

Synthesis of Novel Amphiphilic pH-Sensitive Polyurethane Networks through W/O Soap-Free Emulsion Polymerization Process. II. Mechanical Property and Biphasic Swelling Behaviors

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ABSTRACT: Amphiphilic urethane acrylate anionomer (UAA) chains exhibited very different solution properties in various solvents, such as water, dioxane, and dimethyl sulfoxide (DMSO). UAA chains showed a polyelectrolyte effect in a highly polar solvent, DMSO, but gave constant viscosity at various concentrations in aqueous solution, because of the microstructural difference of the UAA chain formed in solvents. In polar solvents (water and DMSO), the swelling of UAA networks prepared with water and dioxane strongly depended on the properties of the hydrophilic domains. In low and nonpolar solvents (dioxane and methylene chloride), the swelling of UAA networks was only dependent on the property of the hydrophobic segments. In the polar solvent medium, UAAG networks prepared with water exhibited greater swelling than UADG networks prepared with dioxane. Concerning swelling in a nonpolar solvent, however, UADG networks showed greater swelling than UAAG networks. This is because of the microstructural difference between these networks, which was confirmed by the mechanical property measurement. UAAG networks, having highly microphase-separated structures, had higher modulus and transition temperatures than the UADG networks, because of the microstructural difference between UADG and UAAG networks. Both the UAAG and UADG networks take up two immiscible solvents simultaneously within their hydrophobic and hydrophilic domains. Equilibrium swelling ratio of these networks in two immiscible solvents strongly depends on their hydrophilic/hydrophobic balance that is controlled by the type of solvent used in the network synthesis. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 621–630, 2001

Key words: microphase separation; urethane acrylate anionomer; amphiphilic networks; microstructure

INTRODUCTION

Amphiphilic networks, which exhibit both hydrophilic and hydrophobic properties, have attracted

much attention because of their interesting physical properties as well as their potential technological applications.^{1–4} The conventional approach to control the hydrophilic/hydrophobic balance in amphiphilic polymer networks is to control the molar ratio of hydrophilic/hydrophobic monomers during the crosslinking reaction.^{5,6} However, little work has been reported on tuning

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or controlling the network properties by controlling the degree of microphase separation present in a precursor chain using the same amphiphilic precursor chains. In our previous work, we could achieve very different network structures from the same precursor chains by changing the structure of a precursor solution via a change in the amount of solvent and/or the nature of the solvent.^{7–11} pH-sensitive amphiphilic networks have been synthesized from urethane acrylate anionomer (UAA) precursor chains. The microstructure of these networks was very sensitive to the nature of, and the amount of, solvent used during crosslinking. Whereas dioxane formed a relatively homogenous solution, water preferentially interacted with the hydrophilic segment of UAA chains, causing microphase separation between hydrophilic moieties and hydrophobic main chains. This microphase separation was locked in by a crosslinking reaction, largely enhancing the hydrophilicity of UAA networks and the hydrophobic aggregation. Because UAAG and UADG gels prepared at different conditions have completely different microstructures, these gels exhibited quite different swelling behavior in the same swelling medium. (Microstructural differences between UADG and UAAG gels were confirmed by contact angle to water, and their morphology was examined by scanning electron microscopy.)

The incorporation of a small concentration of ions into organic polymers has been shown to lead to microphase separated ionic domains that greatly influence the properties of the polymers. The nature of the ionic groups, compatibility with the hydrophobic backbone, and the length of the spacer in side-chain ionomers have all been shown to have important effects on the morphology and properties of the polymer.^{12–20} However, little work has been reported on the effect of the solvent used during crosslinking on the mechanical properties of the ensuing ionomer networks. In our previous reports,^{7–10} we could achieve drastically different structures of the ionomer network from the same ionomer precursor chains by changing the structure of a polymer solution via a change in the amount of solvent and/or the nature of the solvent. This approach can provide an alternative approach to the modification of the properties of the ionomer network without modifying the chemical structure of the ionomer precursors. In this report, we present the mechanical properties of amphiphilic UAA networks, measured by a dynamic mechanical analyzer, to dem-

onstrate the microstructural difference of amphiphilic UAA networks prepared with different solvents.

In general, polymer gels do not take up two immiscible solvents at the same time. Amphiphilic polymer networks, however, can absorb two immiscible solvents because these networks have hydrophilic and hydrophobic segments at the same networks. So, our research group has been applying these amphiphilic polymer networks for the removal of organic solvents that are not miscible or are sparingly miscible in water. In this report, we present biphasic swelling behavior of amphiphilic UAA networks in two immiscible solvents to examine possible application of UAA networks in the waste-water treatment process. In addition, hydrophilic/hydrophobic balance of UAA networks are also discussed in conjunction with the biphasic swelling behavior.

EXPERIMENTS

Materials

In the synthesis of UAA precursor chains, poly(tetramethylene glycol) (PTMG) ($M_w = 1000$; Hyosung BASF, Korea), 2,4-toluene diisocyanate (TDI) (Junsei Chemical Co., Japan), 2-hydroxyethyl methacrylate (2-HEMA) (Aldrich Chemical Co., USA), and dimethylol propionic acid (DMPA) (Shinyo Chemicals, Japan) were used. Dioxane, acetone, dimethyl sulfoxide (DMSO), and methylene chloride were purchased from Aldrich Chemical Co. Potassium persulfate (KPS) (Wako Pure Chemical Co., Japan) and 2,2-azobisisobutyronitrile (AIBN) (Aldrich Chemical Co., USA) were recrystallized from distilled deionized (DDI) water and absolute ethanol, respectively. *N*-methyl-2-pyrrolidone (NMP) (Junsei Chemical Co., Japan) was used as a solvent for DMPA and as a viscosity thinner of the synthesized precursors.

Synthesis of UAA

UAA was synthesized by using a previously published three-step process.^{7–10} PTMG, DMPA, and NMP were placed into a 500-mL 4-necked vessel with a stirrer, a thermometer, a reflux condenser, and an inlet system for nitrogen gas. The molar ratios of PTMG/DMPA/TDI/2-HEMA used in the synthesis of the UAA precursors are summarized in Table I. To neutralize the carboxylic groups, triethylamine (Aldrich Chemical Co., USA) was

Table I Recipes for the Synthesis of UAA Precursor Chains

Symbols	Molar Ratios of Reactants (PTMG/DMPA/TDI/2-HEMA)	M_n	M_w	PDI
UAA28	0.2/0.8/1.5/1.5	2842	4774	1.669
UAA37	0.3/0.7/1.5/1.5	3449	6267	1.817
UAA46	0.4/0.6/1.5/1.5	3500	6180	1.765
UAA55	0.5/0.5/1.5/1.5	3958	6929	1.750
UAA64	0.6/0.4/1.5/1.5	4856	9343	1.924

added at room temperature with stirring for 30 min. The resulting product was a 90% solution of UAA precursors in 10% NMP to be used as is in network synthesis. The detailed synthesis conditions and characterization of UAA chain precursors were described previously.⁷⁻⁹ The proposed structure of the chain is illustrated in Figure 1. The polystyrene equivalent molecular weights obtained using the above formulation are summarized in Table I.

Network Synthesis

UAA in NMP precursor solutions were mixed with a solvent (dioxane or DDI water) and initia-

tor (AIBN or KPS) and were transferred into test tube molds (inner diameter of 1.5 cm) to perform the gelation. After the gelation was complete, the samples were taken out, fully washed with a large amount of DDI water, and methanol. These gels were put into an extracting medium to be washed for 72 h and then dried in a convection oven for 24 h. For the UAA gels prepared in dioxane (UADG), UAA in NMP solution (10 g) were dissolved in various amounts of dioxane. The composition ratio UAA solution/dioxane was varied from 5:1 to 5:7. For the gel prepared in water (UAAG), soap-free emulsions of UAA-NMP solution were first prepared; these emulsions were then poured into test tubes to perform the gelation. The composition ratios of UAA solution to water mixtures were identical to UAA solution to dioxane ratios used in the synthesis of UADG. Table II presents the amount of reactants used in the synthesis of UAA gels. Symbol UAAG37-5 and UADG37-5 represent UAA gel prepared with 5 g of UAA37 precursor chain in 7 g of water and 7 g of dioxane, respectively.

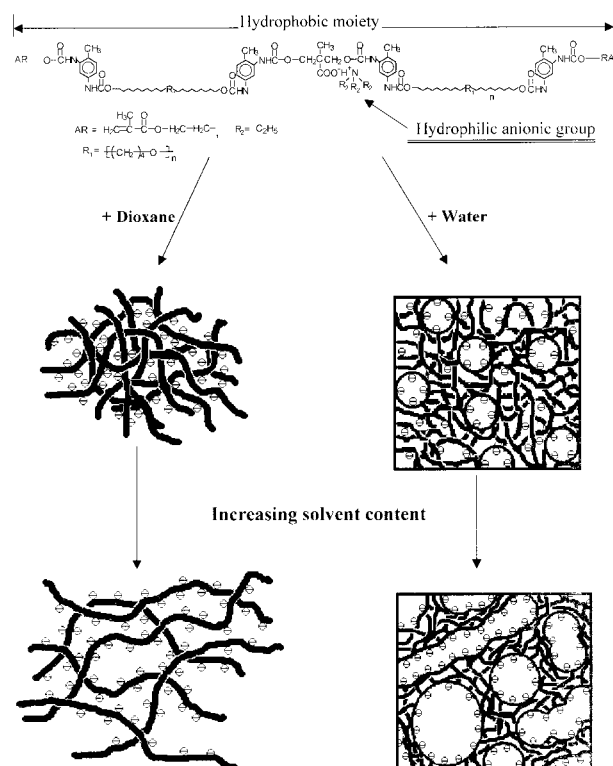


Figure 1 Proposed molecular structure of UAA and the schematic figure of microstructures of UAA networks prepared at different conditions.

Swelling Measurement in Pure Solvents and Biphasic Swelling Measurement

The swelling ratios of dried UAA gels were determined in various pure solvents, such as pH 11 buffer solution, methylene chloride (MC), dioxane, and DMSO at 25°C. Dried network samples were placed in the bottoms 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 swelling of these samples defined as weight absorbed/dried weight \times 100 was determined using gravimetric methods.

The biphasic swelling ratio of UAA gels was also examined to determine the swelling ratio in a

Table II Formulation for Preparation of UAAG and UADG Networks

Recipe	UAA/NMP	DDI Water	Dioxane	KPS	AIBN	Symbol
A	5	1		0.0015		UAAG-1
	5	3		0.0015		UAAG-2
	5	5		0.0015		UAAG-3
	5	6		0.0015		UAAG-4
	5	7		0.0015		UAAG-5
B	5		1		0.0015	UADG-1
	5		3		0.0015	UADG-2
	5		5		0.0015	UADG-3
	5		6		0.0015	UADG-4
	5		7		0.0015	UADG-5

series of two immiscible solvents (water and MC). At first, dried UAA gels were placed in pH 11 buffer solution for 24 h to obtain equilibrium swelling at aqueous phase. Fully swollen gels in pH 11 buffer solution were then transferred into MC and left for another 24 h to examine the change in swelling ratio.

Measurements

An Amtec VCD Ubbelodhe viscometer was used to measure the reduced viscosity of the UAA solution. The temperature was regulated at $25.0 \pm 0.05^\circ\text{C}$. The reduced viscosity, η_{red} , is defined as the specific viscosity divided by the concentration:

$$\eta_{\text{red}} = \frac{\eta_{\text{sp}}}{c} = \frac{t - t_0}{ct_0}$$

where c is the concentration (gdl^{-1}), and t and t_0 are the measured flowing times of the UAA solution and of the pure solvent, respectively.

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 $2^\circ\text{C}/\text{min}$ in the temperature range $25\text{--}200^\circ\text{C}$.

RESULTS AND DISCUSSION

Viscosity of UAA Chains at Various Solvents

Figure 2 shows the reduced viscosity of UAA chain in various solvents (water, DMSO, and dioxane) as a function of the concentration of UAA chain in solutions. UAA/DMSO solution shows a greater reduced viscosity than UAA-in-water and UAA-in-dioxane solutions, indicating that DMSO

is a better solvent for the UAA chain than water and dioxane. It is generally accepted that ionomer structures formed in solution can be explained by observed viscosity.^{21–24} Ionomer solutions show two types of behavior depending on the polarity of the solvents used. In nonpolar solvent, ionomers tend to form aggregates because of the attraction between ion pairs. The reduced viscosity of ionomer at low polymer concentrations is lower than that of its nonionic polymer because of the dominant intramolecular association of ion pairs, whereas the reduced viscosity at high polymer concentrations is higher than that of its nonionic polymer because of the dominant intermolecular

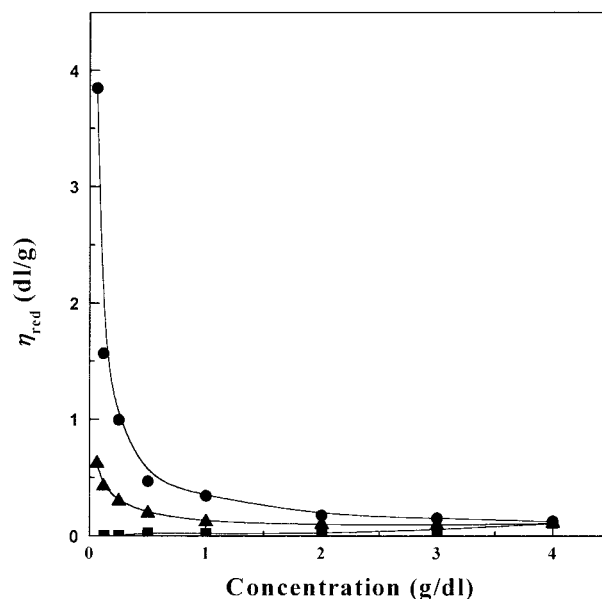


Figure 2 Reduced viscosity of UAA chain at various solvents as a function of the concentration of UAA chain in solutions (■, water; ●, DMSO; ▲, dioxane).

association of ion pairs. In polar solvent, ionomers show polyelectrolyte behavior because of coulombic interactions and exhibit a dramatic increase in reduced viscosity with decreasing polymer concentrations.^{21–24} According to a recently published report,²⁴ in high polar solvent, such as NMF ($\epsilon = 182$) and water ($\epsilon = 78.39$), polyurethane (PU) does not exhibit polyelectrolyte behavior. That is because highly polar solvents (NMF or water) do not dissolve the hydrophobic backbone of PU (polyurethane). Therefore, hydrophobic segments of PU ionomer phase-separate and aggregate to form colloidal particles, resulting in the decrease of the hydrodynamic volume of the polymer chain in solution.

For UAA solutions, un-neutralized UAA does not dissolve in water, whereas neutralized UAA chains form dispersions in water, where the size of the UAA dispersion in water is 40–60 nm, i.e., the water is a poor solvent for UAA chain and a nonsolvent for hydrophobic soft segments as well. Because the water does not dissolve the whole UAA chain but dissolves anionic hard segments only, nonionic soft segments are separated from hard segments with the addition of water and aggregate to minimize interfacial energy. This hydrophobic aggregation in water results in a lower viscosity compared with UAA/DMSO and UAA/dioxane solutions. Also, UAA/water solu-

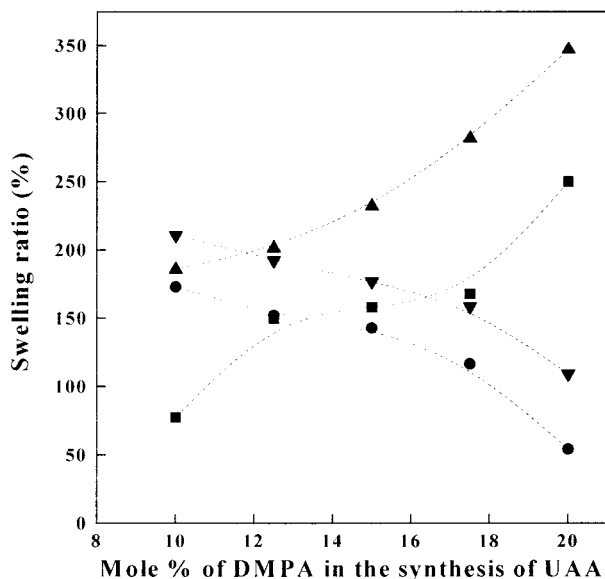


Figure 3 Swelling ratio of UAAG networks prepared using the largest amount of solvent in formulation (Table I) at various pure solvents, measured as a function of mol % of DMPA in the synthesis of UAA chain (■, pH 11 buffer solution; ●, dioxane; ▲, DMSO; ▼, MC).

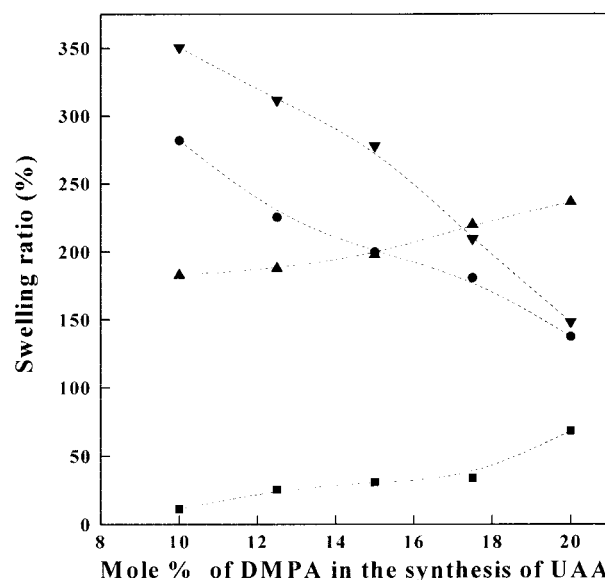


Figure 4 Swelling ratio of UADG networks prepared using the largest amount of solvent in formulation (Table I) at various pure solvents, measured as a function of mol % of DMPA in the synthesis of UAA chain (■, pH 11 buffer solution; ●, dioxane; ▲, DMSO; ▼, MC).

tions do not exhibit polyelectrolyte behavior. Because DMSO and dioxane dissolves both segments of the UAA chain, the hydrodynamic volume of UAA chains in DMSO and dioxane is larger than that of the UAA chain in water, leading to greater viscosity. In addition, the higher polyelectrolyte effect and viscosity of the UAA/DMSO solution than the UAA/dioxane solution can be interpreted as due to a difference of polarity between DMSO and dioxane. Because DMSO has a higher dielectric constant ($\epsilon = 37$) than dioxane ($\epsilon = 2.209$), DMSO has a stronger ability to solvate the counterions of carboxylic complex than dioxane, which results in higher polyelectrolyte effect and viscosity. Therefore, it can be tentatively concluded that DMSO is a better solvent for UAA chains than water or dioxane.

Swelling of UAA Networks in Pure Solvents

Figures 3 and 4 show the equilibrium swelling ratio for UAAG and UADG networks in various pure solvents, measured as a function of mol % of DMPA in the synthesis of UAA chain. In these experiments, all UAA networks having different ionic content were prepared using the largest amount of solvent in formulations (Table II). By increasing mol % of DMPA in the synthesis of UAA chains, the ionic groups per chain increase, resulting in greater hydrophilicity.

For the swelling in pH 11 buffer solution and DMSO, the swelling ratios of UAAG and UADG networks are in proportion to the mol % of DMPA used in the synthesis of UAA chains. For the swelling in dioxane and MC, however, the swelling ratio decreases with the increase in the mole % of DMPA used in the synthesis of UAA chains. These quite different swelling behaviors can be interpreted as due to the difference of solvent polarity between water (or DMSO) and MC (or dioxane). Because water and DMSO, having high dielectric constants, can dissolve the ionic groups of the UAA networks as discussed previously, the swelling in pH 11 buffer or DMSO medium is dependent of the ionic content of the networks. In addition, DMSO can dissolve both the hydrophilic anionic segments and hydrophobic soft segments, so that DMSO can be absorbed by both segments simultaneously, which results in a higher equilibrium swelling ratio than pH 11 buffer solution. The swelling in highly polar DMSO also increases with increase in the mol % of DMPA in the synthesis of UAA chains.

For the swelling in dioxane and MC, low-polarity and nonpolar solvents, the swelling ratios are independent of the ionic content of the UAA networks; that is, the swelling ratio decreases with the increase in the mol % of DMPA in the synthesis of UAA chains. This swelling behavior can be explained in terms of the low polarity of dioxane and MC. Because dioxane and MC have a very low ability to solvate the hydrophilic anionic groups in the UAA chain, MC and dioxane are absorbed by the hydrophobic segments only. So, the swelling ratio in MC and dioxane is strongly influenced by the molecular weight between crosslinks of UAA chains. As the mol % of DMPA increases in the synthesis of the UAA chain, the molecular weight of the UAA chain decreases; that is, the molecular weight between crosslinks of UAA networks decreases (see Table I). As a consequence, the equilibrium swelling ratio in dioxane and MC decreases.

In highly polar solvent media (DMSO and water), UAAG networks show greater swelling ratios than do UADG networks. In low polarity and nonpolar solvents media (dioxane and MC), however, UAAG networks exhibit smaller swelling ratios. These results indicate that UAAG networks have higher hydrophilicity and lower hydrophobicity than UADG networks and vice versa, even though these network were prepared with the same UAA chain. This is because UAAG and UADG networks have very different micro-

structures. In our previous article,^{7,8,10} we showed that UAA networks had very different microstructures depending on the solvent type used. UAAG networks prepared with water during the crosslinking reaction had dispersed hydrophilic domains in a hydrophobic UAA matrix, which was confirmed by scanning electron microscopy and contact angle measurements. These microphase separated hydrophilic domains collapse to form ionic clusters that act as superabsorbents for water, i.e., the hydrophilicity of UAA networks is greatly increased by the hydrophilic/hydrophobic microphase separation in the presence of water. This is schematically presented in Figure 1. For UADG networks prepared with dioxane, the microstructure of the networks was relatively homogeneous, and the hydrophilicity was much smaller than UAAG networks (see Fig. 1). Thus, for UAAG networks, the greater swelling ratio in buffer solution and DMSO is due to the improved hydrophilicity and the smaller swelling ratio in MC and dioxane is due to the aggregation of the hydrophobic segments and the improved hydrophilicity as well. In the case of UADG networks, the greater swelling of UADG networks in MC and dioxane is due to the greater decrease in the chain entanglement by dioxane used in the preparation of networks.

Mechanical Property of UAA Networks

We have explained the swelling behavior of UAAG and UADG networks in terms of the microstructural differences between UAAG and UADG networks. In this section, we report on the elastic modulus of UAA networks studied by a dynamic mechanical analyzer to confirm the microstructural difference between UAAG and UADG networks.

It is well established that aggregation of ionic groups into microdomains, acting as physical crosslinks, gives rise to many of the unique properties of ionomers.²⁵⁻²⁹ Ionic aggregation in ionomers has been confirmed by small-angle X-rays and inferred from mechanical measurements using dynamic mechanical analyzers. Both the elastic modulus and the glass transition temperature of ionomers have been shown to increase with increasing ionic content of a sample, in agreement with the expectation of an increase in ion clusters.

In Figures 5 and 6, we show the storage modulus as a function of temperature E' for UAAG and UADG networks, respectively. All the networks were prepared in the same total amount of

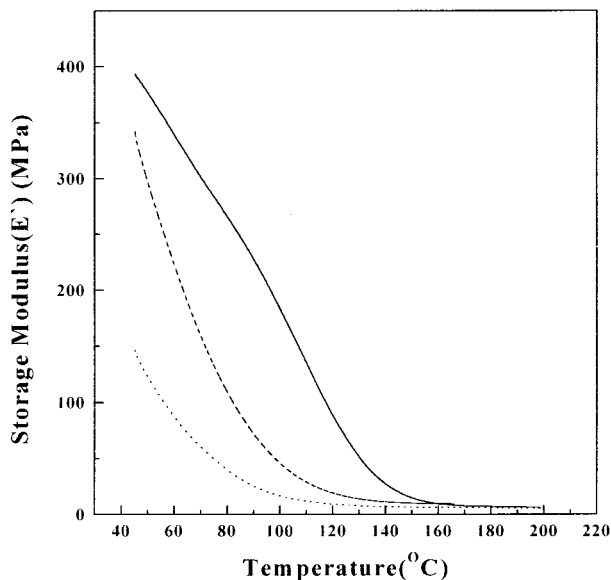


Figure 5 Storage modulus E' versus temperature measured at 2 Hz for UAAG networks (—, UAAG37-5; —, UAAG55-5; ·····, UAAG64-5).

solvent. The modulus of UAA networks was found to increase in the order of UAAG64 (or UADG64), UAAG55 (or UADG55), and UAAG37 (or UADG37). This can be interpreted as due to the increase in the ionic content of UAA networks exerting coulombic forces and hydrogen bonding. The larger the ionic groups in UAA networks, the

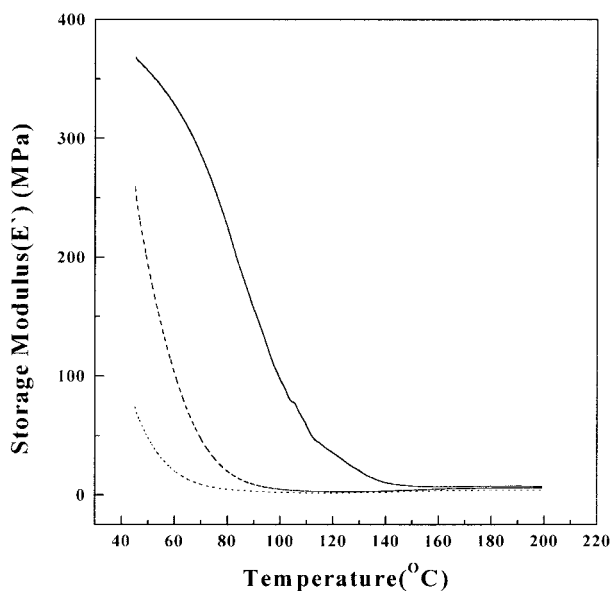


Figure 6 Storage modulus E' versus temperature measured at 2 Hz for UADG networks (—, UADG37-5; —, UADG55-5; ·····, UADG64-5).

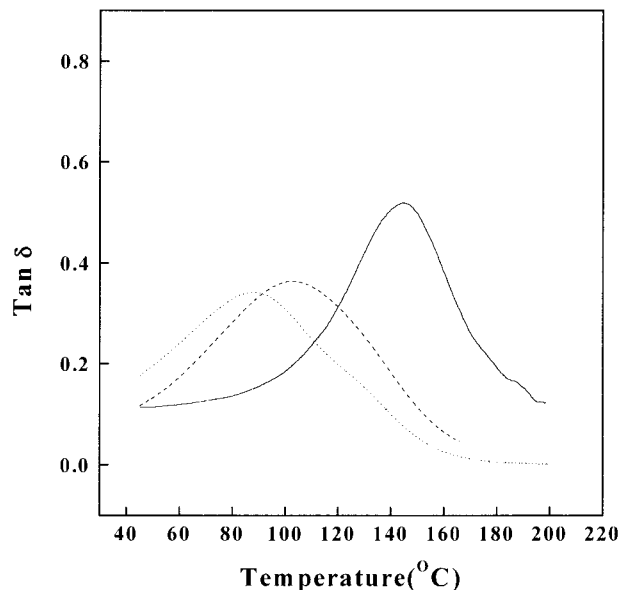


Figure 7 $\tan \delta$ versus temperature curves measured at 2 Hz for UAAG networks (—, UAAG37-5; —, UAAG55-5; ·····, UAAG64-5).

greater is the effect of the physical crosslinks exerted by ionic groups. For the modulus of UAAG and UADG networks prepared with the same UAA chain, the UAAG networks prepared with water during crosslinking reaction have higher modulus than UADG networks prepared with dioxane. In general, the increase in the modulus of the ionomers results from the increase of the ionic contents in the polymer backbone. However, these networks, having the same ionic content, exhibit different moduli. The higher modulus of UAAG networks is due to the greater ionic clustering formed by the hydrophilic-hydrophobic microphase separation by the presence of the water during crosslinking reaction. So, the modulus of UAA networks can be increased by increasing the hydrophilic-hydrophobic microphase separation without increasing the ionic content in the polymer backbone.

Figures 7 and 8 present $\tan \delta$ as a function of temperature for UAA networks. The main relaxation peak, assigned to the transition temperature to a rubbery plateau, of UAA networks was also found to increase in the order of UAAG64 (or UADG64), UAAG55 (or UADG55), and UAAG37 (or UADG37). That is, as the mol % of DMPA increased, the transition temperature shifted to a higher temperature. Therefore, the higher transition temperature of UAAG37 or UADG37 networks can also be explained by their higher

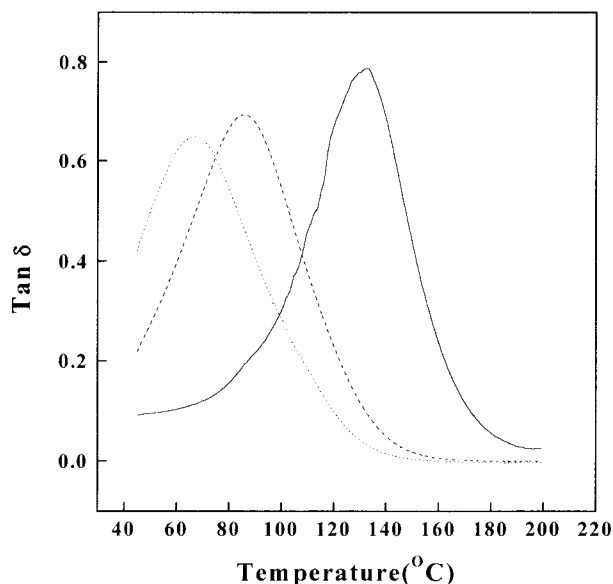


Figure 8 $\tan \delta$ versus temperature curves measured at 2 Hz for UADG networks (—, UADG37-5; ---, UADG55-5; ·····, UADG64-5).

DMPA contents. For UAAG37 and UADG37 networks prepared with the same UAA chain (UAA37), however, UAAG37 networks have a 10-degree higher transition temperature than UADG37 networks. This can also be interpreted as due to the microstructural difference between UAAG and UADG networks. The greater ionic clustering in UAAG networks increases the transition temperature without increasing DMPA content of UAA chains. Therefore, it can be concluded that the modulus and transition temperature of UAA networks is increased by the increase of the hydrophilic-hydrophobic microphase separation without increasing the ionic contents of the networks.

Biphasic Swelling Behaviors

We have considered above the swelling behavior of UAA networks in pure solvents. UAA networks can be swollen in two immiscible solvents, water and MC. However, these two immiscible solvents are sorbed by the hydrophilic and hydrophobic segment, separately. So, we expect UAA networks to take up pH 11 buffer solution in its hydrophilic domains and MC in the hydrophobic matrix simultaneously, because of their heterogeneous network structure. Therefore, we also expect that UAA networks can have applications in the removal of organic solvents that are immiscible or sparingly miscible in water. We report in this

section on the biphasic swelling behaviors of UAA networks. In addition, we intend to evaluate the hydrophilic/hydrophobic balance of UAA networks prepared with different solvents by examining the swelling ratio of swollen UAA networks in MC.

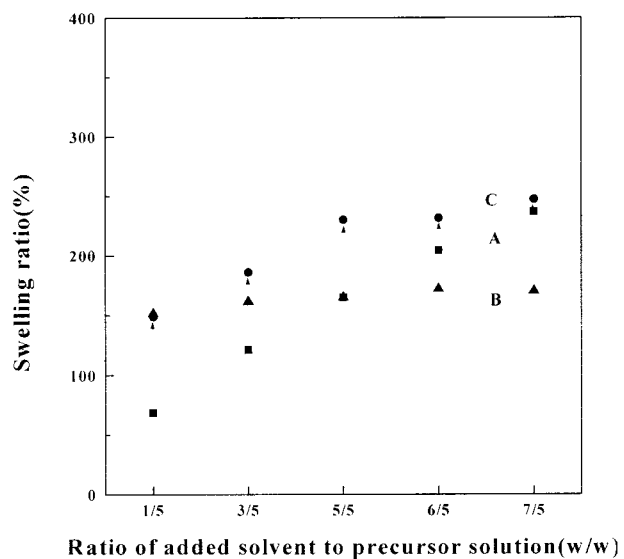
In Figure 9, we show the biphasic swelling results of UAAG and UADG networks as a function of the amount of solvent used in the preparation mixture. Curve A shows the swelling ratio in pure pH 11 buffer solution as a function of the water content during the crosslinking reactions. When these networks, swollen in the buffer solution, are placed in MC, they take up MC because of the hydrophobic matrix. The results are represented by curve C. UAA networks swollen in neat MC yield the results presented by curve B. The difference between curves A and C corresponds to the swelling ratio in MC after swelling in buffer solution.

As expected, all of the UAA networks swell by two mechanisms in two immiscible solvents. Generally, one network absorbs a solvent giving one equilibrium swelling ratio. However, UAA networks absorb two immiscible solvents and exhibit two equilibrium-swelling ratios with one network. When dried UAA networks are placed in pH 11 buffer solution, the hydrophobic segments remain unswollen but the hydrophilic segments absorb water. After these swollen networks in buffer solution are transferred into MC, these networks take up MC in their hydrophobic domains and swell again, whereas the swollen hydrophilic domain containing water remains unchanged. This is schematically presented in Figure 10. Although all the UAA networks showed such consecutive swelling behavior, that is biphasic swelling, we represent only the results for UAAG28 and UADG28 networks in this work.

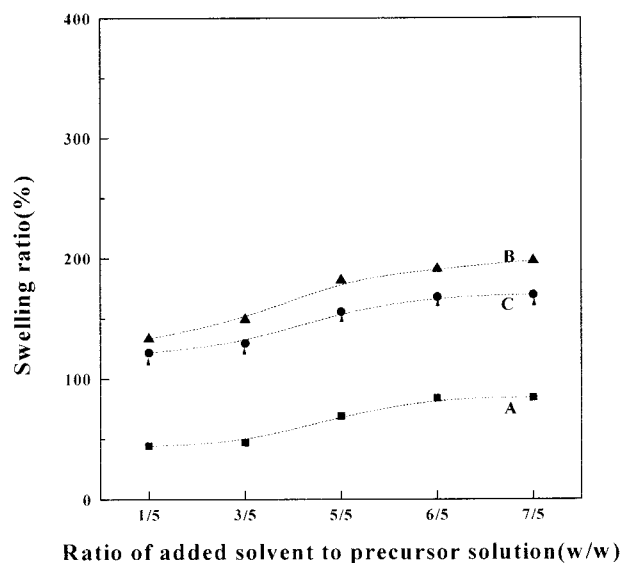
When the UAAG28 and UADG28 networks swollen in buffer solution are placed in MC, swollen UADG networks [Fig. 9(b)] in buffer solution take up a larger amount of MC than swollen UAAG networks [Fig. 9(a)]. Swollen UAAG28 networks, prepared with the higher water content, hardly take up any MC. This different biphasic swelling of UAA networks can be explained in terms of the microstructural differences.

Because UAAG28 networks have a larger hydrophilic domain formed by the hydrophilic/hydrophobic microphase separation, as discussed in our previous articles,^{8,10} UAAG28 networks are highly swollen in pH 11 buffer solution by sorbing water in their hydrophilic domains. When these

swollen UAAG28 networks are placed in MC, these highly swollen hydrophilic domains in the hydrophobic matrix exert greater osmotic pressure. This pressure prevents the networks from taking up MC despite the favorable interaction of MC with UAA chain backbone. For UADG networks, having less hydrophilicity, a smaller amount of water is absorbed and the osmotic pres-



(a)



(b)

Figure 9 Swelling ratio of UAA networks in pH 11 buffer solution (curve A) and subsequently in methylene chloride (curve C) versus the amount of solvent in the preparation of UAA networks. Curve B represents swelling in pure methylene chloride. (a) UAAG28-5; (b) UADG28-5.

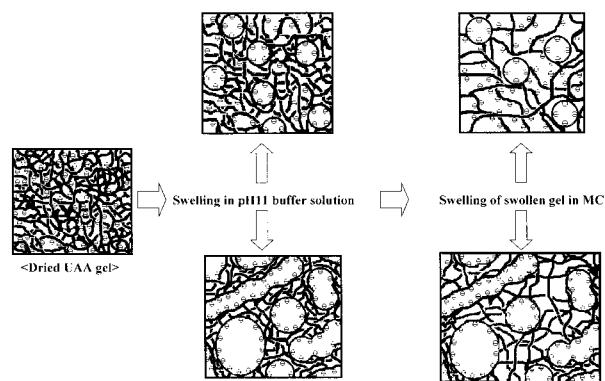


Figure 10 Schematic figure of biphasic swelling of UAA gels in pH 11 buffer solution and MC.

sure exerted by swollen hydrophilic domains is smaller. As a consequence, swollen UADG networks in buffer solution take up a larger amount of MC. The biphasic swelling results also show the difference of microstructure and the hydrophilic/hydrophobic balance between UAAG and UADG networks. Also, the practically constant swelling ratio of the dry UAAG networks in MC indicates that the hydrophobic matrix of the UAAG networks remains essentially unmodified by the presence of water used during the crosslinking reactions.

CONCLUSIONS

Amphiphilic ionomer, urethane acrylate anionomer chains showed very different solution properties in various solvents. UAA chains showed the highest polyelectrolyte behavior and viscosity in highly polar solvent, DMSO. This is because DMSO is a good solvent for the hydrophobic segment as well as the hydrophilic segment of UAA chains. For UAA-in-water solution, UAA chains formed a very fine dispersion in the aqueous phase, because water is a nonsolvent for hydrophobic segments and a good solvent for ionic hydrophilic segments. Therefore, we can conclude that the solution property of UAA chains is strongly dependent on the nature of the solvent, that is, the polarity of the solvent. Also, the swelling behavior of UAA networks in various pure solvents, such as DMSO, MC, water, and dioxane, strongly depended on the nature of the solvent and the microstructural difference of UAA networks. The swelling in polar solvent (DMSO and water) was greatly influenced by the properties of

the hydrophilic domains. But the swelling in non-polar solvent (dioxane and MC) was strongly dependent on the molecular weight and the hydrophobicity of UAA chains. The microstructural difference between UAAG and UADG networks was confirmed by dynamic mechanical measurement. UAAG networks had the higher transition temperature and modulus because of the microphase separated hydrophilic domains in the hydrophobic continuous phase. Both UAAG and UADG networks took up two immiscible solvents simultaneously within their hydrophobic and hydrophilic domains. Equilibrium swelling ratio of these networks in two immiscible solvents strongly depends on their hydrophilic/hydrophobic balance that is controlled by the solvent type used in the network synthesis. Therefore, we are studying the removal of organic solvent dissolved in groundwater using these amphiphilic polyurethane anionomer networks. These networks exhibit good extraction results of pollutant from contaminated soil, which will be reported in our accompanying article.

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