

Effect of Solvent Interactions on Swelling and Microstructure of Amphiphilic Polyurethane Networks

JU-YOUNG KIM,¹ KYUNG-RAN MOON,² JOON-WOO LEE,² KYUNG-DO SUH²

¹ Department of Material Engineering, Samchok National University, Samchok, Kangwon, 245-711, Korea

² Department of Industrial Chemistry, College of Engineering, Hanyang University, Seoul 133-791, Korea

Received 3 January 2000; accepted 14 February 2000

ABSTRACT: Amphiphilic polyurethane (PU) ionomer networks were synthesized by urethane acrylate anionomer (UAA) precursor chains. These networks were prepared with water, dioxane (DO), and dimethyl sulfoxide (DMSO) and exhibited very different swelling behaviors in water/DO (UAADG) and water/DMSO (UAASG) solvent mixtures, which was due to the different solvent interactions between water/DO and water/DMSO. The additional important factor influencing the swelling behavior in water/aprotic solvent mixtures was the hydrophilicity of the UAA networks, which was different than the water–UAA network interaction. The microstructure of UAA networks prepared with the water/aprotic solvent mixtures was greatly influenced by the water–solvent interactions. Unlike the water/DO mixtures, which had a relatively weak water–DO interaction, the strong water–DMSO interaction largely restricted the ability of DMSO to solvate the UAA chain, which resulted in an increase in the aggregation of the hydrophobic segment and the hydrophilic/hydrophobic microphase separation. Thus, UAASG and UAADG networks showed very different swelling behaviors in the same swelling medium because of the microstructural difference between these gels, which was confirmed by dynamic mechanical measurements. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 608–620, 2001

Key words: solvent interactions; swelling; microstructure; amphiphilic polyurethane networks

INTRODUCTION

Much attention has been paid recently to the volume phase transitions of hydrogels because of their engineering and scientific importance. A discontinuous volume change can be induced by continuous variation of the surrounding conditions such as a solvent composition, salt concentration, pH, electric field, and temperature.^{1–7} Several researchers reported the temperature-induced collapse transition

of poly(*N*-isopropyl acrylamide) (PIPAAm) gels, which were interpreted in terms of the change in hydration and hydrophobic aggregation with temperature.^{8–10} Reentrant swelling behaviors of PIPAAm gels in mixtures of water and organic solvents were also extensively studied.^{11–16} PIPAAm gels showed shrinking in a water-rich solvent composition and reswelled with the increase in the organic solvent content in the solvent composition, which was interpreted in terms of the change of the interactions between the solvents as a function of the concentration.^{14–16} Most studies on the volume transition of polymer gels focused on the swelling behaviors of PIPAAm gels in water/aprotic solvent mixtures. So, in this present work we present the

Correspondence to: K.-D. Suh (kdsuh@email.hanyang.ac.kr).

Journal of Applied Polymer Science, Vol. 79, 608–620 (2001)
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convex swelling behavior of amphiphilic ionomer networks in water/aprotic solvent mixtures and demonstrate the effect of solvent interactions on the swelling of amphiphilic networks in solvent mixtures.

Because the amphiphilic networks used in this work exhibit both hydrophilic and hydrophobic properties, these networks attracted a lot of attention because of their interesting physical properties, as well as their potential technological applications.^{17–22} In general, the hydrophilic/hydrophobic balance of amphiphilic networks is controlled by varying the molar ratio of the hydrophilic to hydrophobic monomers in the synthetic process.^{21,22} However, in our previous study we dramatically changed the amphiphilicity and mechanical properties of polyurethane (PU) networks via controlling the degree of hydrophilic/hydrophobic microphase separation in various solvents. The amphiphilicity of PU networks prepared with a poly(ethylene glycol) modified urethane acrylate (UA) and UA anionomer (UAA) was dramatically changed with the solvent type used in the preparation of the networks.^{23–26} This is because the interaction between the precursor chains and solvent used in the network synthesis greatly influences the amphiphilicity of PU networks. Several researchers reported on the solution properties of ionomers in various solvents, such as a polar solvent, a nonpolar solvent, and their mixtures.^{27–35} The type of solvent used has a strong effect on the structure and morphology of ionomers when they are cast using different solvents, which results in a dramatic change in the thermal and mechanical properties. However, very little work is reported on the water/aprotic solvent interaction effects on the mechanical properties and amphiphilicity of polymer networks. In this article we present the swelling of amphiphilic UAA ionomer networks prepared in water/aprotic solvent mixtures and demonstrate the important role played by the water/aprotic solvent interactions in the structure and properties of the networks formed. We also present the mechanical properties of these networks as measured by dynamic mechanical analysis to complement the swelling measurements.

EXPERIMENTAL

Materials

In the synthesis of the UAA precursor chains we used poly(tetramethylene glycol) (PTMG, $M_w = 1000$, Hyosung BASF), 2,4-toluene diisocyanate

(TDI, Junsei Chemical Co.), 2-hydroxyethyl methacrylate (2-HEMA, Aldrich Chemical Co.), and dimethylol propionic acid (DMPA, Shinyo Chemicals). Dioxane (DO), dimethyl sulfoxide (DMSO), and methylene chloride (MC) were purchased from Aldrich Chemical Co. Potassium persulfate (KPS, Wako Pure Chemicals Co.) and 2,2-azobisisobutyronitrile (AIBN, Aldrich) were recrystallized from distilled deionized (DDI) water and absolute ethanol, respectively. *N*-Methyl-2-pyrrolidone (NMP, Junsei Chemical Co.) was used as a solvent for DMPA and as a viscosity thinner of the synthesized precursors. PTMG was dried and degassed at 80°C and 3–5 mmHg for 2 days. DMPA was dried overnight at 80°C under a vacuum of 3–5 mmHg. TDI, 2-HEMA, DMSO, DO, and triethylamine (TEA) were dried over 4 Å molecular sieves before use.

Synthesis of UAA

The UAAs were synthesized by using a previously published four-step process.^{23,25} PTMG, DMPA, and NMP were placed in a 500-mL four-necked vessel with a stirrer, a thermometer, a reflux condenser, and an inlet system for nitrogen gas. The molar ratio of the PTMG/DMPA/TDI/2-HEMA used in the synthesis of the UAA precursors was 0.3/0.7/1.5/1.5. TEA (Aldrich) was added at room temperature with stirring for 30 min to neutralize the carboxylic groups. The details of the synthesis conditions and characterization of UAA chain precursors were described previously.^{23,25} The proposed structure of the chain is illustrated in Figure 1. The polystyrene equivalent molecular weight obtained of UAA was a 6267 weight-average molecular weight with a polydispersity of 1.8.

Network Synthesis and Swelling Measurements

UAA chains were mixed with a solvent or solvent mixtures and an initiator (AIBN or KPS) and were transferred into test tube molds (1.5-cm inner diameter) to carry out the gelation. After the gelation was complete, the samples were taken out and fully washed with a large amount of DDI water and methanol. These gels were put into an extracting medium and washed for 72 h and then dried in a convection oven for 24 h. For the UAA gels prepared in DO (UADG) or DMSO (UASG), UAA precursors were dissolved in various amounts of DO or DMSO. The weight ratio of UAA:DO or DMSO was varied from 5:1 to 5:9. For the gel prepared in water

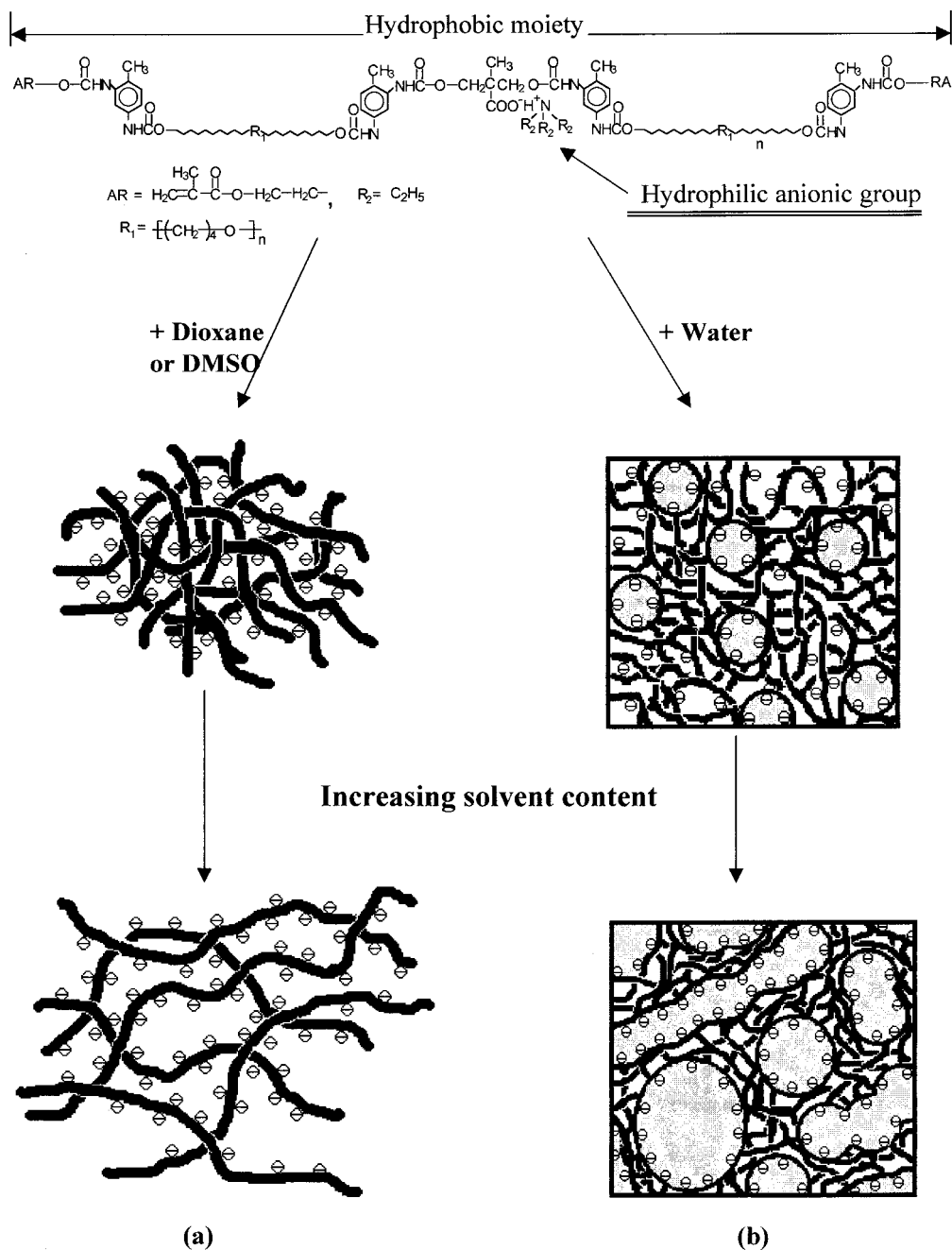


Figure 1 Proposed molecular structures of the UAA chain and a schematic of the microstructure of UAA networks: (a) UADG or UASG networks and (b) UAAG network.

(UAAG), soap-free emulsions of UAA precursor were first prepared; these emulsions were then poured into test tubes to carry out the gelation. The weight ratio of UAA precursor/water was changed from 5:1 to 5:6. The maximum weight ratio of water/UAA was 5/6. Beyond this point, no wall to wall network formation is possible.²³ Table I represents the amount of reactants used in the synthesis of

UAA gels. Also, the swelling ratios of the UAA gels prepared in pure solvents in water and the MC were determined by the gravimetric method and are summarized in Table I.

UAA gels were synthesized using water-DO (UAADG) or water-DMSO mixtures (UAASG). The solvent composition used in the preparation of these networks is summarized in Table II. The

Table I Recipe for Preparation of UAAG, UADG, and UASG Gels and Their Swelling Ratios in Water and MC

Symbol	UAA (g)	Water (g)	DO (g)	DMSO (g)	Swelling Ratio (%)	
					Water	MC
UAAG1	5	1	—	—	67	150
UAAG2	5	2	—	—	123	162.5
UAAG3	5	3	—	—	165	174
UAAG4	5	4	—	—	205.5	175
UAAG5	5	6	—	—	238.4	175
UADG1	5	—	1	—	23.8	122.7
UADG2	5	—	2	—	32.4	136.5
UADG3	5	—	3	—	55.7	179.5
UADG4	5	—	4	—	62.1	192.3
UADG5	5	—	6	—	68.6	212.4
UADG6	5	—	7	—	72.7	213.3
UADG7	5	—	8	—	81.1	227.7
UADG8	5	—	9	—	87.7	244.3
UASG1	5	—	—	1	36.1	122.4
UASG2	5	—	—	2	45.4	140.6
UASG3	5	—	—	3	52.3	153.3
UASG4	5	—	—	4	60.9	174.0
UASG5	5	—	—	6	87.6	191.4
UASG6	5	—	—	7	89	195.4
UASG7	5	—	—	8	100.3	210.5
UASG8	5	—	—	9	114.3	222.5

The initiators AIBN and KPS were used in the preparation of UAAG and UADG (or UASG) gels, respectively.

Table II Recipe for Preparation of UAADG and UAASG Gels

Symbol	UAA (g)	Water (g)	DO (g)	DMSO (g)	X_{water}	X_{DO}	X_{DMSO}
UADG5	5	6	0	—	1	0	—
UAADG1	5	6	1	—	0.967	0.033	—
UAADG2	5	6	2	—	0.9362	0.0638	—
UAADG3	5	6	3	—	0.9072	0.0928	—
UAADG4	5	6	4	—	0.88	0.12	—
UAADG5	5	6	5	—	0.8544	0.1456	—
UAADG6	5	6	6	—	0.8302	0.1698	—
UAADG7	5	6	7	—	0.8073	0.1927	—
UAADG8	5	6	8	—	0.7857	0.2143	—
UASG5	5	6	—	0	1	—	0
UAASG1	5	6	—	1	0.963	—	0.037
UAASG2	5	6	—	2	0.9286	—	0.0714
UAASG3	5	6	—	3	0.8966	—	0.1034
UAASG4	5	6	—	4	0.8666	—	0.1334
UAASG5	5	6	—	5	0.8378	—	0.1622
UAASG6	5	6	—	6	0.8126	—	0.1874
UAASG7	5	6	—	7	0.788	—	0.212
UAASG8	5	6	—	8	0.7648	—	0.2352

swelling measurement of UAA gels prepared in pure solvents (UAAG, UADG, and UASG gels) was also carried out in water/DO and water/DMSO solvent mixtures. The solvent composition used in these swelling experiments was identical to the water/DO or water/DMSO ratio used in the preparation of the UAADG and UAASG networks, which were converted as molar ratios of water/DMSO or water/DO and are presented in Table II.

The swelling ratios of the dried UAA gels were determined in DDI water and MC at 25°C. Dried network samples were placed in the bottom of 20-mL glass bottles. An accurately known initial volume of pure solvent or of a solvent mixture was added. After the bottles were sealed, they were left in a constant temperature insulated box for 2 days. The networks were then removed from their containers and weighed. Any solvent on the gel surface was dried before a weight reading was taken. The percentage of swelling of these samples, defined as the weight absorbed/dried weight $\times 100$, was determined using gravimetric methods.

Measurements

Dynamic mechanical measurements on the dry networks were performed by using a Perkin-Elmer DMA7e in the extension mode at 1 Hz and a heating temperature of 2°C/min in the 25–200°C temperature range. DDI water was dropped on the dried UAA gels, and the contact angle was determined by a model G-1 Erma contact angle meter.

RESULTS AND DISCUSSION

Swelling of UAA Gels in Water–Aprotic Solvent Mixtures

The swelling behavior of UAA gels in mixtures of an aprotic solvent (DO) and water as a function of the molar ratio of DO (X_{DO}) in the solvent mixture is shown in Figure 2. All UAA gels (UAAG5, UADG5, and UASG5) were prepared using the same amount of solvent in the formulation (Table I).

All of the UAA gels exhibited an increase in the swelling ratio with the increase in the molar ratio of DO in the swelling medium and showed a greater swelling ratio in solvent mixtures than in pure water ($X_{DO} = 0$). The UAA gel prepared in

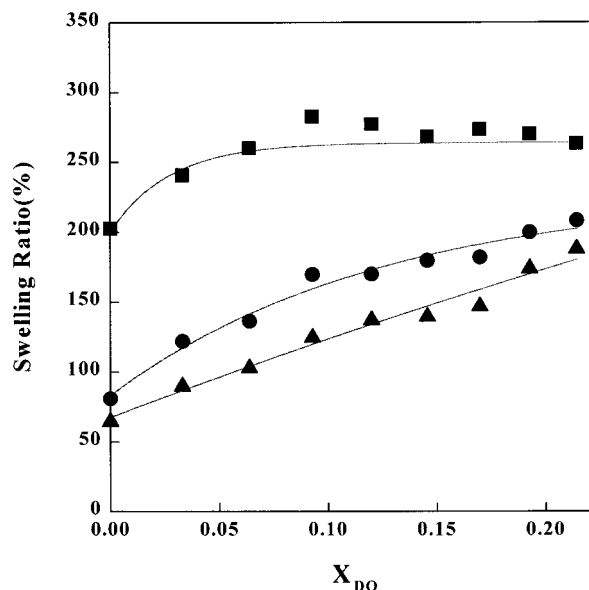


Figure 2 The swelling ratio of UAA networks in water/DO mixtures as a function of the mole fraction of DO (X_{DO}): (■) UAAG gel, (▲) UADG gel, and (●) UASG gel.

water (UAAG5) showed a greater swelling ratio than the gels prepared in DO (UADG5) or DMSO (UASG5). Two arguments can be advanced to explain these results; the change of water–water, water–DO, and DO–DO interaction with composition; and the difference in structure between UAAG5 and UASG5 or UADG5 gels.

Several reports have been made regarding the swelling behavior of PIPAAm networks in tetrahydrofuran, DO, and acetonitrile–water mixtures were interpreted in terms of the change of the interactions between the solvents as a function of the molar ratio in the solvent component.^{14–16} The PIPAAm gels showed an increase of the swelling ratio with the increase of water–water interaction and the decrease of the water–aprotic solvent (DO or acetone) interaction in the water-rich region. Mukae et al. interpreted the swelling results of PIPAAm in terms of the variation of the Kirkwood–Buff parameter as representing the varying solvent–solvent interactions.^{14,15} Matteoli and Lepori reported values of the Kirkwood–Buff parameter (G_{ij}) for the water–DO mixtures.³⁶ The G_{ij} is defined as

$$G_{ij} = \int (g_{ij}(r) - 1) 4\pi r^2 dr$$

where $g_{ij}(r)$ is the radial distribution function between species i and j . Figure 3 shows G_{11} , G_{12} ,

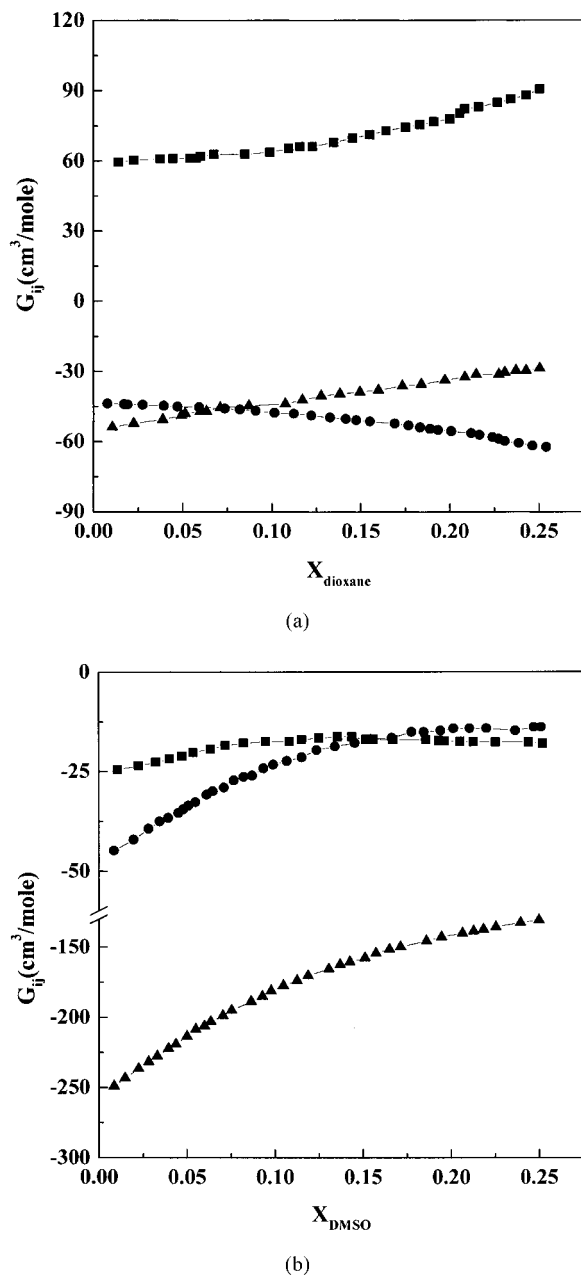


Figure 3 Solvent interactions (G_{ij}) in water and aprotic solvent mixtures as a function of the molar fraction of the aprotic solvent in the solvent mixtures, which is replotted from Matteoli and Lepori's report³⁶: (a) water/DO mixture and (b) water/DMSO mixture; (■) G_{11} , (▲) G_{22} , and (●) G_{12} .

and G_{22} in water/DO and water/DMSO mixtures in which water is represented by 1 and DO (or DMSO) by 2. These values were replotted from the literature.³⁶ The G_{11} and G_{22} exhibit a maximum (strong attractive interaction) and G_{12} exhibits a corresponding minimum around a DO

mole fraction (X_{DO}) of 0.45.³⁶ According to Mukae et al.'s results,^{14,15} PIPAAm gels showed an increase in the swelling ratio with the increase of the G_{11} values and the decrease of the G_{12} values in the range of $X_{\text{DO}} = 0.0-0.25$. This is because G_{12} , which hinders the solvation of the networks by solvents, is decreased while G_{11} and G_{22} are increased in this solvent composition.

Thus, the results of the UAA gels in Figure 2 may be interpreted in terms of the variation of the solvent-solvent interactions as a function of the solvent composition. Like the swelling of PIPAAm in water/aprotic solvent mixtures, UAA gels showed an increase in the swelling ratio in the range of $X_{\text{DO}} = 0.0-0.25$ where the G_{11} and G_{22} values increased but the G_{12} values decreased (Fig. 3). Thus, this result may be interpreted as being due to the weaker water-DO attractive interaction (G_{12}). As the molar ratio of DO increased from 0.033 to 0.2143 in the solvent mixtures, the G_{12} hindering interaction between the solvent and gel polymer network decreased; as a consequence, the ability of solvents, water, and DO to swell the networks increased. The highest swelling of the UAA gel prepared in water (UAAG5) in a water/DO mixture can be interpreted as attributable to the strong interaction between water and hydrophilic domains because of the highly improved hydrophilicity of the UAAG5 gel formed by the microphase separation between hydrophilic and hydrophobic segments in UAA chains. The improved hydrophilicity of UAAG networks allows them to take up a larger amount of water and absorb more DO, because the good miscibility of DO in water allows the DO to penetrate into the hydrophilic pockets formed during the preparation. This leads to the near flat dependence of swelling on solvent composition in Figure 2.

According to our previous experimental results,^{23,25} UAA gels prepared in water (UAAG5) have microphase separated hydrophilic domains in a continuous hydrophobic matrix. For UAA gels prepared in DO (UADG) or DMSO (UASG), the microphase separation between the hydrophilic and hydrophobic segments is relatively small, so these networks have homogeneous microstructures [see Fig. 1(a)]. For preparation of UAA gels in water, the water is a nonsolvent for the hydrophobic segment but dissolves carboxylate anionic groups, so water in UAA emulsification is caused by the microphase separation between hydrophilic and hydrophobic segments of the chains. The carboxylate anion groups orient

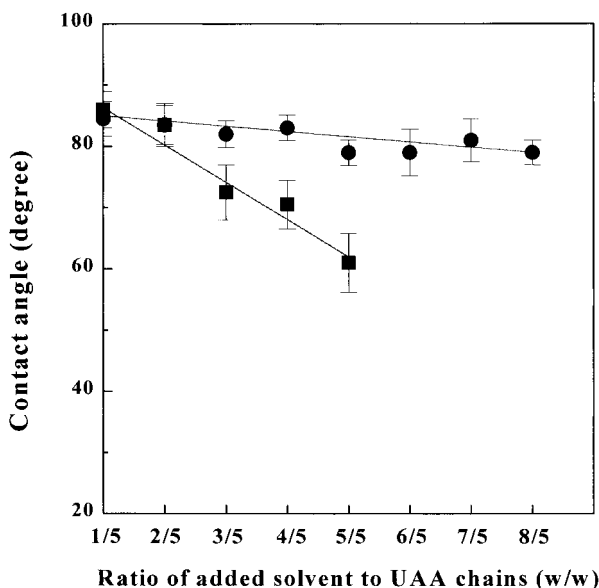


Figure 4 Contact angles of UAAG and UADG gels to water as a function of the weight ratio of the solvent (water or DO) in the network formulation: (■) UAAG gel and (●) UADG gel.

toward the water phase to form hydrophilic ionic groups in a continuous hydrophobic phase. This is schematically illustrated in Figure 1(b). When the gelation of the water in the UAA emulsion was carried out with KPS, the initiator radicals formed in the aqueous phase penetrated into the oil phase to initiate the crosslinking reaction between vinyl end groups. So, this microphase separated microstructure is locked in by the crosslinking reaction. These hydrophilic domains acted as a superabsorbent for water and exhibited a greater swelling ratio in water than the UAA gels prepared in DO (UADG). In addition, UAA gels prepared in water preferentially absorbed the water in the water/acetone mixture, which was due to their improved hydrophilicity. The greatly improved hydrophilicity of these UAA gels was also confirmed by the dynamic mechanical measurements.²³

The contact angles of the UAA gels used in this study are summarized in Figure 4 to demonstrate the differences in the hydrophilicity between UAA gels. The contact angles of UAA gels prepared in water are smaller than those of the UAA gels prepared in DO, indicating that UAA gels prepared in water have greater hydrophilicity than the gels prepared in DO, even though these gels are prepared with the same UAA precursor chain. Thus, it can be postulated that the hydro-

philicity, which is the interaction between the water and hydrophilic segments, should be considered as an important factor influencing the swelling of amphiphilic polymer networks in the water and aprotic solvent mixture.

The swelling results of the three UAA gel networks in water/DMSO mixtures are reported in Figure 5. As the molar ratio of DMSO in the solvent composition increases, the swelling ratio of UAA gels prepared in DO or DMSO slightly decreases. These gels show smaller swelling ratios in the water/aprotic solvent mixture than in pure water. However, the swelling ratios of UAA gels prepared in water increase with the increase in the molar ratio of DMSO in the solvent composition. These results are not simply interpreted by the theory for UAA gels in the water and DO solvent mixture. The water–DO interaction (G_{12}) is weaker than the water–water (G_{11}) and DO–DO (G_{22}) interactions, and the water–DMSO interaction (G_{12}) is stronger than the water–water (G_{11}) and DMSO–DMSO (G_{22}) interactions in the range of $X_{\text{DMSO}} = 0.0-0.25$ (Fig. 3).¹⁴⁻¹⁶ Because the two hydrophilic methyl groups in DMSO reinforce the water structures, strong hydrogen-bonding formation between DMSO and water molecules occurs in this solvent composition.¹⁴⁻¹⁶ This strong water–DMSO interaction was confirmed by the large exothermic enthalpy

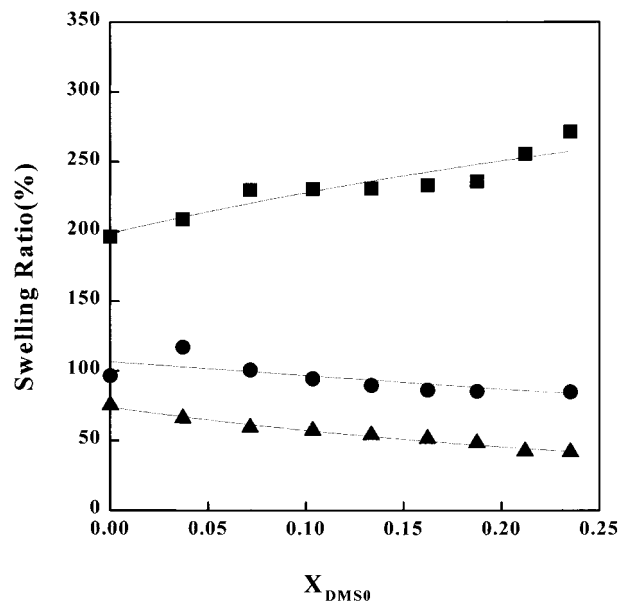


Figure 5 The swelling ratio of UAA networks in water/DMSO as a function of the mole fraction of DMSO (X_{DMSO}): (■) UAAG gel, (▲) UADG gel, and (●) UASG gel.

change on mixing of DMSO with water due to the strong hydrogen bonding formation between DMSO and water molecules in the range of $X_{\text{DMSO}} = 0.0-0.25$.^{14-16,36,37} This leads to an increase in the G_{12} in contrast to the decrease in the G_{11} in this solvent composition. Thus, the decrease in the swelling ratio of UAA gels prepared in DO or DMSO can be explained by the strong water-DMSO interaction. DMSO/water mixtures are hardly solvated to the gel polymer networks and produce the decrease in the swelling ratio, because of this strong water-DMSO interaction in this solvent composition.

UAA gels prepared in water exhibit a very different trend than the gels prepared in DO or DMSO in the DMSO mixtures. Another factor must be playing an important role in the swelling of UAA gels prepared in water in this solvent mixture. This difference is again due to the greater hydrophilicity of UAA gels prepared in water (UAAG5) because of the microphase separation between the hydrophilic/hydrophobic segments' water discussed above. So, the interactions between the water and these hydrophilic domains are stronger than the water-DMSO interactions; as a consequence, the swelling in DMSO-water mixtures increases as DMSO is added to the solvent mixture. The improved hydrophilicity of UAA networks prepared in water as a function of the water in the network preparation allows more DMSO to be absorbed because the good miscibility of DMSO in water allows DMSO to penetrate into the hydrophilic pockets formed during the preparation. This leads to the much greater swelling of UAA gels prepared in water in this solvent composition.

Swelling Behavior of UAA Gels Prepared with Water-Aprotic Solvent Mixtures

We considered above the swelling behavior of UAA networks in water-aprotic solvent mixtures. According to the swelling results, the water-aprotic solvent interaction strongly influences the swelling of UAA gels. The interaction between the solvents and the UAA chain can be greatly changed with G_{11} , G_{12} , and G_{22} in the solvent mixtures. We report the effect of solvent interactions on the microstructure of amphiphilic UAA gels. UAA gels were prepared with various water-aprotic solvent (DO or DMSO) mixtures, and the swelling ratios in MC and DDI water were measured. The molar ratio of water/aprotic solvent in the solvent mixtures used in the prepara-

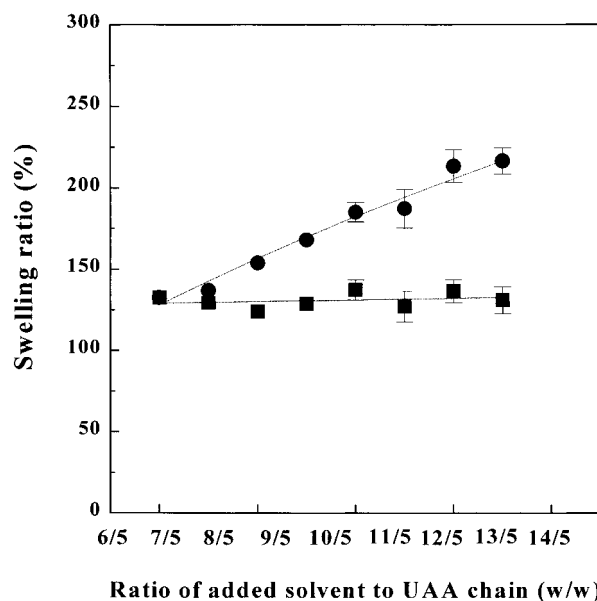


Figure 6 The swelling ratio of UAA networks in MC vs the weight ratio of solvent mixtures/UAA chain in the preparation of networks: (●) UAADG gel and (■) UAASG gel.

tion of networks was identical to the molar ratio of water/aprotic solvent used in the swelling measurement of UAA gels prepared in pure solvents (UAAG5, UADG5, and UASG5 gels; Table II).

For the preparation of UAA gels composed of a water/DO (UAADG) or water/DMSO (UAASG) solvent mixture, the weight ratio of the solvent mixture/UAA chain in the network formulation was varied from 6/5 to 13/5, whereas the amount of water in the solvent mixture was fixed but the DO or DMSO content in the solvent mixtures was varied. The increase in the weight ratio of added solvent to UAA precursor chain in the preparation of UAADG and UAASG gels meant an increase in the added amount of DO or DMSO with the constant amount of water in the solvent compositions. The results for the swelling of these gels in MC are shown in Figure 6. Although UAA gels prepared in water/DO (UAADG) showed the increase in the swelling ratio with increasing solvent content in the network formulation, the gels prepared using water/DMSO (UAASG) exhibited a practically constant swelling ratio at various solvent contents. At the same weight ratio of solvent/UAA chain, the UAASG gels showed much smaller swelling ratios than the UAADG gels, even though these networks were prepared with the same UAA precursor chain, indicating that the hydrophobic domains of these networks have

very different properties. According to our previous articles,^{23,25} although amphiphilic UAA networks were swollen in water and MC immiscible with water, these two immiscible solvents were separately absorbed by the hydrophilic and hydrophobic domains of the UAA network. That was because the water cannot be taken up by the hydrophobic segments of the UAA networks. Because the swelling in MC only depended on the property of the hydrophobic domains and was independent of the hydrophilic domains of the UAA networks, the swelling ratio in MC merely indicated the properties of the hydrophobic domains of the UAA networks. Thus, two arguments can be advanced to explain these results: the different solvent interactions between water/DO and water/DMSO and the different microstructures of UAASG and UAADG networks.

As discussed above, the DO–water interaction (G_{12}) was weaker than water–water (G_{11}) and DO–DO (G_{22}) interactions in this solvent composition, and the interaction of the water with the hydrophilic segments and the DO with the hydrophobic segments was not hindered by a water–DO attractive interaction. Thus, the solvation of the UAA chain by DO in the solvent mixture was not hindered by the water–DO interaction in this water/DO solvent composition used in the preparation of network, so that the chain entanglement of the UAA chain decreased with the increase in DO content in the solvent mixture. This decreased chain entanglement caused the increase in the swelling ratio in the MC. These results are discussed later in conjunction with the mechanical properties of the networks.

However, DMSO–water (G_{12}) interactions were stronger than water–water (G_{11}) and DMSO–DMSO (G_{22}) interactions, which resulted in very different swelling behaviors in water–DO mixtures as mentioned above. So, the constant swelling ratio of UAA gels prepared in water/DMSO mixtures (UAASG) in MC can be also interpreted as being due to the strong water/DMSO interaction. As presented in Table I, the swelling ratio of UAA gels prepared in DMSO only (UASG) increased with the increasing amount of DMSO used, because of the decrease in the chain entanglements. For the gels prepared using the water/DMSO mixture, however, the swelling ratio was practically constant with the increase in the amount of DMSO used in the preparation of networks, indicating that the chain entanglements of the hydrophobic segments remained unmodified. This can be interpreted as resulting from the

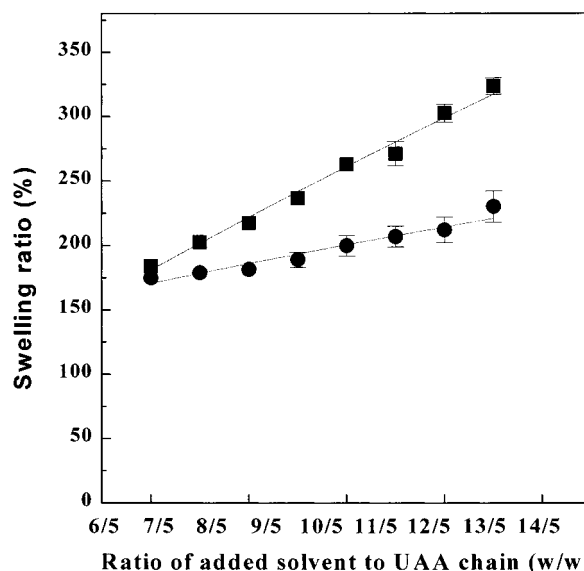


Figure 7 The swelling ratio of UAA networks in water vs the weight ratio of solvent mixtures/UAA chain in the preparation of networks: (●) UAADG gel and (■) UAASG gel.

strong water/DMSO interaction. Because the solvation of hydrophobic segments in UAA chains by DMSO is largely restricted by this strong water/DMSO interaction, the DMSO in the water/DMSO mixture cannot reduce the chain entanglement of UAA, leading to the almost constant swelling ratio in MC. In other words, DMSO in the solvent mixture prefers interacting with water to dissolving the hydrophobic segments of the UAA chain, because of the strong water/DMSO interaction in this solvent composition.

The degree of the swelling of UAA gels prepared using the mixture of water–DO and water–DMSO in water are plotted as a function of the ratio of the added solvent to UAA chain in the network formulation in Figure 7.

The UAA gels exhibited increases in the swelling ratio with the increase in the amount of solvent used during the crosslinking reaction. Unlike UAA gels prepared in water/DO, they had a greater swelling ratio and increase of the swelling ratio in MC than did the gels synthesized in water/DMSO. UAA gels prepared in the water/DMSO mixture showed a greater swelling ratio in water than the gels prepared in water/DO at the same weight ratio of solvent/UAA chain. The increase in the swelling ratio of the gels prepared in water/DMSO was also much greater compared to the gels synthesized in water/DO. These results can also be interpreted in terms of the microstruc-

tural differences attributable to the difference of the solvent interactions between water/DMSO and water/DO.

We reported in our previous articles that the hydrophilicity of UAA networks was greatly increased by maximizing the hydrophilic/hydrophobic microphase separation, not by decreasing the chain entanglement of UAA networks.^{23–25} UAA networks prepared in water had highly microphase separated structures, so these networks showed a much greater swelling ratio in water than the network synthesized in pure DO or DMSO (Table I). Because the weaker water–DO interaction does not hinder the solvation of UAA chains by DO, the chain entanglement of the networks was decreased by the presence of DO in the solvent mixtures, leading to the greater swelling ratio in MC. But the degree of the hydrophilic/hydrophobic microphase separation was not increased by the water/DO mixtures used in the preparation of the networks, even though water and DO were mixed homogeneously. As a consequence, these networks exhibited a smaller swelling ratio in water than the networks prepared in water/DMSO mixtures.

For UAA gels prepared in water/DMSO, the greater swelling ratio can be explained in terms of strong water–DMSO attractive interactions. This strong solvent interaction restricted the solvation of UAA chains by DMSO, so the DMSO in the solvent mixtures preferably interacted with water, causing microphase separation rather than interacting with the hydrophobic segments. Thus, this strong water/DMSO interaction enhanced the hydrophilic/hydrophobic microphase separation, leading to the formation of larger hydrophilic domains in the networks. These larger hydrophilic domains in the networks take up a larger amount of water, resulting in the greater swelling ratio in water compared to the networks prepared in water/DO mixtures. The difference in the swelling in these gels prepared in water/DO or water/DMSO mixtures is also explained in the following section in conjunction with the mechanical properties of these networks.

Mechanical Properties of UAA Networks Prepared with Solvent Mixtures

We explained the swelling behavior of UAA networks prepared in different solvent mixtures in terms of the microstructural differences of these networks, which are due to the difference between water/DO and water/DMSO interactions.

This section reports on the mechanical properties of UAA networks studied by dynamic mechanical analysis to confirm the microstructural differences between these networks. It is well established that aggregation of ionic groups into microdomains, which act as physical crosslinks, gives rise to many of the unique properties of ionomers. Ionic aggregation in ionomers was confirmed by small-angle X rays and inferred from mechanical measurements using dynamic mechanical analysis.^{38–43} The elastic modulus and the glass-transition temperature of ionomers both increased with the increase in the ionic content of a sample, which agreed with the expectation of an increase in ion clusters.

In our previous work we reported that UAA networks prepared with water had higher modulus and glass-transition temperature to a rubbery plateau than the networks prepared with DO.²³ That was because UAA networks prepared in water had larger ionic domains formed by hydrophilic/hydrophobic microphase separation, even though UAA networks were synthesized with the same UAA chain. These ionic domains formed by ionic clustering after drying and acted as physical crosslinks, leading to the increase in the modulus and glass-transition temperature.

In Figure 8 we show the $\tan \delta$ as a function of temperature for networks prepared using pure DO (UADG) or water/DO mixtures (UAADG). Detailed recipes for the preparation of these networks are represented in Tables I and II. With the increase in the weight ratio of solvent/UAA chain during crosslinking reactions, both of these networks exhibited a decrease in the main relaxation peak assigned to the transition temperature to a rubbery plateau, which was due to the decrease in the chain entanglements. Thus, it can be concluded that the increase in the swelling ratio of these gels with an increasing amount of solvent used was due to the decrease of the chain entanglement of the networks (Table I, Figs. 6, 7). However, the networks prepared with the water/DO solvent mixtures had higher transition temperatures than the networks synthesized in pure DO, even though a larger amount of solvent was used in the preparation of UAADG gels synthesized using water/DO mixtures. This result can be interpreted as being due to the ionic clusters formed by the presence of water in the preparation of UAADG networks. The water used in the preparation of UAADG networks caused hydrophilic/hydrophobic microphase separation during the crosslinking reaction. Once the UAADG networks

were dried, the hydrophilic domains collapsed and formed higher ionic clusters acting as physical crosslinks in the UAADG network matrix, which resulted in the increase in the transition temperature. These results thus indicate that the greater swelling ratio of UAADG gels than UADG gels in water was not due to the difference in the amount of solvent used but was instead due to the hydrophilic domains formed by the presence of the water during the crosslinking reaction.

Figure 9 presents the $\tan \delta$ as a function of temperature for the networks prepared in pure DMSO (UASG) or water/DMSO mixtures (UAASG). Like UAADG networks, UAASG networks had higher transition temperatures than UASG networks, which was due to the ionic clusters formed by the presence of water during the crosslinking reaction. This result confirmed that the larger ionic clustering formed in the UAASG network resulted in greater swelling of UAASG gels in water compared to UASG gels (Figs. 6, 7). Unlike the transition temperature of the UAA network prepared in water/DO mixtures, which decreased with the increase in the amount of the solvent used, the network synthesized in water/DMSO mixtures exhibited an increase in the transition temperature with the increase in the amount of DMSO in the network formulation: the UAADG2 network prepared with a smaller amount of solvent had a higher transition temperature than the UAADG4 networks (Table II,

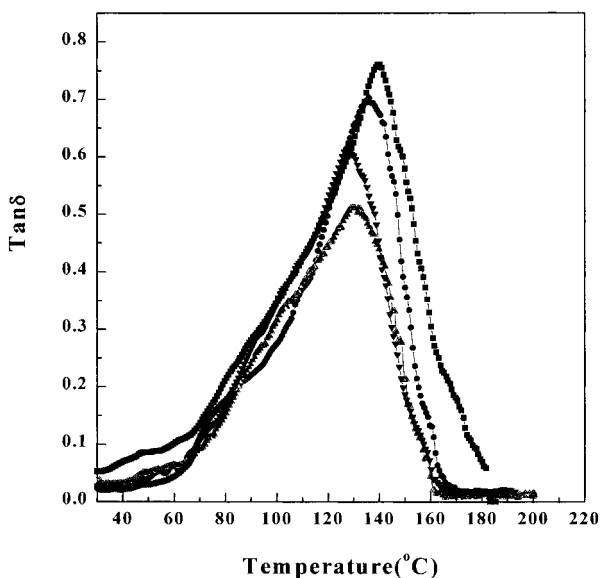


Figure 8 The $\tan \delta$ vs temperature curves measured at 1 Hz for UAADG and UADG networks: (■) UAADG2 gel, (●) UAADG4 gel, (▲) UADG2 gel, and (▼) UADG4 gel.

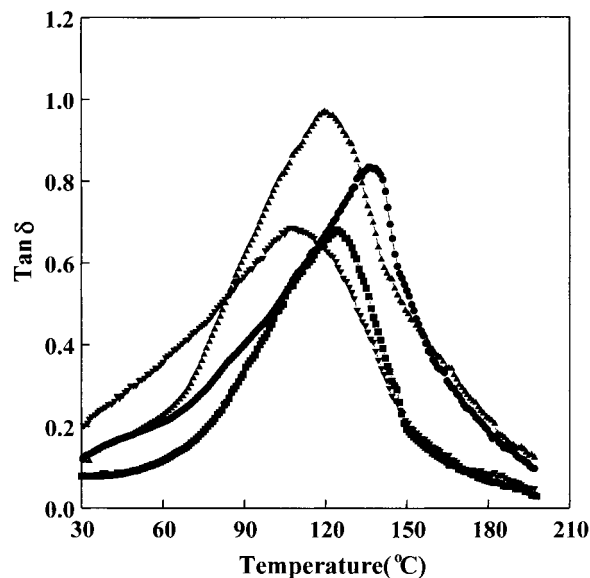


Figure 9 The $\tan \delta$ vs temperature curves measured at 1 Hz for UAASG and UASG networks: (■) UAASG2 gel, (●) UAASG4 gel, (▲) UASG2 gel, and (▼) UASG4 gel.

Fig. 8), but the UAASG4 network prepared with a larger amount of DMSO had a higher transition temperature than the UAASG2 network. This result indicated that the formation of ionic clusters was enhanced by the increase in the amount of DMSO in the network formulation. This can be explained by the strong water/DMSO interaction in this solvent composition. As mentioned previously, this strong solvent interaction reduced the ability of DMSO to solvate the UAA chain, but a water–DMSO mixture enhanced microphase separation between hydrophilic and hydrophobic segments. Consequently, the ionic clustering and aggregation of the hydrophobic segments in UAA chains increased. This increased ionic clustering, which acted as physical crosslinks, caused an increase in the glass-transition temperature. So, it can be concluded that the constant swelling in MC and the increase of the swelling in water with the increasing amount of water/DMSO mixture used were due to the increase of the ionic clustering from this strong water/DMSO interaction.

CONCLUSION

Amphiphilic PU ionomer networks prepared with water, DO, and DMSO exhibited very different swelling behaviors in water/DO and water/DMSO solvent mixtures, which were attributable to the

different solvent interactions between water/DO and water/DMSO. The hydrophilicity of UAA networks should also be considered as one of the important factors in interpreting this peculiar swelling behavior in solvent mixtures. The microstructure of UAA networks was greatly influenced by the water-solvent interactions. Unlike the water/DO mixtures with relatively weak water-DO interactions, the strong water-DMSO interaction largely restricted the ability of DMSO to solvate the UAA chain, which resulted in an increase in the aggregation of the hydrophobic segment and hydrophilic/hydrophobic microphase separation. Thus, UAA networks prepared using different solvent mixtures (water/DO and water/DMSO) showed very different swelling behaviors in the same swelling medium because of the microstructural difference between these gels. The networks prepared using water/aprotic solvent mixtures had higher transition temperatures than the networks synthesized using pure solvents, because of the ionic clustering acting as physical crosslinks, which were formed by the presence of water during the crosslinking reaction. For UAA networks prepared in water/DO mixtures, the transition temperatures of the networks decreased with the increase in the DO content in the network formulation. In the networks synthesized using water/DMSO, however, there was a greater increase in the transition temperature that was brought about by increasing the DMSO content in the preparation of the networks. That was because the strong water-DMSO interaction largely increased the hydrophilic/hydrophobic microphase separation and decreased the solvation of the hydrophobic segments by DMSO. This increase in microphase separation consequently caused an increase in ionic clustering in the networks. Thus, the networks prepared in water/DMSO mixtures had higher transition temperatures at larger DMSO contents and exhibited a constant swelling ratio in MC.

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