Colloid & Polymer Science Colloid Polym Sci 272:655–663 (1994)

Swelling of poly(N-isopropylacrylamide) gels in water-aprotic solvent mixtures

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Abstract: The swelling volume of poly(N-isopropylacrylamide) (PIPAAm) gel in aprotic solvents (acetonitrile (AcN)-, tetrahydrofuran (THF)-, 1,4-dioxane (DO)- and dimethylsulfoxide (DMSO)) -water mixtures was measured at 25 °C. The gel swollen in water shrank first and then reswelled with addition of the aprotic solvents. At an intermediate mole fraction (XDMSO) range of DMSO-water mixtures, the gel demonstrated a "reentrant" swelling phenomenon: the hydrated gel shrank first on addition of a small amount of solvent, showed a typical wide reentrant transition, and gradually reswelled in the range near pure solvent. On the other hand, the gels in AcN-, THF-, and DO-water mixtures demonstrated a "reentrant-convex" swelling phenomenon: the gels reswelled after a reentrant phase transition in low Xorg (XAcN, XTHF and XDO), showed a maximum swelling in the intermediate Xorg region, and shrank again gradually in the high Xorg region. Such a swelling behavior of the gel was interpreted by correlating with solution properties of the aqueous aprotic solvent mixtures.

The strength of hydrogen bonding around amide groups of the homopolymer was examined in pure solvents (water, THF, and DMSO) and in all proportion of aqueous THF to observe the relation with swelling behavior of gel by spectrum analysis of the amide I and II bands of Fourier Transform Infrared Spectroscopy (FT-IR). The swelling properties of gels in solvents and the aqueous mixtures were well correlated with the peak shifts of amide groups of the homopolymer.

Key words: Aprotic solvent – reentrant swelling phenomenon – reentrant-convex swelling phenomenon – solubility parameter – Kirkwood-Buff parameter

Introduction

It is well known that poly(*N*-isopropylacrylamide) (PIPAAm) homopolymer and PIPAAm gel exhibit a lower critical solution temperature (LCST) around 32 °C in pure water [1, 2]. The phase transition phenomenon of the gels has attracted much attention [3–6]. It is of interest to see how the addition of organic compounds affects the transitions.

Cononsolvency for the homopolymer and its gel in water-polar solvent mixtures has been reported and is one of interesting physical phenomena [7–10]. Namely, the homopolymer demonstrates intriguing phase separation phenomena in methanol [8]-, tetrahydrofuran (THF)- and 1,4-dioxane (DO) [10]-water mixtures at various temperatures: the homopolymer is soluble in water and in the polar solvents at room temperature, but precipitates from the aqueous mixtures in the intermediate composition and/or on raising temperature. Similar curious swelling behaviors of the gel in alcohol [9, 11, 12] and dimethylsulfoxide (DMSO)-water mixtures [7, 13] have also been reported as a "reentrant" swelling phenomenon. Several authors [11, 12] have treated theoretically the solvent effect on the swelling mechanisms by a single compound approximation. However, it is not yet clear why the gel shows such a characteristic reentrant swelling phenomenon although the behavior is qualitatively interpreted in terms of the attractive interactions between water and solvent molecules, and hydrogen bonding between polymer chains in the reentrant swelling region of the gel.

In a previous paper [14], we reported the swelling of gel in alcohol-water mixtures and discussed the relationship between the gel swelling and the solvent properties such as thermodynamic activities and partial molar volumes of components in the aqueous solvent mixtures.

In this paper, we will report on the swelling behavior of the gels in the aprotic solvent (acetonitrile(AcN), THF, DO and DMSO)-water mixtures where the gels demonstrate the swelling phenomena different from those in aqueous alcohol mixtures.

Here, we select two groups of the solvent-water mixtures: one is DMSO [15], which is known to strongly interact with water molecules, and others consist of AcN, THF, and DO which tend to associate with same species in the aqueous solution [16–18].

Firstly, the swelling behavior of the gels in the aprotic solvents are discussed in relation to the solubility parameters of PIPAAm and the solvents.

Secondly, Kirkwood-Buff parameters (G11, G12 and G22) are found to be useful parameters which may display a specific aprotic solvent-water structure in the aqueous mixtures. Essentially, the mechanism of swelling of gels in the aprotic solvent-water mixtures should be discussed by a three component system (aprotic solvent, water and polymer network). However, we tentatively correlated the swelling behavior of the gels and Kirkwood-Buff parameters of the aprotic solvent-water mixtures which were equilibrated outside the gels and obtained a kind of correlation in a certain concentration region.

Hydrogen bonding around the amide groups of the homopolymer was also analyzed by Fourier Transform Infrared Spectroscopy (FT-IR) to obtain insight into the nature of the interactions between PIPAAm gel networks and the solvent molecules.

Experimental

Materials

N-isopropylacrylamide(IPAAm) (mp = 63–65 °C), ethyleneglycol dimethacrylate (EGDMA) (bp = 83–85 °C/1 mm Hg), and 2,2′-azobis (isobutyronitrile) were purchased from Polysciences Inc. (Warrington, PA, USA). AcN and THF of spectroscopic grade were purchased from Wako Pure Chemical Industries, Ltd (Osaka, Japan). DMSO and DO of spectroscopic grade were also purchased from Kanto Chemical Co., Inc. (Tokyo, Japan). EGDMA was distilled before use, and the other chemicals were used without further purification.

Synthesis

PIPAAm gel and its homopolymer were polymerized by free radical polymerization. The detailed synthesis conditions and the preparation method of the gel disk were described previously [14].

Swelling volume measurements

All gel disks (30 mg) were placed into vials filled with solvent-water mixtures (20 ml). The vials were kept in a thermostat for 1 week to insure complete swelling. After equilibrium, the gels were removed from the vials, blotted with a tissue to remove surface solvents and then weighed. The degree of swelling was defined as the weight of solvent-uptake (gram) per unit mass (gram) of dried polymer (Ws/Wp).

FT-IR study of PIPAAm solution

Solutions of PIPAAm homopolymer were examined by FT-IR. All spectra of the solutions (100 mg/ml) were taken with the use of Micro Circle Cell (Openboat type) [19] in a Perkin Elmer model 1760 FT-IR spectrophotometer

(Norwalk, CT, USA) equipped with a Perkin-Elmer model 7300 computer for sample analysis. The data were transformed and averaged after 10 scans. The differential spectrum was obtained by subtracting the spectrum of solvent from that of polymer solution. A KBr disk containing 1% homopolymer was also submitted for FT-IR measurement for comparison with the infrared spectra of the homopolymer in solution.

Results

In Fig. 1, the degree of swelling of PIPAAm gels in the aprotic solvent (AcN, THF, DO and DMSO)-water mixtures is plotted as a function of solvent mole fraction (Xorg (XTHF, XDO, XAcN, and XDMSO)). The swelling profiles are classified into two groups. Namely, one is the swelling type observed in DMSO-water mixtures where the gel swells when XDMSO is either very small or high, but shrinks in a wide intermediate XDMSO range. Another is the "reentrant-convex" type observed with THF-, DO-, and AcN-water mixtures: the gels swell more or less when the solvent medium is either pure water or the pure aprotic solvents, although the degree of swelling (Ws/Wp) in the aprotic solvents is generally smaller than in water. In low Xorg region, the swollen gel shrinks on addition of a very small amount of solvent into water and attains a swelling minimum. Then, the shrunk gel swells again, passing through a swelling maximum in the intermediate Xorg region, and gradually decreases again down to the equilibrated swollen values in the pure aprotic solvents.

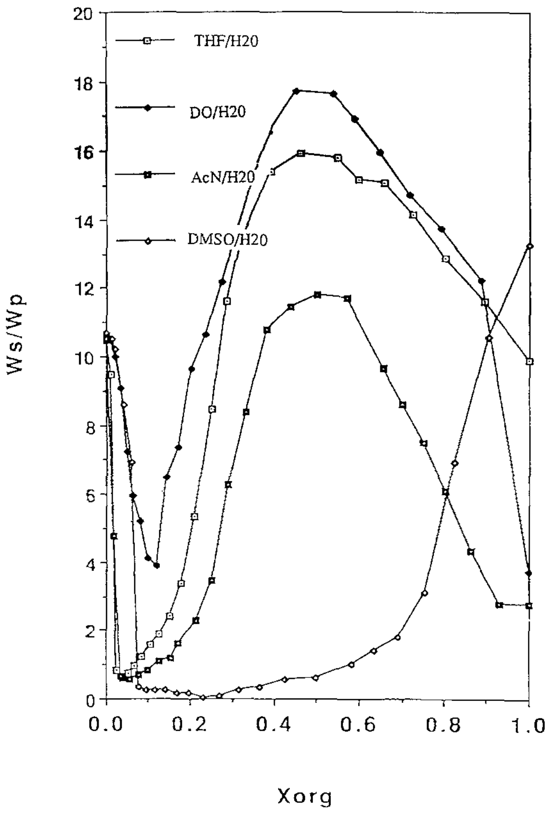

Fig. 1. Swelling curves of PIPAAm gels in aprotic solvent (AcN, THF, DO, and DMSO)-water mixtures

In our results, we are not sure whether the behavior of phase transition of gels in the dilute region of the organic solvent is discontinuous or continuous, although some researchers [7, 13] reported that the change of a phase transition of gel was discontinuous. This reason may be partly due to our different gel with a different hydrophobic crosslinker [7, 13].

In DMSO-water mixtures, however, the gel shows a drastic abrupt shrinking after a minute decrease between XDMSO = 0.00 and 0.1 and has a broad shrunk domain between XDMSO = 0.07 and 0.7. The degree of swelling at the lowest swelling was 0.052 at XDMSO = 0.25. After passing through the plateau shrunk domain, the gel rapidly swells from XDMSO = 0.7 up to 1.0.

At low XAcN, XTHF, and XDO regions of AcN, THF, and DO-water mixtures, the gels also show a drastic abrupt shrinking between XAcN = 0.00 to 0.04, a drastic abrupt shrinking after a minute decrease between XTHF = 0.00 and 0.03, and a moderate shrinking after a slight shoulder-like decrease between XDO = 0.00 and 0.12. The minimum degrees of swelling of gels are 0.71, 0.61, and 4.2 at XTHF = 0.04, XAcN = 0.052, and XDO = 0.12, respectively. The broad convex swelling maxima in AcN, THF and DO-water mixtures are also observed in the intermediate Xorg range. The degrees of swelling at the convex swelling maxima of the gels are 17.7, 15.9 and 11.9 at XDO = 0.54, XTHF = 0.46 and XAcN = 0.50. After passing through the convex swelling maxima of the gels, the swollen gels decrease their volume until the degrees of swelling reach 9.93, 3.74 and 2.75 in pure THF, DO and AcN, respectively.

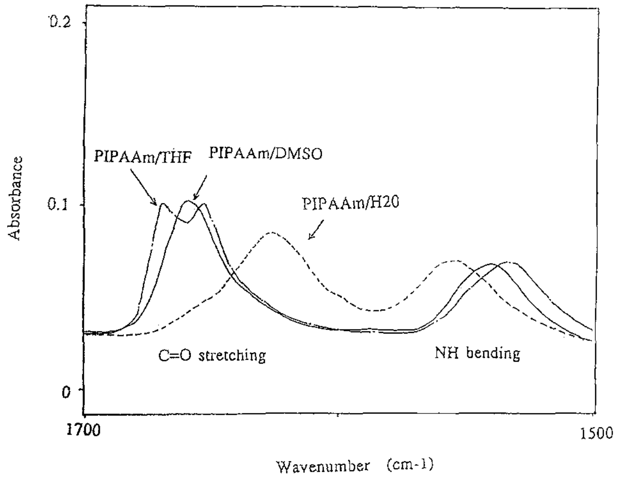

Fig. 2. IR spectra of amide I and II bands of PIPAAm in THF, DMSO and water between 1500 and 1700 (cm^{-1})

Figure 2 shows spectra of amide I (C=O stretching) and amide II (N-H bending) regions of the homopolymer in pure THF, DMSO, and water. The infrared spectrum of the homopolymer in THF is taken as an example of the solvents in which the gel shows a "reentrant-convex" swelling phenomenon. The absorption frequency maximum of amide I of the polymer in pure DMSO is 1657 cm^{-1} and that in water is 1637 cm^{-1}. Absorption spectrum of the homopolymer in THF is split into two peaks in amide I region, one is 1669 cm^{-1}, and another 1651 cm^{-1}.

The absorption maxima of amide II of the homopolymer are 1559, 1540, and 1536 cm^{-1} in water, DMSO, and THF, respectively. The frequencies of amide I and amide II of bulk polymer in a KBr disk are 1652 and 1548 cm^{-1}.

Figure 3 shows the concentration dependence of peak frequencies of amide I and amide II of the homopolymer in THF-water mixtures. In water-rich region, the amide I shifts from 1637 cm^{-1} in water down to 1627 cm^{-1} at XTHF = 0.011. At high XTHF region, the peak frequency of amide I moves from 1641 cm^{-1} at XTHF = 0.287 to the higher frequencies with two maxima of 1651 and 1669 cm^{-1} as XTHF increases to XTHF = 1.0. The peak wavenumber of amide II in THF-ater mixture decreases monotonically from 1559 cm^{-1} in pure water to 1534 cm^{-1} in THF as XTHF increases. Polymer precipitation prevented the IR measurements between XTHF = 0.02 and 0.28.

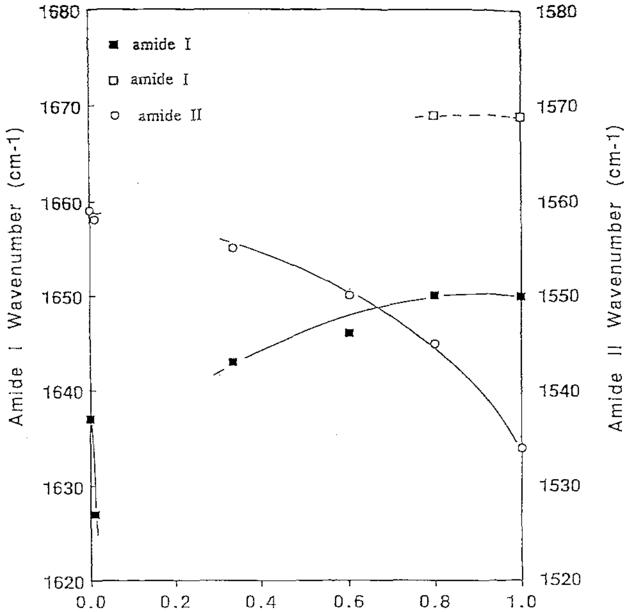

Fig. 3. Central frequency dependencies of amide I and II bands of PIPAAm in THF-water mixture

Discussion

In Fig. 1, it is seen that PIPAAm gels in DMSO-water mixtures demonstrate a "reentrant" swelling phenomenon and, in the other aprotic solvent (THF, AcN and DO)-water mixtures, undergo a "reentrant-convex" swelling phenomenon.

Firstly, we consider the swelling of PIPAAm gel in pure solvents. The gel in pure water swells about 10 times as much as the dried gel weight. In the case of DMSO, the gel swells about 13 times higher than the dried gel. On the other hand, in the pure organic solvents of THF, AcN, and DO, the gel swells to various degrees depending on the kind of solvents, and the degree of swelling is always smaller than that in pure water.

The swelling of gels in the pure aprotic solvents may be interpreted in terms of solubility parameters [20] which are shown in Table 1.

In the analysis of swelling of PIPAAm gel in water-alcohol mixtures of our previous paper [14], we interpreted that the swelling of gel in water may be caused by a strong hydration with a large enthalpy change and the swelling in alcohol may be caused by solvation of alcohol with less thermal enthalpy change. Therefore, in this

Table 1. Solubility parameters of solvents and PIPAAm $[(\mathrm{cal/cm^3})^{1/2}]$

Solvent	δ	δ_d	δ_p	δ_h
AcN	11.9	7.50	8.8	3.0
THF	9.5	8.2	2.8	3.9
DO	10.0	9.30	0.9	3.6
DMSO	12.9	9.0	8.0	5.0
PIPAAm	9.6			

paper, the solubility parameter was very helpful to discuss the swelling of gels in aprotic solvents except for water as discussed in the previous paper. The solubility parameter (δ) can be also divided into three components

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 ,$$

where δ_d, a contribution from the dispersion force, δ_p, a contribution from the polar force, and δ_h, a contribution from the hydrogen bonding. Table 1 shows the solubility parameters together with the three-dimensional components of the solubility parameter of the solvents [20] used. The solubility parameter (δ) of linear PIPAAm was calculated by Fedor's method [21]. In pure solvents, the gel swells consistently in the order of the component from hydrogen bonding of AcN, DO, THF, and DMSO. Similar observations [22] are reported. It was considered that the hydrogen bonding component may be predominant in swelling behavior of the gel in various organic solvents.

Secondly, the reentrant swelling behavior of the PIPAAm gel in low Xorg region (AcN-, THF-, DO-, and DMSO-water mixtures) may be explained by the low solvation to gel polymer network due to the strong interactions between solvent and water molecules around the mole fraction region of the reentrant transition.

In this paper, we also considered that the shrinking of PIPAAm gel in water rich region may be interpreted in terms of highly cooperative dehydration of water molecules from the hydrated gel network and the reentrant phase transition of PIPAAm gels in water aprotic solvent mixtures may be caused by the strong interaction between water and aprotic solvent in water rich region where PIPAAm polymer chains interact intermolecularly through hydrogen bonding and take a compact conformation as discussed in the previous paper [14].

Namely, hydrogen bonding as a component of interactions between solvents and water molecules may be helpful for the above discussion. In the intermediate XDMSO region, DMSO behaves as a water structure maker since the two hydrophobic methyl groups reinforce the water structure [23]. The large exothermic enthalpy change on mixing with water [23] implies strong hydrogen bonding formations between DMSO and water molecules in the XDMSO region. On the contrary, the hydrogen bonding in water rich region, as a component of interactions between DO and water, may be weaker than those of THF-water mixtures as judged from the lower enthalpy change of mixing [24]. Moreover, the entropy loss may be much smaller because the two polar ether oxygens on DO prevent water molecules from cluster formation [25]. THF, which has only a single oxygen atom, is a stronger water-structure maker than DO which has two oxygen atoms [26–28]. AcN is also a hydrophobic solute behaving as a strong water structure maker [29, 30], although the enthalpy change on mixing with water is small [31]. It is interesting that the composition of DO-water mixtures where the gel begins to reswell after the minimum swelling, is quite consistent with the mole fraction point where the concentration fluctuations begin to increase in the light scattering measurement [26].

The Kirkwood Buff parameter may be helpful to explain the swelling behavior of PIPAAm gel in the aprotic solvent-water mixtures. The Kirkwood Buff parameter is expected to display the amount of molecular association more sensitively than activity [32]. Namely, the Kirkwood Buff parameter; Gij is defined [33] as

$$\mathrm{Gij} = \int_0^\infty (\mathrm{gij}(r) - 1)\, 4\pi r^2 dr ,$$

where gij(r) is the radial distribution function between species i and j. In a binary solution of water (1) and solvent (2), G11, G12 and G22 can bring about information on water-water, water-solvent, and solvent-solvent interactions, respectively.

Figure 4 shows G11, G22, and G12 in THF-, AcN-, DO-, and DMSO-water mixtures. These values were replotted from the literature [34]. In the case of DMSO-water mixtures, the G12 in the intermediate XDMSO region indicates the high affinity between DMSO and water molecules

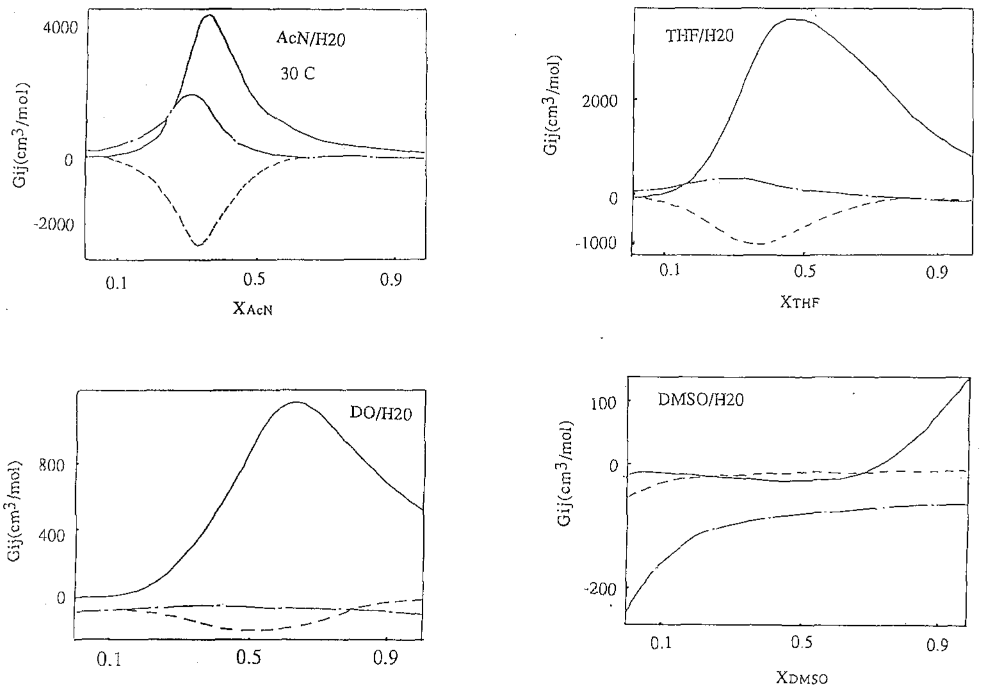

Fig. 4. Gij functions vs the mole fraction of aprotic solvent (AcN, THF, and DO): XAcN, XDO, and XTHF. G11: ——; G22: —; G12: -----

while G12 values in the same Xorg region of THF, AcN, and DO-Water mixtures are low. Generally, DMSO is an aqueous mixture has a specific tendency [35, 36] to interact with water molecules in the wide range of intermediate XDMSO region. Therefore, the aqueous solvent mixtures are hardly solvated to the gel polymer network and produces a wide shrunk bottom in the swelling profile.

In high XDMSO region, it is interesting that the degree of swelling and G11 synchronize as XDMSO increases from XDMSO = 0.5 to 1.0 in Fig. 4. The stronger interaction between water molecules in the high XDMSO region results in a much more effective swelling.

On the contrary, the convex swelling phenomena in AcN-, THF-, and DO-water mixtures may be caused when cohesive tendencies of water and these organic solvents are stronger than the water-organic solvent interactions. A similar microheterogeneity was reported on molecular aggregation of solvent and/or water molecules in AcN- and THF-water mixtures [31, 37].

Figures 5, 6 and 7 show the relationship between Ws/Wp and G11, G22, and G12 values at high Xorg region (AcN-, THF-, and DO-water mixtures). Near Xorg = 1.0, the order of the G11 values was consistent with the degree of swelling for all the pure solvents (AcN, THF and DO). Moreover, we generally observe that the G11 values are relatively higher than the G12 and G22 values in the region where the gels show the convex maxima of swelling in the mixtures. Similar to the above discussion on the relationship between G11 and swelling behavior, the gel shows the convex maximum when the G22 values are relatively higher at a definite Xorg region. On the other hand, the G12 values are lower in the intermediate Xorg region where the gel shows the convex swelling maxima. It is seen that the gels decrease their volume when the G11 and G22 values decrease, but G12 values increase in the region of Xorg = 0.5–1.0.

It is noted that the concentration dependence of partial molar volumes of water in the AcN-, THF-, and DO-water mixtures [38–40] are also very characteristic and different from those in alcohol-and DMSO-water mixtures [38, 41]. Namely, the profiles of partial molar volume of water in these aqueous mixtures have a minimum point in the intermediate Xorg range. Probably, promoted water structure may not be entirely destroyed and remain even in the high Xorg region.

In Fig. 2, the amide I of the homopolymer in DMSO has a single peak, while it gives double

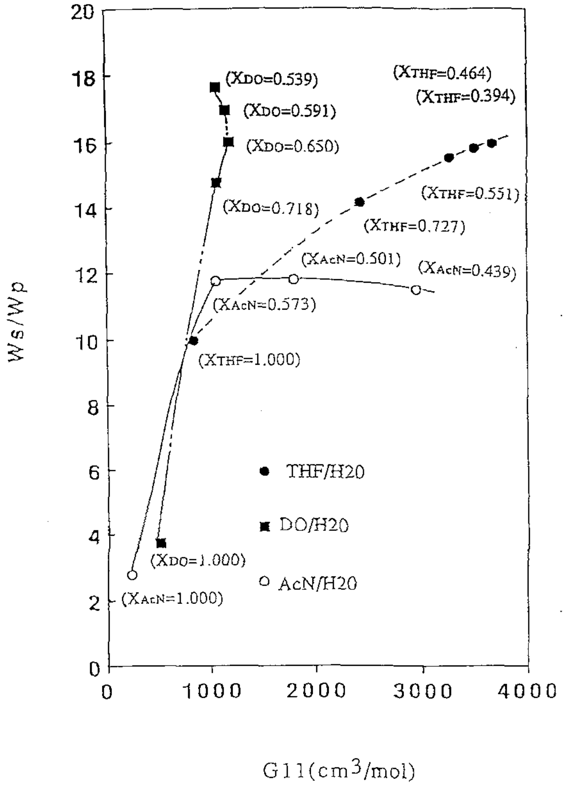

Fig. 5. Deswelling curve of PIPAAm gels vs G11 in rich Xorg region

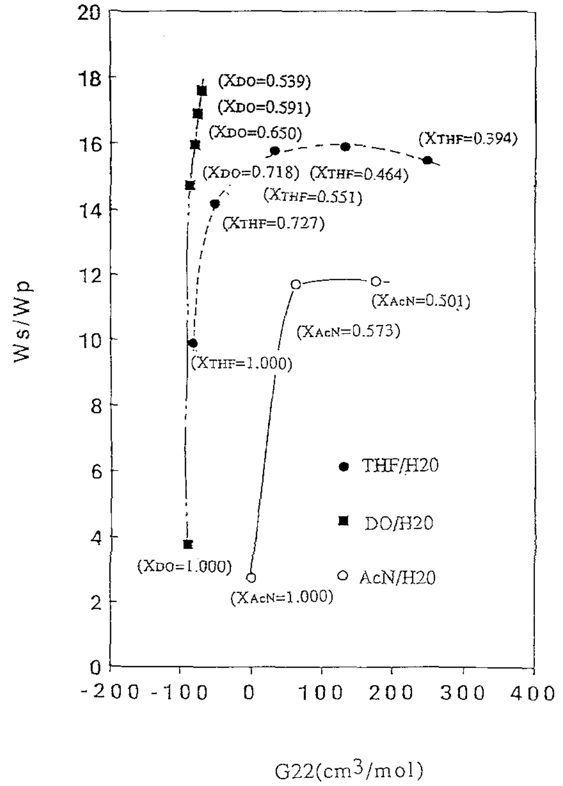

Fig. 6. Deswelling curve of PIPAAm gels vs G22 in rich Xorg region

peaks which indicate that motion mode of amide I consists of the two types in pure THF.

Kobayashi et al. [42] studied the hydration of N-monosubstitute amides in dioxane-water focusing upon the amide I infrared spectra. Peak stretching frequency of amide I shifts to a higher frequency as water fraction decreases. Several other researchers [43, 44] reported a similar infrared spectra of stretching of carbonyl group by solvation. Generally, the stretching mode shifts to a lower frequency as hydrogen bonding increases. Therefore, the vibration mode of amide I in DMSO indicates the carbonyl of amide groups in the polymer is less polar than in water. In THF, the two frequencies of amide I also indicate that the strength of hydrogen bond of carbonyl group is weaker than in water and solvation to polymer chains may consist of two types.

The peak frequency of amide I of the bulk polymer in a KBr disk is 1652 cm^{-1}, which is higher than in water, but lower than in pure THF or DMSO. This observation implies that the carbonyl group in a KBr disk is still a hydrogen bonded state which is less than in water, but is also more than in THF or DMSO.

Hydrogen bonding effect on amide II of some chemicals was discussed in terms of the bending frequency shift [45], especially amide II [46] as discussed with the amide I. Generally, the bending shifts to the higher frequency as hydrogen bonding increases. The peak frequency of amide II of the homopolymer indicates that the strength of hydrogen bond in THF or DMSO is weaker than in water. The amide II of the bulk polymer in a KBr disk has a higher wave number than in DMSO or THF, and hence the microenvironment indicates a stronger hydrogen bonded NH group in the bulk polymer than in DMSO or THF.

In Fig. 3, the frequency shift of amide I indicates that the hydrogen-bonding circumstance of the carbonyl group in the polymer gel network becomes stronger around the reentrant phase transition between XTHF = 0.0 to 0.07. In other words, this observation suggests an increase of the intermolecular hydrogen bonding of PIPAAm gel network from XTHF = 0.0 to 0.07 of THF-water

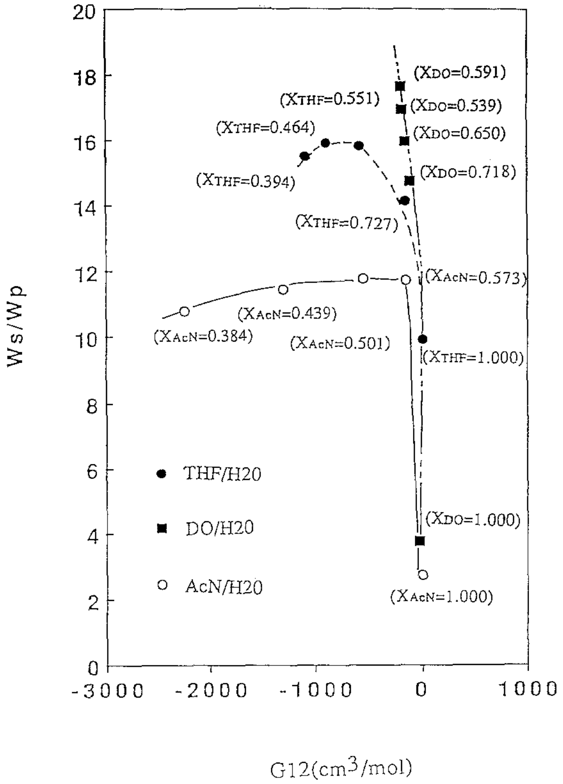

Fig. 7. Deswelling curve of PIPAAm gels vs G12 in rich Xorg region

mixtures. The frequency increase of amide I of polymer from XTHF = 0.12 to 1.0 should suggest the reduction of the intermolecular hydrogen bonding in PIPAAm gel network.

In Fig. 3, the frequency shift of amide II in THF-water mixtures indicates that the strong microenvironmental hydrogen-bonded state of NH group in pure water gradually decreases as XTHF increases and finally attains a lowest state in THF, which is even weaker than that of bulk polymer in a KBr.

Conclusion

The swelling of PIPAAm gels in aprotic solvent (AcN, THF, DO, and DMSO)-water mixtures is strongly dependent on the properties of solvent component. The reentrant swelling phenomena of the gels in the aprotic solvent-water mixtures were interpreted that the gel polymer network could not be solvated by the aqueous aprotic solvent mixtures due to strong interactions between aprotic solvent and water, and due to an intermolecular interaction of polymer network in a certain intermediate Xorg region. On the other hand, the convex swelling phenomena of gel in AcN-, THF- and DO-water mixtures were considered to be due to that the gel swells even when interaction between water and the aprotic solvents is relatively weak and the self-association of the same compound occurs in the aqueous binary solution around the convex swelling region.

The FT-IR studies of the homopolymer suggested that polymer chains of gel around the reentrant transition may take a compact conformation where the polymer chains interacted with themselves by intermolecular hydrogen bonding. Polymer chains loose their hydrogen bonding of amide group in the high Xorg region. It is also interesting that two maxima of amide I of the homopolymer in pure THF may indicate the existence of two-types of solvated carbonyl groups of gel network in high Xorg region where gel shows "reentrant-convex" swelling behavior.

Acknowledgment

The Authors thank Mr. Hirotaka Nakatomi, Mr. Minoru Nakata, Dr. Shuji Sato (Hisamitsu Pharm. Co., Inc.), Dr. Yoshiro Kaminoh (University of Utah), and Dr. Teruo Okano (Tokyo Women's Medical College) for strong support and useful discussions.

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Received March 26, 1993;
accepted October 7, 1993

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