Synthesis of Novel Amphiphilic pH-Sensitive Polyurethane Networks through Water-in-Oil Soap-Free Emulsion Polymerization Process. I. Microstructural Differences and Swelling Behaviors

JU-YOUNG KIM,[1] SEUNG-HWAN SONG,[2] DAE-SOO KIM,[1] KYUNG-DO SUH[2]

[1] Department of Material Science and Engineering, Samchok National University, Samchok, Kangwon, 245-711, Korea

[2] Department of Industrial Chemistry, Hanyang University, Seoul 133-791, Korea

Received 21 September 1999; accepted 16 November 1999

ABSTRACT: pH-sensitive amphiphilic networks are synthesized from urethane acrylate anionomer (UAA) precursor chains. The microstructures of these networks are very sensitive to the nature of and the amount of solvent used during crosslinking. Whereas dioxane forms relatively homogenous solution, water preferentially interacts with hydrophilic segment of UAA chains, causing the microphase separation between hydrophilic moieties and hydrophobic main chains. This microphase separation was locked-in by crosslinking reaction, enhancing largely the hydrophilicity of UAA networks and the hydrophobic aggregation. The UAA gels, prepared with water (UAAG) and/or dioxane (UADG), exhibit quite different swelling behaviors in the same dissolution medium because of their completely different microstructures. The improved hydrophilicity of UAAG gels due to the hydrophilic/hydrophobic microphase separation is confirmed by measuring the contact angle to water. These microphase-separated hydrophilic domains on UAA gel matrix, which are observed by scanning electron microscopy measurement, influence the mechanical property of dried UAA gels as well.
 J Appl Polym Sci 76: 2115–2127, 2000

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

INTRODUCTION

Amphiphilic networks, which exhibit both hydrophilic and hydrophobic properties, have attracted a lot of 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.[5–7] However, little work has been reported on tuning 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 works, we achieved 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.[8–10] Polyethylene glycol–modified urethane acrylate (PMUA) precursor chains made up very different solutions in water and dioxane. Whereas PMUA formed homogeneous solution in dioxane,

Correspondence to: K.-D. Suh.

Journal of Applied Polymer Science, Vol. 76, 2115–2127 (2000)

the water interacted with only the polyoxyethylene (POE) group of PMUA and made up highly microphase-separated. Such structures could be locked-in by crosslinking, leading to very different network properties achievable using the same precursor chains.

In this article, we present the synthesis of new pH-sensitive amphiphilic polyurethane networks by the use of urethane acrylate anionomer (UAA) precursor chains. Generally, pH-sensitive networks are synthesized by the crosslinking polymerization of water-soluble monomers, such as acrylic acid, methacrylic acid, sodium styrenesulfonate, aminoethyl methacrylate, and vinylpyridine.[11–14] However, little work has been reported on the synthesis of pH-sensitive amphiphilic polymer networks by the use of ionomer precursor chains.[9] Keszler and Kennedy[15] reported the synthesis of pH-sensitive amphiphilic polymer networks using copolymerization of 2-sulfoethylmethacrylate and methacrylate-ditelechelic polyisobutylene. They controlled the hydrophilicity of networks by varying molar ratio of 2-sulfoethylmethacrylate in the synthesis. In our previous work, by maximizing microphase separation between POE and the hydrophobic main chain via soap-free, water-in-oil (W/O) emulsification, we could greatly enhance the hydrophilicity of urethane acrylate precursor chains.[10] Thus, in this work, we present a new approach to the preparation of pH-sensitive amphiphilic networks using ionomer precursor chains and demonstrate the important role played by the nature and amount of the solvent on the microstructure and properties of the ionomer networks formed.

The incorporation of a small concentration of ions into organic polymers has been shown to lead to microphase separated ionic domains that influence greatly the properties of the polymers. The nature of the ionic groups and their 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.[16–20] However, little work has been reported on the effect of the solvent used during crosslinking on the properties of the ensuing ionomer networks. By changing the structure of a polymer solution via a change in the amount of solvent and/or the nature of the solvent, one can achieve, after crosslinking, drastically different structures of ionomer network from the same ionomer precursor chains. 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 article, we investigate the different properties of ionic polymer networks prepared from the same precursor chain, UAA, in different solvents. We shall first describe swelling behavior of these UAA networks in two immiscible solvents, water and methylene chloride (MC), and discuss it in relation to the different microstructures anticipated for these networks. We shall then present the swelling behavior of these networks in polyethylene glycol (PEG) aqueous solution to investigate the different microstructures locked-in during crosslinking. Finally, the tensile strength of these networks obtained using Instron will be interpreted in light of the swelling measurements.

EXPERIMENTS

Materials

In the synthesis of UAA precursor chains, poly(tetramethylene glycol) (PTMG, MW 1000; Hyosung BASF), 2,4-toluene diisocyanate (TDI; Junsei Chemical Co.), 2-hydroxyethyl methacrylate (2-HEMA; Aldrich Chemical Co., Milwaukee, WI), and dimethylol propionic acid (DMPA; Shinyo Chemicals) were used. Dioxane, acetone, dimethylsulfoxide, and MC were purchased from Aldrich Chemical Co. Potassium persulfate (KPS; Wako Pure Chemicals Co.) and 2,2-azobisiso-butyronitrile (AIBN; Aldrich Chemical Co.) 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. PEG (MW 600, 2,000, 4,000, 6,000, and 20,000) was purchased from Wako Chemicals Co.

Synthesis of UAA

UAA precursors were synthesized by using a previously published three-step process.[21–23] PTMG, DMPA, and NMP were placed into 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 PTMG/DMPA/TDI/2-HEMA used in the synthesis of the UAA precursors is summarized in Table I. To neutralize the carboxylic groups, triethylamine (TEA; Aldrich Chemical Co.) was

Table I Recipes for the Synthesis of UAA Precursor Chains

Symbols	Molar Ratio 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 precursor chains were described previously.[21–23] The proposed structure of the chain is illustrated in Figure 1. The polystyrene equivalent molecular weight obtained using the above formulation is summarized in Table I.

Network Synthesis and Swelling Measurement

UAA in NMP precursor solution were mixed a solvent (dioxane or DDI water) and 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, 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) was dissolved in various amounts of dioxane. The composition ratio of UAA solution to 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, and then these emulsions were poured into test tubes to carry out the gelation. The composition ratios of UAA solution–water mixtures were identical to UAA solution–dioxane ratios used in the synthesis of UADG. Table II represents the amount of reactants used in the synthesis of UAA gels. Symbol UAAG28-5 represents that UAA gel is prepared with 5 g of UAA28 precursor chain in 7 g of water. In addition, NUADG gel is prepared with the un-neutralized UAA chain in dioxane.

The swelling ratio of dried UAA gels were determined in a pH 11 buffer solution, in MC at 25°C. Dried networks 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 swelling of these samples, defined as weight absorbed/dried weight $\times$ 100, was determined using gravimetric methods.

The swelling ratio of UAA gels in PEG solution (50 wt %) were also measured at 25°C. Dried UAA networks samples were placed in a 20-mL glass bottle. PEG solution containing different molecular weight of PEG (600, 2000, 4000, 6000, and 20,000) was added. After the bottles were sealed, they were left for 2 days. The swollen networks were then blotted with filter paper to remove surface solvent and were weighed. After measuring the change in the weight of networks, UAA networks sorbing PEG solution were freeze-dried for 2 days. The morphology of dried networks was examined by scanning electron microscopy (SEM; Philips C. KL-30; Mahwah, NJ).

Measurements

DDI water was dropped on dried UAA gels, and the contact angle was determined by a contact angle meter (Erma contact angle meter; model G-1). Tensile strength of dried networks was measured using Hounsfield Model Instron (serial no. R10001231). Crosshead speed was 10 mm/min. All samples were measured five times.

RESULTS AND DISCUSSION

Hydrophilicity and pH Sensitivity of UAA Networks

The effect of the amount of water (or dioxane) used in the preparation of UAAG (or UADG) networks on the swelling properties of the dried networks in pH 11 is shown in Figures 2 and 3, respectively. When UAAG and UADG gels were swollen at the same swelling medium, that is, pH 11, these gels showed different swelling behaviors. Both of UAAG and UADG gels exhibited an increase in the swelling with the in-

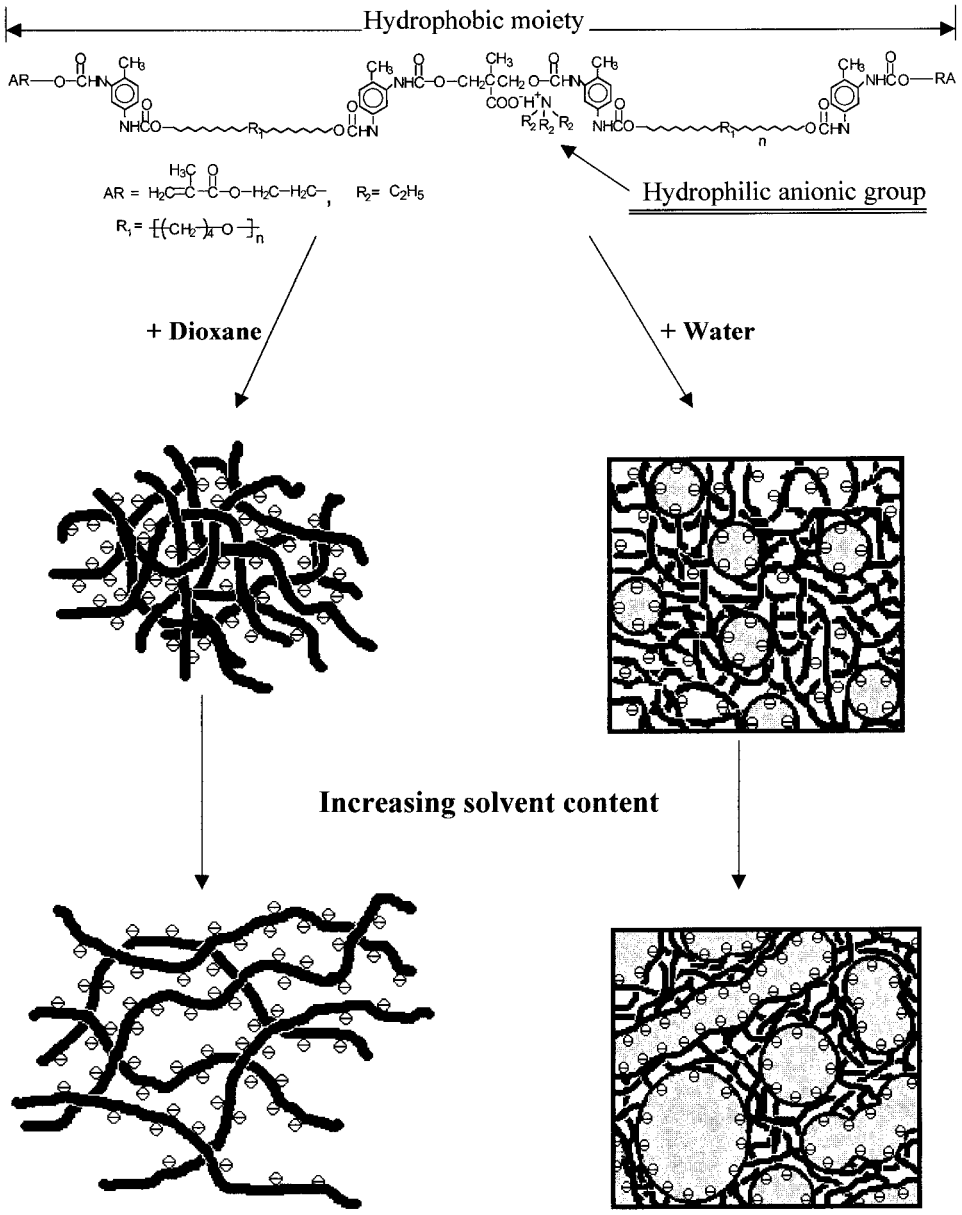

Figure 1 Proposed molecular structure of UAA and the microstructures of UAA networks prepared at different conditions.

crease in the amount of solvent used in the preparation of networks. By increasing the amount of solvent used, the UAAG gels exhibited a more drastic change in swelling in pH 11 than UADG, even though these two gels were prepared with the same UAA precursor chains having the same molecular weight and ionic content. When the swelling of UAAG and UADG gels prepared with the same precursor chain were compared, that is, UAAG28 versus UADG28 or UADG64 versus UADG64, UAAG gels showed greater swelling ratio than UADG gels.

Many researchers suggested a model describing equilibrium swelling of a charged network synthesized with solvent present, based on the Flory–Huggins thermodynamic theory, the rubber elasticity theory, and ionic interaction deviations.[24–32] Their expression is

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

$$\frac{V_1}{4I}\left[\frac{\upsilon_{2,S}}{\bar{\upsilon}}\right]^2\left[\frac{K_a}{10^{\mathrm{pH}}+K_a}\right]^2 = \ln(1-\upsilon_{2,S}) + \upsilon_{2,S} + \chi_1\upsilon_{2,S}^2 + \left[\frac{V_1}{\bar{\upsilon}\bar{M}_c}\right]\left[1-\frac{2\bar{M}_c}{\bar{M}_n}\right] \times \upsilon_{2,r}\left[\left(\frac{\upsilon_{2,S}}{\upsilon_{2,r}}\right)^{1/3} - \frac{1}{2}\left(\frac{\upsilon_{2,S}}{\upsilon_{2,r}}\right)\right] \quad (1)$$

where $\bar{M}_n$ is the number average molecular weight before crosslinking, $\bar{M}_c$ is the molecular weight between the crosslink, υ is the specific volume of the polymer, V_1 is the molar volume of the swelling agent, $\upsilon_{2,S}$ the polymer volume fraction in the equilibrium-swollen polymer, $\upsilon_{2,r}$ is the polymer volume fraction in the nascent state, χ_1 is the Flory polymer–solvent interaction parameter, I is the ionic strength, and K_a is the dissociation constant. According to their expression, when charged networks having the same ionic group content and M_c are swollen in the same dissolution medium, the equilibrium swelling of charged network is in proportion to the decrease in the volume fraction of polymer at nascent state, $\upsilon_{2,r}$, that is, the increase in the amount of solvent used during crosslinking. Thus, the increase in the swelling ratio of UAAG and UADG gels in pH 11 buffer solution can be interpreted in terms of the

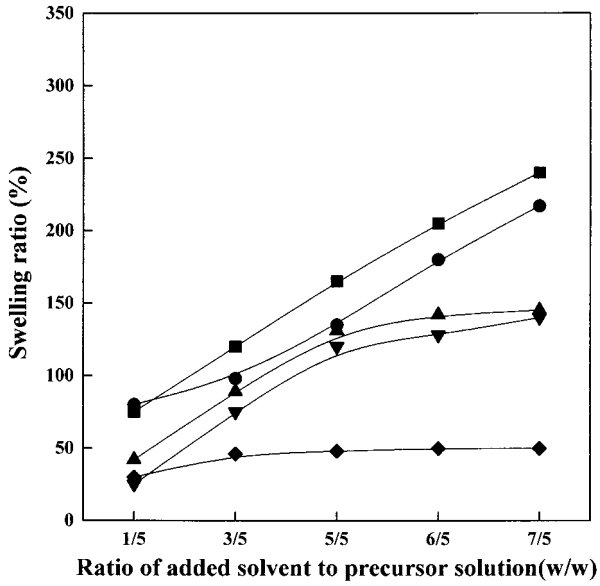

Figure 2 Swelling ratio of UAAG networks in pH 11 buffer solution vs. the amount of water used in the networks preparation: (■) UAAG28; (●) UAAG37; (▲) UAAG 46; (▼) UAAG55; (♦) UAAG64.

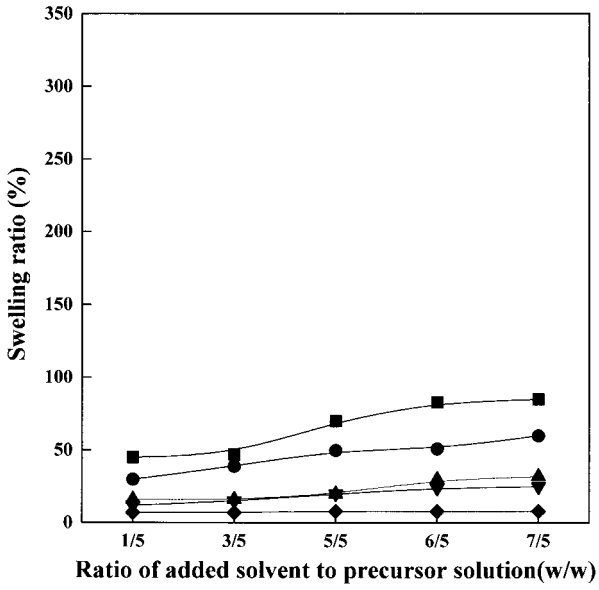

Figure 3 Swelling ratio of UADG networks in pH 11 buffer solution vs. the amount of dioxane used in the networks preparation: (■) UADG28; (●) UADG37; (▲) UADG 46; (▼) UADG55; (♦) UADG64.

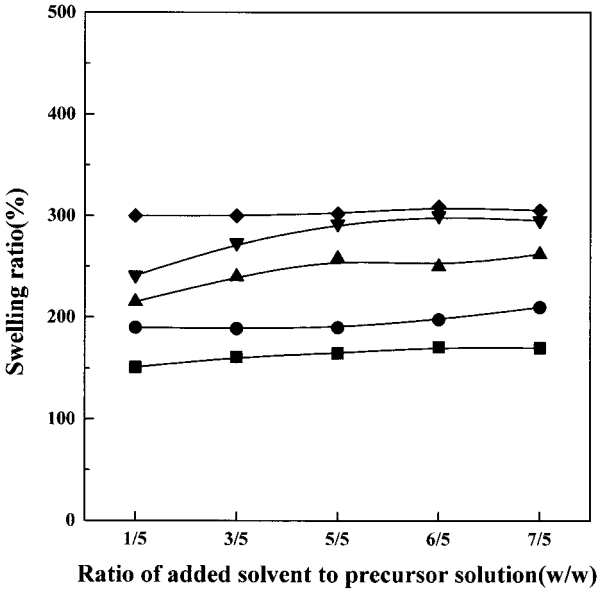

Figure 4 Swelling ratio of UAAG networks in methylene chloride vs. the amount of water used in the networks preparation: (■) UAAG28; (●) UAAG37; (▲) UAAG46; (▼) UAAG55; (♦) UAAG64.

increase of the chain mobility of UAA networks with the increase in the amount of solvent used. Because UAAG gels showed the greater swelling ratio and the greater increase in the swelling ratio with the increase of the solvent content relative to UADG gels, it might be assumed by the swelling results that water is a better solvent for UAA precursor chains than dioxane.

At the same amount of solvent in the network formulation, the swelling ratio of UAA is in proportion to the molar ratio of DMPA in the synthesis of UAA chains. For UAAG gels, the swelling ratio in pH 11 buffer solution was found to increase in the other UAAG64, UAAG55, UAAG46, UAAG37, and UAAG28 gels. UADG28 and UADG64 gels also exhibited the highest and lowest swelling ratio, respectively. As illustrated in Table I, the molecular weight of UAA precursor chain decreased with the increase in the molar ratio of DMPA in the synthesis of UAA chain, leading to the decrease of molecular weight between crosslinks (M_c). According to above-mentioned model,[26] the swelling ratio of charged network is in proportion to M_c, M_n, and ionic content of networks. However, the swelling ratio of UAA networks in pH 11 buffer solution is not dependent on M_c and M_n, but dependent on ionic content of UAA networks. We can tentatively conclude that for the swelling in ionic solution, the hydrophilicity of UAA networks played more important role than M_c of UAA networks.

In addition, the swelling ratio of UAAG55 prepared with UAA55 is greater than that of UADG28 prepared with UAA28, indicating that UAAG55 network is more hydrophilic than UADG28 networks, even though UAA28 has the larger amount of ionic groups than UAA55 (see Table I). In other words, the hydrophilicity of UAAG 55 gels containing smaller ionic groups is greater than that of UADG28 gels having greater ionic groups. Thus, the greater swelling of UAAG gels compared to UADG gels cannot be simply interpreted as due to the difference in the interaction between water–UAA and dioxane–UAA chains.

Although UAA gels were swollen by a pH 11 aqueous solution, UAA gels were also swollen by MC, which is immiscible with water, because UAA gels have hydrophilic and hydrophobic segment in the same network. In Figures 4 and 5, the swelling ratio of UAAG and UADG gels in hydrophobic solvent, MC is plotted as a function of the amount of solvent (water or dioxane) used in the preparation of the networks. UAAG and UADG gels exhibited quite different swelling behavior in MC even though these gels were prepared in the same precursor chains. The swelling ratio of UADG gels in MC increased with the increase in

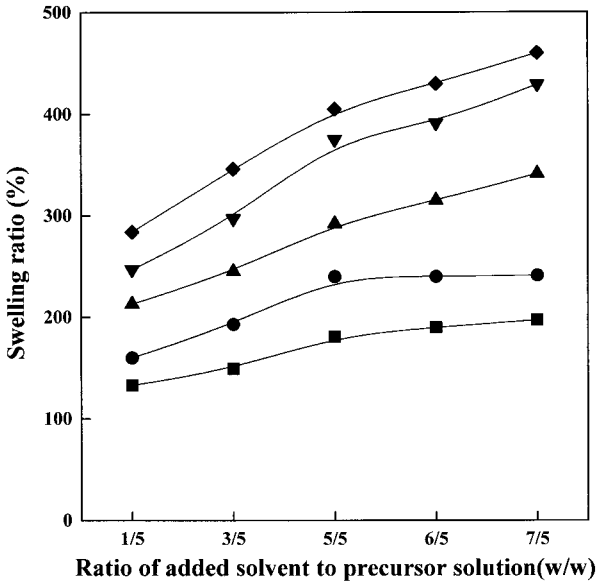

Figure 5 Swelling ratio of UADG networks in methylene chloride vs. the amount of dioxane used in the networks preparation: (■) UADG28; (●) UADG37; (▲) UADG 46; (▼) UADG55; (♦) UADG64.

the amount of dioxane used in the network preparation. UAAG gels showed a practically constant swelling ratio with increasing water content in the network preparation, even though the swelling ratio of UAAG gels dramatically increased in pH 11 buffer solution with the increase of water content in the network formulation.

The swelling behavior of UAA gels in MC should be explained by the model expressing the swelling of uncharged networks (eq. 2),[24–26] because the swelling of these gels in MC is related to only the uncharged hydrophobic segments of UAA networks.

$$\frac{1}{\bar{M}_c} = \frac{2}{\bar{M}_n} - \frac{(\bar{v}/V_1)[\ln(1 - v_{2,S}) + v_{2,S} + \chi_1 v_{2,S}^2]}{v_{2,r}\left[\left(\frac{v_{2,S}}{v_{2,r}}\right)^{1/3} - \frac{1}{2}\left(\frac{v_{2,S}}{v_{2,r}}\right)\right]} \quad (2)$$

The swelling of UADG gels in pH 11 and MC can be explained by above-mentioned models [eqs. (1) and (2)]. The increase in the swelling ratio of UADG gels in MC and pH 11 buffer solution can be interpreted as due to the increase in the chain mobility of UAA networks by increasing dioxane content in the network formulation. However, the swelling behavior of UAAG gels in MC is not simply interpreted as due to the change of chain mobility. Because hydrophobic segments of UAA networks do not absorb water but these segments are swollen by sorbing MC, the swelling ratio in MC indicates the chain mobility of their hydrophobic segments. Thus, the increase in the swelling ratio of UADG gels in MC chain is due to the increase in the mobility of hydrophobic segment of UADG networks. For UAAG networks, their swelling results in MC indicate that the chain mobility of their hydrophobic segment did not change with the amount of water used in the preparation of networks. Thus, it would be better to explain quite different swelling behavior between UAAG gel and UADG gels in terms of the difference in microstructures between these gels.

Many researchers have reported that ionomer solutions make up quite different microstructures with solvent type.[33–36] Schlick et al.[37] reported that in aqueous phase, ethylene-methacrylic acid (EMAA) ionomers had the aggregates comprised of hydrophobic core, an intermediate layer, and hydrophilic region. Cooper et al.[36] also reported on the hydrophobic aggregation of polyurethane ionomer solutions at various solvents. The degree of hydrophilic or hydrophobic aggregation in ionomer solution is dependent on solvent–ionomer interactions. When a solvent is a poor solvent for the hydrophobic main chain, hydrophobic aggregation stimulates the formation of compact structure interaction, leading to decrease the hydrodynamic volume. In this study, dioxane and water used in the preparation of networks interacts very different UAA precursor chains, so that UAA precursor chains form very different microstructures in water and dioxane. Whereas dioxane is absorbed homogeneously by the precursor chains and the solution is clear, the water is preferentially absorbed by the hydrophilic ionic group and forms scattered dispersed domains in a continuous hydrophobic phase, that is, W/O emulsions are formed. This water-in-UAA emulsification is caused by the microphase separation between hydrophilic and hydrophobic segments of the chains. In the course of emulsification, the carboxylate anions orient toward the water phase to form ionic domains in continuous hydrophobic phase. When the gelation of the W/O emulsion is carried out with KPS, initiator radicals probably first formed in the aqueous phase penetrate into the oil droplets to initiate the crosslinking reaction between vinyl end groups similar to W/O emulsion polymerization. The highly microphase-separated structure of this emulsion is locked-in by the crosslinking reaction. As the amount of water used in the preparation of networks increases, the degree of microphase separation between hydrophilic and hydrophobic segments increases, leading to larger hydrophilic domains in the gel matrix and to increase the aggregation of hydrophobic main chains. This is illustrated schematically in Figure 1. Once the networks are dried, the water droplets collapse to form ionic clusters. These clusters act as superabsorbent centers for water under appropriate external pH conditions, and a large volume change occurs. In the preparation of UADG gels in dioxane, the hydrophilic/hydrophobic microphase separation is negligible, so that relatively homogeneous network is formed by the crosslinking reaction between vinyl end groups. As the amount of dioxane in the network formulation increases, the chain mobility of whole UAA chain increases.

For UAAG gels, as the amount of water used increases in the preparation of networks, the degree of microphase separation between hydrophilic and hydrophobic segments increases, leading to larger microphase-separated hydrophilic domains in the gel matrix. Thus, the increase of the swelling ratio in pH 11 buffer solution can be explained by the increase in the hydrophilicity of

UAAG networks due to the increase in the microphase separated hydrophilic domains. The greater swelling of UAAG gels can be also interpreted in term of the improved hydrophilicity due to the hydrophilic/hydrophobic microphase separation. Since water does not interact with hydrophobic main chain and just causes microphase separation, the chain mobility of hydrophobic segment does not increase with the increase in the amount of water in the preparation mixtures. Thus, the practically constant swelling of UAAG gels in MC at various concentration of water in the preparation of networks can be explained the aggregation of the hydrophobic segments in UAAG networks due to the microphase separations.

For UADG gels, the increase in the swelling ratio in pH 11 buffer solution and MC with the amount of dioxane can be interpreted as due to the increase in the mobility of whole UAA chains. On the other hand, the increase in the swelling ratio in MC with the amount of dioxane used is greater and can be interpreted as due to the greater increase of chain mobility of hydrophobic segment by adding dioxane. This result indicates that dioxane is much better solvent for the hydrophobic main chains than water. The change of the swelling ratio in pH 11 buffer solution and MC with the amount of dioxane used can be explained by eqs. (1) and (2) regarding the swelling of the homogeneous charged and uncharged networks.

In the case of the swelling results for UAAG and UADG gels in MC, the swelling ratio of these gels prepared with the same solvent content decreased in the order of UAAG28 (or UADG28), UAAG37 (or UADG37), UAAG46 (or UADG36), UAAG55 (or UADG55), and UAAG64 (or UADG64). These swelling results are quite different because UAAG28 (or UADG28) showed the greatest swelling in pH 11 buffer solution. The swelling results in MC can be interpreted as due to the increase in the molecular weight between crosslinks of UAA networks. As the molar ratio of DMPA increases in the synthesis of UAA chains, the molecular weight of UAA chains decreases, leading to the decrease in the molecular weight between crosslinks. That is, the swelling in MC of UAA gels is in proportion to M_c, whereas the swelling in pH 11 buffer solution is in proportion to ionic content of networks and independent of M_c of networks. Thus, unlike homogenous charged networks, the swelling of amphiphilic UAA networks in pH 11 buffer solution should be explained by the property of the hydrophilic domains, and the swelling in hydrophobic solvents (MC) must be interpreted by the property of the hydrophobic domains. In other words, the property of hydrophilic domains in UAA networks does not influence the swelling of hydrophobic domains in hydrophobic solvents and vice versa. The main reason for these peculiar swelling behaviors of UAA networks is that the hydrophilic domains sorb water only and the hydrophilic domains take up MC exclusively.

The maximum possible swelling achieved of UAAG gels is limited by the maximum amount of W/O (UAA precursor chain) possible before a phase inversion occurs. Beyond this, no wall-to-wall networks formation is possible, because UAA precursor chains are dispersed in water (oil-in-water emulsion).

Figures 6 and 7 show the equilibrium swelling behavior for UAAG and UADG gels prepared using the largest amount of solvent in formulation, measured as a function of pH at 37°C. For UADG gels prepared with dioxane, the swelling ratio is only slightly pH dependent. UAAG gels, however, exhibit much larger pH sensitivity with an apparent transition around pH 6 or 7. These results can also explained by the difference in the microstructure between UAAG and UADG gels.

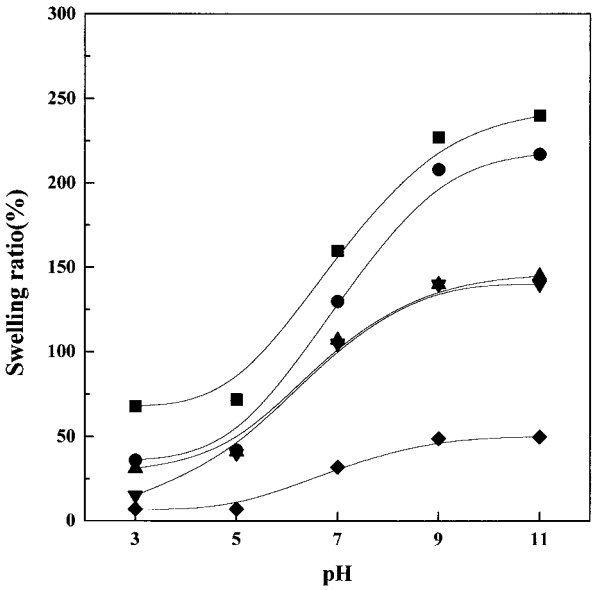

Figure 6 Swelling ratio of UAAG networks prepared at difference conditions as a function of buffer pH: (■) UAAG28-5; (●) UAAG37-5; (▲) UAAG46-5; (▼) UAAG55-5; (♦) UAAG64-5.

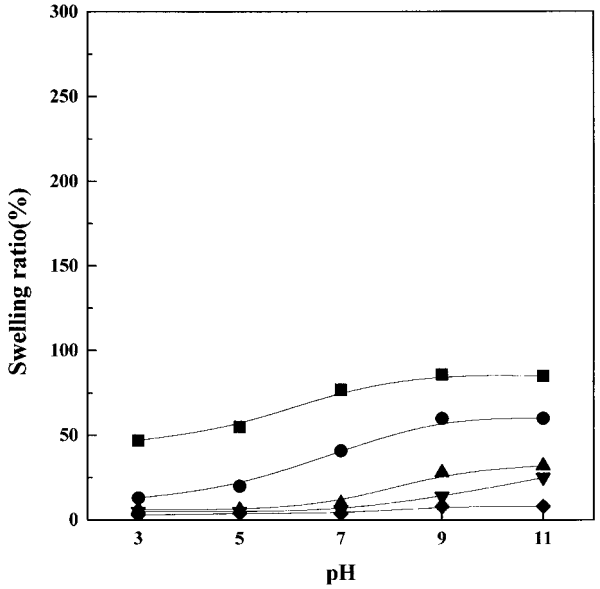

Figure 7 Swelling ratio of UADG networks prepared at difference conditions as a function of buffer pH: (■) UADG28-5; (●) UADG37-5; (▲) UADG46-5; (▼) UADG55-5; (♦) UADG64-5.

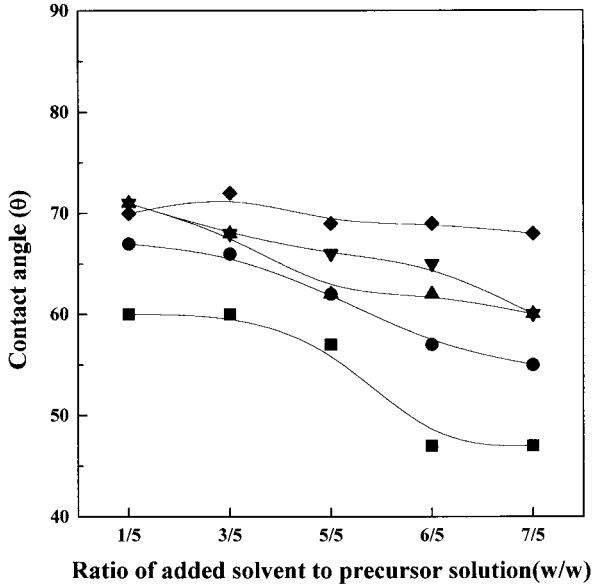

Figure 8 Contact angles of UAAG networks vs. the amount of water used in the preparation of UAAG networks: (■) UAAG28; (●) UAAG37; (▲) UAAG46; (▼) UAAG55; (♦) UAAG64.

Microstructural Difference of UAA Networks

By the results of the swelling measurement of UAA gels in pH 11 buffer solution and MC, it can be assumed that UAAG and UADG network have very different microstructures. To confirm the microstructural difference between these gels, the contact angles of UAAG and UADG gels to water were examined and are illustrated in Figures 8 and 9, respectively. The contact angles of UAAG and UADG networks to water are plotted as a function of the amount of solvent (water or dioxane) used in the network preparation. The contact angle of UADG networks remained unchanged with increasing added amount of dioxane in the network preparation, indicating their hydrophilicity did not change with the added amount of dioxane in network preparation. It can be concluded that the increase in the swelling in pH 11 buffer solution with the increase of added amount of dioxane in the network preparation is due to the increase in chain mobility of hydrophobic domains. For UAAG networks, however, their contact angles are smaller than UADG networks and decrease with the increase in added amount of water in the network preparation. These results indicate that the hydrophilicity of UAAG network is greater than that of UADG network, even though UAAG and UADG network were prepared with the same UAA precursor chains. Thus, it can be thought that greater swelling of UAAG networks in pH 11 buffer solution results from the greater hydrophilicity of UAAG network com-

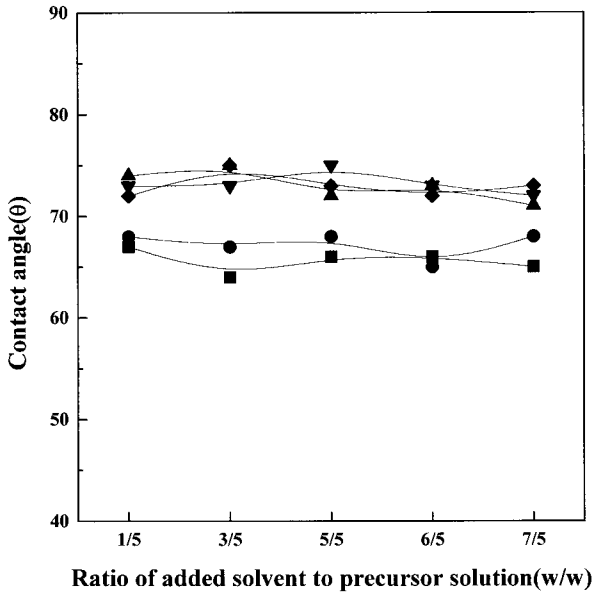

Figure 9 Contact angles of UADG networks vs. the amount of dioxane used in the preparation of UAAG networks: (■) UADG28; (●) UADG37; (▲) UADG46; (▼) UADG55; (♦) UADG64.

pared to UADG network. And, the smaller contact angle of the UAAG network compared to the UADG network can be interpreted as due to the formation of microphase-separated hydrophilic domain in continuous phase.

We assume by the above-mentioned results that UAAG and UADG networks have very different microstructures due to the very different structure of UAA–dioxane and UAA–water solutions. Thus, we can expect that UAAG networks have much bigger mesh size of hydrophilic domains on hydrophobic matrix than UADG networks. To evaluate mesh size of hydrophilic domains on UAA networks, the amount of PEG aqueous solution or PEG sorbed by UAAG37-5 and UADG37-5 gel prepared using the largest amount of solvent in the formulation in various PEG aqueous solutions was measured and shown in Figures 10 and 11, respectively. Because PEG is incompatible with hydrophobic matrix of UAA networks, we assumed that the swollen hydrophilic domains by water only take up PEG. The degree of sorbed PEG aqueous solutions by UAA gels are illustrated as the weight of PEG solution taken-up/the weight of UAA gel (g/g).

As expected, UAAG37 gels exhibited taking-up of larger amounts of the PEG solution than the UADG37 gels. As the molecular weight of PEG increased, the amount of sorbed PEG solution decreased. UADG37 showed very small sorbed amounts at PEG 20,000 solution. In addition, UAAG37 and UADG37 gels sorbing PEG aqueous solution were freeze-dried to investigate amount of PEG entrapped within their hydrophilic domains. Curve B of Figures 10 and 11 indicate the amount of PEG remaining within UAA gels after drying. The amounts of PEG remaining are represented as (the weight of UAA gel sorbing PEG solution − the weight of UAA gel after drying)/the weight of dried UAA gel before swelling (g/g). For UAAG networks, 35–50 wt % of PEG sorbed by hydrophilic domains remained within hydrophilic domains after removing water (curve B in Fig. 10). In the case of UADG37 gels, however, extremely small amounts of PEG remained in their hydrophilic domains (curve B in Fig. 11). Especially, In the case of PEG 6000 and 20,000 solution, there was no remaining PEG within UADG37 gels. These results indicate that the hydrophilic domains of UAAG37 gels have larger mesh size than those of UADG37 gels. Unlike UAAG37 gels took up PEG and water simultaneously by hydrophilic domains, UADG37 gels sorbed water only, because of smaller mesh size of their hydrophilic domains.

PEG is incompatible with the hydrophobic matrix[38] and compatible with hydrophilic domains of UAA networks, so that sorbed PEG would form

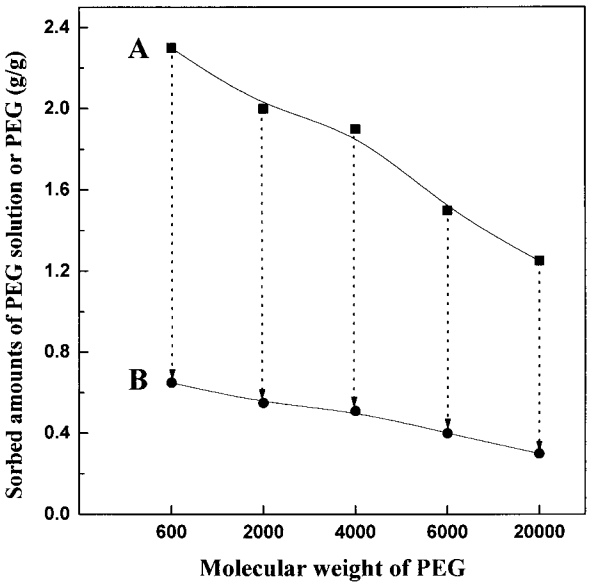

Figure 10 Amounts of sorbed PEG aqueous solution and PEG by UAAG37-5 gel vs. the molecular weight of PEG : (■) amount of sorbed PEG solution; (●) amount of sorbed PEG.

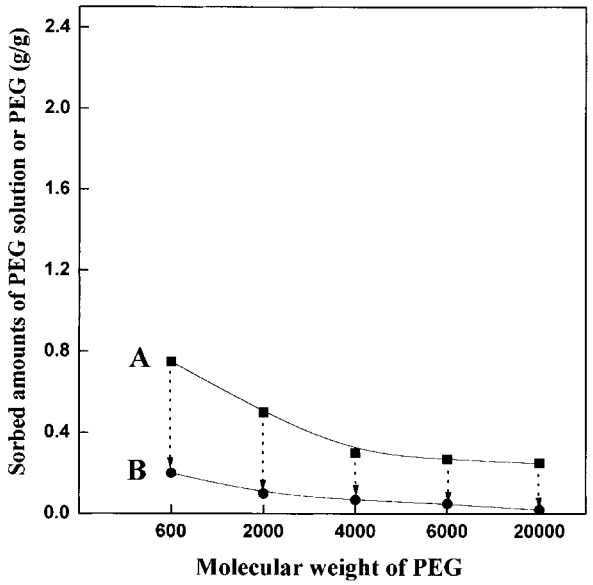

Figure 11 Amounts of sorbed PEG aqueous solution and PEG by UADG37-5 gel vs. the molecular weight of PEG : (■) amount of sorbed PEG solution; (●) amount of sorbed PEG.

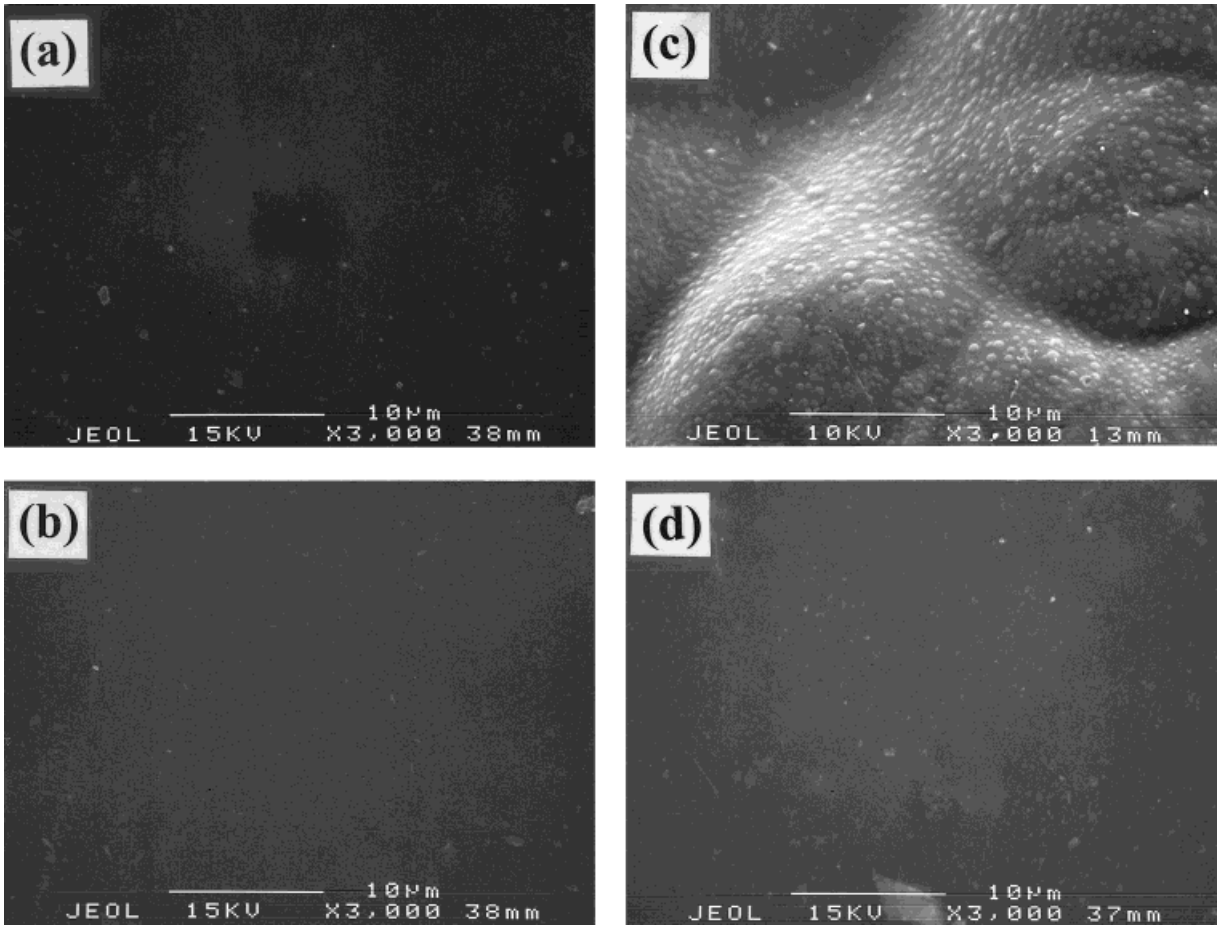

Figure 12 Scanning electron microscopy (SEM) photographs of UAA gels : (a) dried UAAG37- 5, (b) dried UADG37-5, (c) dried UAAG37-5 gel after swelling in PEG solution (d) dried UADG37-5 gel after swelling in PEG solution.

dispersed phase on the hydrophobic matrix after removing water. The morphology of UAAG and UADG networks containing PEG was examined by SEM and is illustrated in Figure 12. In fact, we tried to investigate the morphology of dried UAAG and UADG networks as well. Once the networks dried, swollen hydrophilic domains collapsed to form very small ionic clusters on the hydrophobic matrix. These ionic clusters are too small to be seen by SEM measurement, so that we did not find dispersed hydrophilic domains of UAA networks by SEM [Fig. 12(a,b)**). However, we expected that after removing water, PEG remaining in hydrophilic domains would prevent hydrophilic domains from collapsing. Unlike UADG networks [Fig. 12(d)**) exhibited homogenous morphology, UAAG networks [Fig. 12(c)**) showed that PEG was dispersed on hydrophobic matrix, indicating that hydrophilic domains of UAAG networks have greater mesh size than those of UADG networks, and hydrophilic domains of UAAG37 networks make up dispersed phase on hydrophobic matrix.

It is well established that the aggregation of ionic groups into microdomains acting as physical crosslinks give rise to many or the unique properties of ionomers. Ionic aggregation in ionomers has been inferred from mechanical measurements using dynamic mechanical analyzers.[39–44] Both the elastic modulus and the glass transition temperature of ionomers were shown to increase with the increase in the ionic content of a sample in agreement with the expectation of an increase in ion clustering. Figure 13 shows the tensile strength of UAA networks as a function of added amounts of solvent in the network preparation. UAAG46, UADG46, and NUADG46 networks were prepared with the same precursor chain (UAA46). UAAG46 and UADG46 networks were prepared with neutralized UAA46 precursor

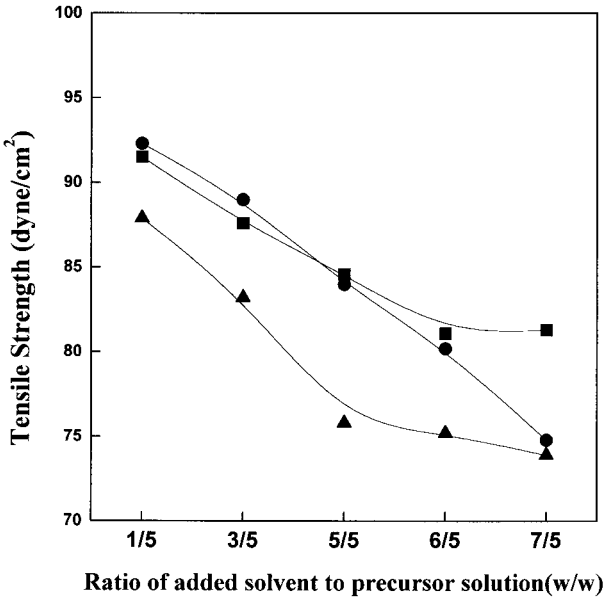

Figure 13 Tensile strength of dried UAAG, UADG and NUADG gels: (■) UAAG46-5; (●) UADG46-5; (▲) NUADG46-5.

chains by TEA, but un-neutralized UAA46 precursor chain was used in the NUADG46 networks. At the same solvent content, NUADG46 networks have smaller tensile strength than any other UAA networks. Navratil and Eisenberg[18] have reported that un-neutralized carboxylic groups suppress ionic clustering and decrease the role of ionic multiples as effective crosslinks. Thus, it can be thought that the higher tensile strength of UADG46 networks prepared under identical conditions as the NUADG46 networks indicates some probable ionic clustering in these networks. According to previous results, such as SEM and the swelling in pH 11 buffer solution, UAAG46 networks has larger ionic clustering on the hydrophobic matrix than other networks, so that we can conclude that this larger ionic clustering give rise to the highest tensile strength of UAAG46 networks. All of UAA networks exhibited the decrease in tensile strength with the increase of the solvent content in the network preparation. Unlike UADG46 and NUADG46 showed rapid decrease in tensile strength with the increase of dioxane content, the decrease in tensile strength of UAAG46 networks with the amount of water used was much smaller than UADG46 and NUADG46 networks. In addition, as the amount of water used in the network formulation increased, the difference of tensile strength between UAAG46 networks and the other networks UADG46 increased, because of the greater ionic clustering on UAAG networks resulted from the hydrophilic/hydrophobic microphase separation. The decrease in the tensile strength of UAAG networks with the amount of water used is probably due to the presence of TEA in the preparation of networks. That is, neutralization agent, TEA can act as a solvent for UAA chains as well.

CONCLUSION

pH-sensitive amphiphilic networks have been synthesized from 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 relatively homogenous solution, water preferentially interacted with hydrophilic segment of UAA chains, causing the microphase separation between hydrophilic moieties and hydrophobic main chains. This microphase separation was locked-in by the crosslinking reaction, enhancing largely the hydrophilicity of UAA networks and the hydrophobic aggregation. Since UAAG and UADG gels have completely different microstructures, these gels exhibited quite different swelling behavior in the same swelling medium. The swelling results for UAAG gels in pH 11 and MC cannot be explained by the model suggested by earlier researchers, because UAAG gels have heterogeneous microphase separated structures. Microstructural difference between UADG and UAAG gels were confirmed by contact angle to water and the morphological difference measured by SEM. Also, UAAG and UADG gels exhibited different mechanical property because of their microstructural differences. We show that the property of amphiphilic networks can be controlled by the degree of microphase separation between hydrophilic and hydrophobic segments.

In the next article in this series, we shall present the biphasic swelling behaviors in MC and water to investigate amphiphilic property of UAA gels. That is, we expect that UAA gels can sorb two immiscible solvents in the same network at the same time. We will also represent the difference of microstructures of UAA gels with the solvent type by the results of mechanical property measurements using DMA. The effect of type of counterions on the microstructure and amphiphilicity of UAA networks will be also considered in the next article.

REFERENCES

1. Yu, H.; Grainger, D. W. Macromolecules 1994, 27, 4554.
2. Ivan, B.; Kennedy, J. P.; Mackey, P. W. In Polymeric drugs and delivery systems; Dunn, R. L.; Ottenbrite, R. M., Eds.; ACS Symposium Series 469; American Chemical Society: Washington, DC, 1991; p 194.
3. Yu, H.; Grainger, D. W. In Proceedings of the 20th International Symposium on Controlled Release of Bioactive Materials; Roseman,T. J.; Peppas, N. A.; Grabelnick, H. L., Eds.; Controlled Release Society: Deerfield, IL, 1993; p 28.
4. Yu, H.; Grainger, D. W. Polym Prepr Am Chem Soc Div Polym Chem 1993, 34, 820.6.
5. Chen. D.; Kennedy, J. P.; Allen, A. J. J Macromol Sci Chem 1988, A25, 387.
6. Keszler, B.; Kennedy, J. P.; Mackey, P. W. J Controlled Release 1993, 25, 115.
7. Katakai, R.; Yoshida, M.; Hasegawa, S.; Ijima, Y.; Yonezawa, N. Macromolecules 1996, 29, 1065.
8. Kim, J. Y.; Suh. K. D. Colloid Polym Sci 1996, 274, 1025.
9. Kim, J. Y.; Suh. K. D. Polym Bull 1997, 38, 297.
10. Kim, J. Y.; Suh. K. D. ; Kim, J. R. J Appl Polym Sci 1997, 65, 821.
11. Harland, R. S.; Prud'homme, R. K. Polyelectrolyte Gels, American Chemical Society, Washington, DC, 1992; p 285.
12. Ricka, J.; Tanaka, T. Macromolecules 1984, 17, 2916.
13. Kou, J. H.; Amidon, G. L.; Lee. P. I. Pharm Res 1988, 5, 592.
14. Siegel, R. A.; Firestone, B. A. Macromolecules 1988, 21, 3254.
15. Keszler, B.; Kenedy, J. P. J Polym Sci Polym Chem 1994, 32, 3153.
16. Eisenberg, A.; King, M. Ion-containing Polymers; Academic: New York, 1977.
17. MacKnight, W.; Earnest, T. R., Jr. J Polym Sci Macromol Rev 1981, 16, 41.
18. Navratil, M.; Eisenberg, A. Macromolecules 1974, 7, 84.
19. Brockman, N. L.; Eisenberg, A. J Polym Sci Polym Phys Ed 1985, 23, 1145.
20. Lundberg, R. D.; Marowski, H. S. In Ions in Polymers; Eisenberg, A., Ed.; Advances in Chemistry 187; American Chemical Society: Washington, DC, 1980, p 22.
21. Song, M. E.; Kim, J. Y.; Suh, K. D. J Appl Polym Sci 1996, 62, 1775.
22. Allan, N. S.; Johnson, M. A.; Oldring, P. K. T.; Salim, S. In Prepolymer and Reactive Diluents for UV and EB Curable Fomulations; Oldring, P. K. T., Ed.; Selective Industrial Training Associates Ltd: London, 1991; Vol 2.
23. Kim, J. Y. Ph.D. Thesis, Department of Industrial Chemistry, Hanyang University, Seoul, Korea, 1996.
24. Peppas, N. A. Hydrogels in Medicine and Pharmacy. CRC Press: Boca Raton, FL, 1987.
25. Peppas, N. A.; Merrill, E. W. J Polym Sci Polym Chem 1976, 14, 441.
26. Brannon-Peppas, L.; Peppas, N. A. Chem Eng Sci 1991, 46, 715.
27. Katchalsky, A.; Michaell, I. J Polym Sci 1955, 15, 69.
28. Hasa, J.; Ilavsky' J Polym Sci Polym Phys 1975, 13, 263.
29. Hooper, H. H.; Baker, J. P.; Blach, H. W.; Prausnitz, J. M. Macromolecules 1990, 23, 1096.
30. Skouri, R.; Schosseler, F.; Munch, J. P.; Candau, S. J. Macromolecules 1995, 28, 197.
31. Rubinstein, M.; Colby, R. H.; Dobrynin, A. V.; Joanny, J. F. Macromolecules 1996, 29, 398.
32. Vasheghani-Farahani, E.; Vera, J. H.; Cooper, D. G.; Weber, M. E. Ind Eng Chem Res 1990, 29, 554.
33. Ding, Y. S.; Register, R. A.; Yang, C. Z.; Cooper, S. L. Polymer 1989, 30, 1204.
34. Chen, S. A.; Chan, W. C. Makromol Chem 1988, 189, 1204.
35. Chen, S. A.; Chan, W. C. Polymer, 1988, 29, 1995.
36. Nomula, S.; Cooper, S. L. J Colloid Polym Sci 1998, 205, 331.
37. Kutsumizu, S.; Hara, H.; Schlick, S. Macromolecules 1997, 30, 2320.
38. Paul, D. R. Polymer Blends; Academic Press: New York, 1978, Vol. 2.
39. Kim, J. S.; Yoshikawa, Y.; Eisenberg, A. Macromolecules 1994, 27, 6347.
40. Eisenberg, A.; Navratil, M. Macromolecules 1973, 6, 604.
41. Visser, S. A.; Cooper, S. L. Macromolecules 1991, 24, 2576.
42. Weiss, R. A.; Fitzgerald, J. J.; Kim, D. Macromolecules 1991, 24, 1071.
43. MacKnight, W. J.; McKenna, L. W.; Read, B. E. J Appl Phys 1967, 38, 4208.
44. Chu, B. Ionomers, Characterization, Theory, and Applications; Schlick, S., Ed.; CRC Press: Boca Raton, FL, 1995; p 7.