pure water plotted as a function of temperature.

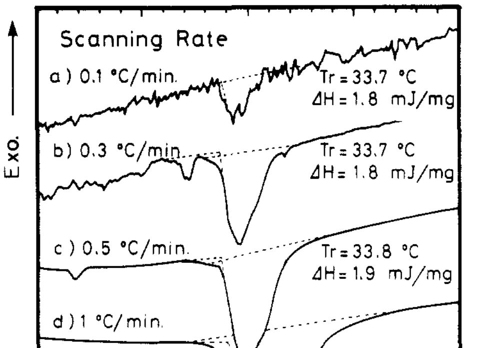

Figure 3. Effect of the temperature scanning rate on the shape of the DSC thermograms of gels.

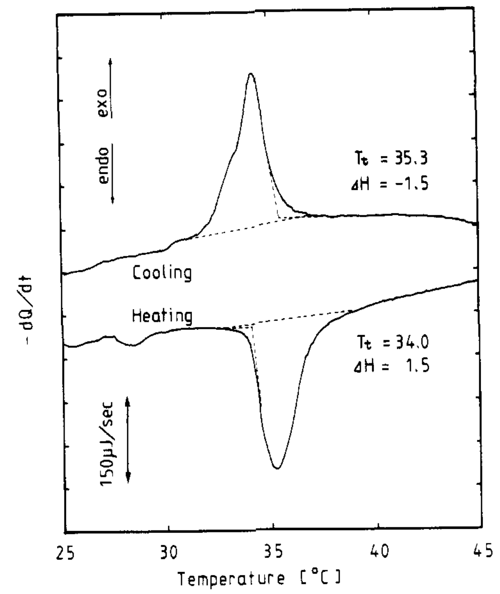

Figure 4. DSC thermograms of a NIPA gel (run 1), illustrating the existence of an endotherm of gel shrinking and an exotherm of gel swelling. The temperature scanning rate is 0.5 °C/min.

Figure 3 shows the effect of the scanning rate on the DSC thermograms of the NIPA gel samples (sample 14 of Table I). The transition temperature was determined from the intersection of the baseline and the leading edge of the exotherm, as illustrated in the figure. As shown in the Figure 4, although the slow scanning rate gave large fluctuations on the DSC thermogram, the fast scan of temperature decreased the precision for the determination of the transition temperature and heat. Thus, we determined that a scanning rate of 0.5 °C/min for gel samples gave clear DSC thermograms and almost the same transition temperature as for a scanning rate 0.1 °C/min.

Figure 4 shows typical DSC thermograms for a NIPA gel sample in water (run 1). During both heating and cooling processes, a single, sharp peak was observed. The experimental conditions and results of all DSC analyses and cloud point measurements are summarized in Table II. In this table, the sample number is the same as in Table I. The transition temperature of NIPA gels obtained from the DSC analyses in the low DMSO concentration region (runs 6–8) was almost the same as those obtained from the swelling experiments shown in Figure 1. On the other hand, in the high DMSO concentration region, there was no indication of a phase transition. In an earlier paper,[24] we determined the spinodal temperature of the NIPA gel, and it was slightly higher than that obtained from the DSC analysis. Thus we regarded the transition temperature obtained from the DSC analysis as the binodal temperature.

From the data numbered 1–5 in Table II, it is clear that the transition temperature of NIPA gels was independent of the monomer unit concentration of the gels. This is quite different from the behavior of acrylamide/sodium acrylate copolymer gels,[6] whose transition temperature is largely depend on the amount of BIS. It is also obvious from the table that the major transition heat becomes higher with increasing swelling ratio (a large swelling ratio corresponds to the low monomer unit concentration).

Figure 5 shows the intensity of the light scattered from the aqueous solution of sample 5 with a concentration of 7.8×10^{-5} mol/g of soln at a scattering angle of 90°. In the same figure, the DSC thermogram of this solution is imposed. The scanning rate was 1 °C/min. The tem-

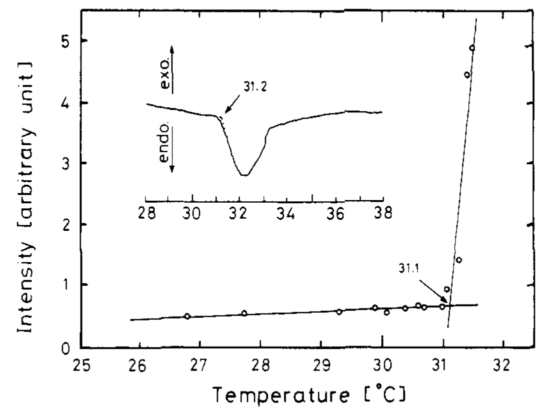

Figure 5. Intensity of light scattered from the PNIPA solution measured at a scattering angle 90°. This polymer is sample 5, and the monomer unit concentration is 7.8 × 10^{-5} mol/g of soln.

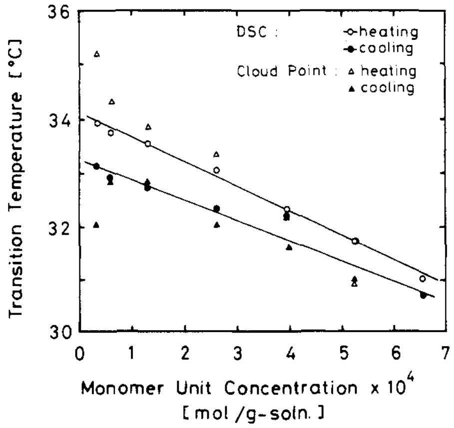

Figure 6. Transition temperature and cloud point of PNIPA solutions plotted as a function of monomer unit concentration. Lines are guides for the eye.

perature obtained from the intersection of two scattering intensity versus temperature lines is almost the same as that of obtained from the DSC measurement. Further, the cloud point obtained visually for this sample was 31.5 °C, almost the same as that obtained from the light scattering and DSC measurements. Thus, in the further DSC analysis of linear polymer solutions, the transition temperatures obtained from the DSC measurements were regarded as the cloud point, or the binodal point, of samples.

Figure 6 shows the transition temperature of PNIPA aqueous solutions obtained by DSC as a function of polymer concentration (runs 15–25). In this article, we described the polymer concentrations as that of monomer units in a unit weight of solution. The cloud points are also plotted in the same figure. As described, the cloud point of PNIPA solutions was almost the same as the transition point. Except for the low concentration region, both the transition temperature and the cloud point became higher when the monomer unit concentration was decreased.

The transition temperature of PNIPA solutions was not dependent on the molecular weight (runs 10–14). However, the transition temperature of run 19 was 2 °C higher than that obtained from runs 10–14. We feel this discrepancy can be attributed to the initiator-originated charges in the PNIPA of no. 19.

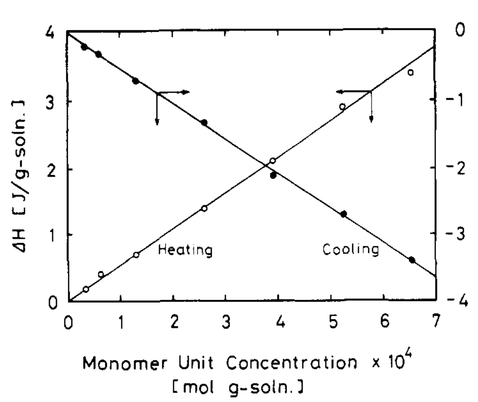

Figure 7. Transition heat of PNIPA solutions plotted as a function of monomer unit concentration. Lines are guides for the eye.

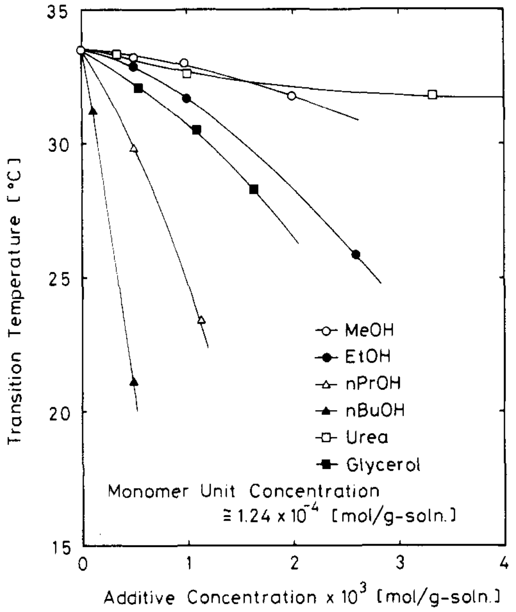

Figure 8. Effect of the low molecular weight additives on the transition temperature depression of the PNIPA solutions.

Figure 7 shows the heat of transition of PNIPA solutions on both heating and cooling as a function of monomer unit concentration (runs 15–25). From the slopes, the average molar heat of phase transition was evaluated to be about 5.0 kJ/mol. On the other hand, for a NIPA gel, the molar transition heat was smaller than that of linear polymer solutions. However, the discrepancy between the molar transition heat of gels and linear polymer solutions became smaller with decreasing monomer unit concentration of the gels (i.e., increasing swelling ratio).

As shown in Table II, the addition of a small amount of DMSO to the solvent largely diminishes the molar heat of phase transition. For the NIPA gels (runs 6–8), it becomes about half of that of a pure water system. While for the PNIPA solutions (runs 22–24), it decreases to two-thirds of that of a pure water systems.

Recently, Hirotsu[14,16,25] and Amiya et al.[22] reported that the addition of alcohols lowers the transition temperature of NIPA gels. The effect of alcohols on the PNIPA solutions was also observed in this study (runs 25–34). Figure 8 shows the effect of alcohols on the transition temperature. In the figure, the influence of the other two water-soluble compounds, urea (runs 35–37) and glycerol (runs 38–40), is also plotted. The transition temperature became lower with increasing number of carbons in the alcohol. However, in contrast to the case of DMSO, the molar transition heat was almost the same as that of the pure water systems.

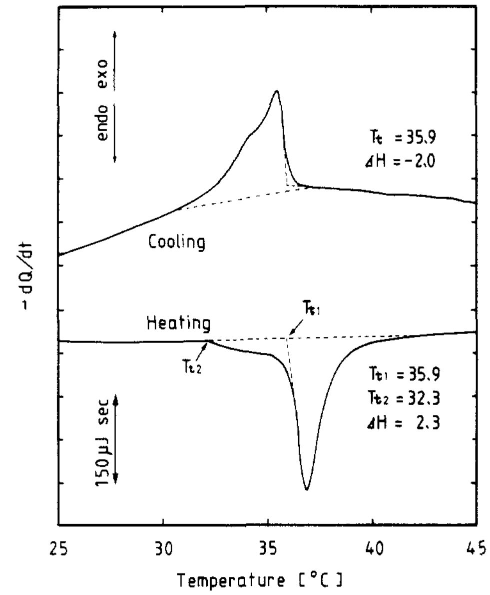

Figure 9. DSC thermograms of a PVME solution (run 26), illustrating the existence of an endotherm on heating and an exotherm on cooling. Temperature scanning rate is 1 °C/min. T_{t1}: Transition temperature determined from the beginning of the shoulder. T_{t2}: transition temperature determined from the main peak.

Figure 9 shows the typical DSC thermogram of a PVME solution (run 43). A clear shoulder was observed just before the peaks of the exo- and endotherm. Such shoulders were also detected for all other PVME samples measured. In Table II, the transition temperatures in parentheses represent the beginning of this shoulder, with which the cloud point also agreed well. Further, the effect of monomer unit concentration, additives, and the molecular weight of polymers on the transition temperature was similar to those of PNIPA solutions (runs 41–50).

In the case of the PSt/cyclohexane system (run 52), there was no indication of a transition in spite of the existence of a cloud point. This might be due to the low polymer concentration we employed.

IV. Discussion

The most important features of the DSC analysis for the discussion of hydrophobic interaction are the followings. The first is the direction of transition heat. Though we could not detect any transition heat for the polystyrene/cyclohexane system, the heat fluxes reported for polymer/nonpolar organic solutions[26,27] have been exothermic, whereas the transition heat from the shrinking of hydrogels or from the sol-to-gel process in linear aqueous polymers was uniformly endothermic in our experiments.

The second feature is the magnitude of the molar heat of phase transition in the experiments, whose value is two to five times greater than that reported for nonpolar organic solutions.[26] Previously, Nemethy and Sheraga[17] presented an equation for the enthalpy of the hydrophobic interaction of amino acid side chains. According to their equation, the enthalpy of the hydrophobic interaction of valine–valine is 3.5 kJ/mol at 33 °C [isopropyl side chain of amino acid, $CH(CH_3)_2$]. On the other hand, the measured transition heat was about 5.0 kJ/mol for PNIPA solutions, which is a value close to the theoretical value that was evaluated by neglecting the existence of the main backbone of the polymer chain.

Both the above mentioned features coincide well with the expectations in section I that the hydrophobic interaction is peculiar to the aqueous system and should be considered in the phase transition of hydrophobic polymers and hydrogels.

Table III
Viscosity *B* Coefficient[a] of Additives (25 °C)[28]

methanol	0.087
ethanol	0.170
1-propanol	0.250
1-butanol	0.300
glycerol	0.225
urea	0.035

[a] L/mol.

As mentioned in section III, the transition temperature of linear polymers was independent of molecular weight, and the transition temperature of NIPA gels was independent of the amount of BIS. These experimental results conclude that there is a strong controlling factor in the aqueous system, for the phase transition of hydrophobic polymers. We feel these results can be explained by the decrease of entropy during the formation of hydrophobic hydration structure, which then forces the solute to associate.

The effects of low molecular weight additives on the transition temperature and heat can also be explained by the hydrophobic hydration and interaction. The hydrophobic and hydrophilic groups in the additives strongly promote the hydration structure around them cooperatively.[12,13] Therefore when the additives are added to an aqueous solution, they interact with the bulk water and decrease the entropy through hydration. This is one reason for the depression of the transition temperature by the addition of low molecular weight additives.

It is known that the "viscosity *B* coefficient"[28] represents the ability of hydration structure formation. The viscosity *B* coefficients of the alcohols, urea, and glycerol at 25 °C are tabulated in Table III. This table and Figure 8 reveal that the order of the viscosity *B* coefficient is in good agreement with the degree of transition temperature depression of the additives. Thus, as a large viscosity *B* coefficient implies the formation of a large hydration structure, this fact also supports the existence of a hydrophobic interaction.

However, the above discussion about the additives is not sufficient to explain the results for DMSO. Addition of DMSO changes not only the transition temperature but also the molar transition heat. This could be due to the nature of DMSO. Differing from alcohols and other additives, DMSO is an aprotic solvent and interacts with the water molecules but in a different way. Probably, the hydrated water molecules may be replaced with DMSO molecules and the replacement decreases the transition heat.

The molar transition heat of PNIPA is greater than that of PVME, which may also be attributed to the structures of water molecules. Namely in the course of hydrophobic association, some of the water molecules become free from the hydration structure, and the number of freed waters will depend on the contact area of the hydrophobic solute. This fact is also one of the reason for the difference in molar transition heat between PNIPA solutions in NIPA gels.

At the same time, the constant molar transition heat (runs 10–21, 25–50) suggests that the additives promote the "excess" hydration structure and that the hydration structure of polymers is maintained until the transition occurs.

The increase in the molar transition heat of NIPA gels with the decrease of BIS could be also attributed to the structure of water, because the existence of cross-linking points will arrest the formation of the hydration structure near the cross-linking points. In fact, the molar transition heat approaches that of linear polymer solutions with decreasing amount of BIS.

The NAPy gel results indicate that a continuous volume change cannot be detected by DSC analysis. This continuous volume change may be attributed to the gradual destruction of hydrogen bonds with C=O and $N(C_4H_8)$ of NAPy.

The transition temperature of NIPA gels is always slightly higher (1–2 °C) than that of linear polymer solutions. For the effect of the cross-linking points on the swelling pressure of gels, Π^{elas}, Tanaka et al.[1,3,4] gave the following expression based on Flory's elastic free energy equation[29]

$$\Pi^{elas} = kT\{0.5(\phi/\phi_0) - (\phi/\phi_0)^{1/3}\}$$

where k is the Boltzmann constant, T is the temperature, ϕ is the volume ratio of polymer segments in the system, and ϕ_0 is the value of ϕ at which the polymer chain has a random flight configuration. According to the equation, existence of a cross-linking point always causes a negative swelling pressure, which makes the gel shrink. However, in our experiments, gels are more stable than linear polymer solutions. This difference in transition temperature could be explained by the following two scores. One is the difference in the "mobility" of the polymer chains. In fact, the apparent diffusion coefficient of NIPA gel[30] has been reported to be less than one-fifth of that of PNIPA solutions.[24] The other is the effect of the surface of polymer grobule in the solution.[31] For the gel samples, the surface free energy could be negligible[32] and will show a higher transition temperature than polymer solutions.

V. Conclusion

In this work, the thermoshrinking-type volume phase transition of gels was connected with hydrophobic interactions by means of thermal analysis. By considering the two interactions, hydrophobic and hydrophilic, the "convexo"-type phase transition,[18,33] which is hard to explain with the ordinary thermal mixing model, can also be explained. The molecular structure of monomers consisting of the gels that undergo a convexo-type volume phase transition contains both hydrophilic and hydrophobic groups. Thus, the swelling at low temperature is attributed to the thermal mixing of molecules,[1,3,4] and the shrinking at high temperature corresponds to the hydrophobic interaction induced association of segments. In another paper, we numerically simulate the effect of the hydrophobic interaction on the thermoshrinking volume phase transition of gels.[34]

At the same time, we suggest the validity of DSC analyses for the detection of the thermoshrinking volume phase transition. Further examination of the effect of the formation of a hydration structure on the volume phase transition will be presented in a forthcoming paper.

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Registry No. (NIPA)(BIS) (copolymer), 90398-43-9; (NIPA) (homopolymer), 25189-55-3; MeOH, 67-56-1; EtOH, 64-17-5; *n*PrOH, 71-23-8; *n*BuOH, 71-36-3; glycerol, 56-81-5; urea, 57-13-6.

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