Consequences of Structural Differences in Ionomer Networks Prepared in Different Solvents

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ABSTRACT: Very different structures and properties result from the preparation of polymer networks from the same weakly charged polyurethane acrylate anionomer (UAA) dissolved in two different solvents, water and dioxane, during cross-linking. The UAA polymer readily dissolves in organic solvents such as dioxane but forms dispersions with water. Networks prepared in water (UAAG networks) and then dried show much higher hydrophilicity (swelling in water of pH 11) than their counterparts (UADG networks), which are cross-linked in dioxane and then dried. The different thermodynamic equilibrium structures achieved in the two polymer/solvent mixtures are locked into different network structures by the cross-linking reaction.

Introduction

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 ionic groups are incorporated either into the molecular backbone or on side chains to improve the physical properties and water dispersibility of hydrophobic organic polymers.[1−5] The nature of the ionic group, its 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. However, little work has been reported on the effect of the solvent used during cross-linking on the properties of the ensuing 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 cross-linking, drastically different network structures from the same polymer. We shall show that this approach can provide an alternative approach to the previously reported modification of the properties of amphiphilic networks via a chemical change in the ratio of hydrophilic to hydrophobic moieties in the chain.[6−8]

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.[9−12] One example has been pH sensitive hydrogels prepared by hydrophobic modification of water-soluble polymers made from monomers such as acrylic acid, methacrylic acid, sodium styrenesulfonate, aminoethyl methacrylate, and vinylpyridine.[13−16] More recently, attempts have included less conventional hydrophilic monomers such as amphiphilic networks prepared by radical copolymerization of methacrylate-telechelic polyisobutylene macromonomers in homogeneous THF solution[10] and *N*-isopropylacrylamide and *N*-alkylacrylamide in water[12] and formation of poly(ethylene glycol)-modified urethane acrylate (PMUA) networks prepared in water dispersions.[17−19]

In this study, we investigate the different properties of ionic polymer networks prepared from the same precursor chain, a polyurethane acrylate anionomer (UAA), in different solvents. The two solvents, dioxane and water, interact very differently with the amphiphilic precursor chains. They lead to different structures that are captured by the end-linking of the precursor chains into networks denoted as UADG and UAAG, respectively. In dioxane, the UAA precursor form a homogeneous solution and their end-linking leads to rather conventional networks. In water, on the other hand, the UAA precursor form a dispersion similar to that previously reported for the poly(ethylene glycol) modified urethane acrylate[17−19] and the micellar copolymerization of *N*-isopropylacrylamide terpolmyer.[9,12] The structure of these dispersions is strongly dependent on the amount of solvent (water) in the dispersion. Such a structure can be locked-in by cross-linking and leads to very different network properties achievable using the same precursor chains.

In this paper, we present the synthesis and characterization of a new pH-sensitive amphiphilic polyurethane gels and demonstrate the important role played by the nature and amount of the solvent on the structure and properties of the networks formed. We shall describe the pH sensitivity of these UAA networks in various buffer ionic solutions and discuss it in relation to the different microstructures anticipated for these networks. We shall also present swelling and preferential solvation behaviors of these networks in different polar solvent/water mixtures to investigate the change of hydrophilicity of the networks caused by the different structures locked-in during cross-linking. Finally, elastic modulus measurements using a dynamic mechanical analyzer will complement the swelling measurements.

Experiments

Materials. In the synthesis of UAA precursor chains, 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 dimethylolpropionic acid (DMPA, Shinyo Chemicals) were used as received. Dioxane, acetone, dimethyl sulfoxide (DMSO), and methylene chloride were purchased from Aldrich Chemical Co. Potassium persulfate (KPS, Wako Pure Chemicals Co.) and 2,2-azobisisobutyronitrile (AIBN, Aldrich Chemical Co.) were recrystallized from distilled deion-

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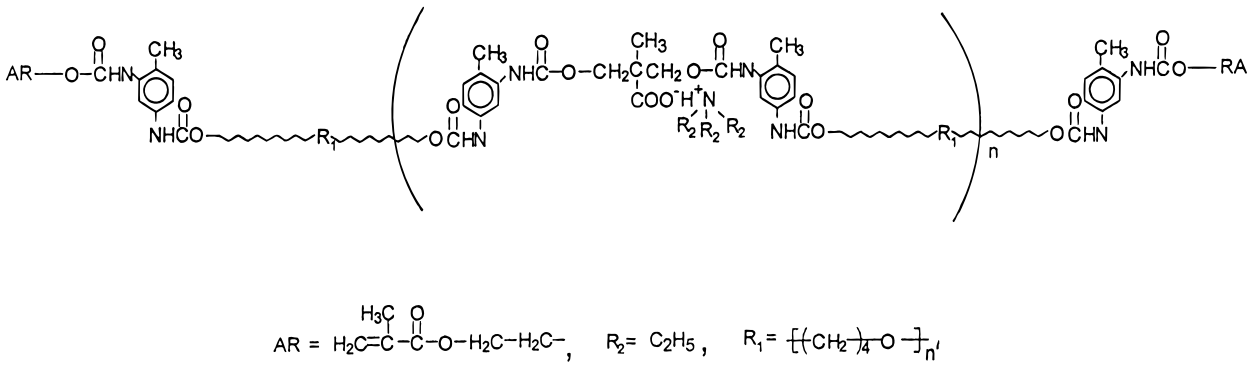

Figure 1. Postulated molecular structure of UAA.

ized (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.

Synthesis of UAA. Urethane acrylate anionomers (UAA) were synthesized by using a previously published four step process.[20−22] PTMG, DMPA, and NMP were placed into a 500 mL four-neck 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 was 0.2/0.8/1.5/1.5. To neutralize the carboxylic groups, triethylamine (TEA, Aldrich Chemical Co.) was 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 the UAA precursor chains were described previously.[7,19,23] The proposed structure of the chain is illustrated in Figure 1. The polystyrene equivalent molecular weight obtained using the above formulation is a 4000 weight average molecular weight with a polydispersity of 1.7.[19,23] Nonionic precursor chains were also prepared by omitting in the formulation the TEA which neutralizes the carboxylic groups.

Network Synthesis. Solvent (dioxane or DDI water) and initiator (AIBN or KPS) were mixed in the UAA and NMP precursor solution. The mixture were transferred then into test tube molds (inner diameter of 1.5 cm) to carry out the gelation. After the gelation was complete (3 h), the networks were soaked in methanol (1 day), DDI water (6 h), and then again in methanol for 3 days with daily solvent replacement. The networks were then dried in a convection oven for 24 h and assumed to be free of sol. For the UAA networks prepared in dioxane (UADG), UAA in NMP solutions (10 g each) were dissolved in various amounts of dioxane. The composition ratio UAA solution: dioxane was varied from 5:1 to 1:1.5. For the networks prepared in water (UAAG), soap-free emulsions of UAA−NMP solutions were first prepared, these emulsions were then poured into test tubes to carry out the gelation (60 min). The composition ratios of UAA solution:water in these mixtures were identical to UAA solution:dioxane ratios used in the synthesis of UADG. Table 1 represents the amounts of reactants used in the synthesis of UAA networks.

Networks were also synthesized from precursor chains with un-neutralized carboxylic acid groups (no TEA added) and were denoted UADU when cross-linked in dioxane.

Swelling Ratio and Preferential Absorption. The swelling ratio of six kinds of dried UAA networks

Table 1. Formulation (g) for the Preparation of UAAG and UADG Gels

recipe	UAA/NMP	DDI water	dioxane	KPS	AIBN	symbol
A	5	1		0.005		UAAG5-1
	5	2		0.005		UAAG5-2
	5	3		0.005		UAAG5-3
	5	4.5		0.005		UAAG5-4
	5	6		0.005		UAAG5-5
B	5		0		0.005	UADG5-0
	5		1		0.005	UADG5-1
	5		2		0.005	UADG5-2
	5		3		0.005	UADG5-3
	5		4.5		0.005	UADG5-4
	5		6		0.005	UADG5-5

were determined in a pH 11 buffer solution, in acetone and in solvent mixtures of buffer and acetone at 25° C with $0 < V°_b < 0.75$, where $V°_b$ is the volume fraction of pH 11 buffer solution in which the networks were swollen. Dried networks samples (of approximately 0.2 g each) were placed in the bottom of 20 mL glass bottles. An accurately known large initial volume of a 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 fully swollen networks were then blotted with filter paper to remove the surface solvent before weighing. The percentage swelling of these samples was defined as (weight swollen/dried weight) × 100. To determine preferential absorption in solvent mixtures, it was necessary to use smaller volume of solvent in the swelling tests. It was determined that pH 11 buffer solution /acetone mixtures show a characteristic acetone maximum absorbance at 267 nm. A Shimadzu UV spectrophotometer was used to determine the preferential absorption of acetone in a network when it was swollen in small amount of solvent mixtures by measuring the initial and final acetone concentration in the external liquid solution.

The volume fraction f_{ac} of acetone inside of the gel after equilibrium swelling was calculated following a procedure described by Aven and Cohen.[24] It is given by

$$f_{ac} = [\mu°_{ac} V° - \mu_{ac} V^{out}]/V^{in} \quad (1)$$

where $\mu°_{ac}$ is the volume fraction of acetone in the solvent mixture originally added to the polymer network and μ_{ac} is the volume fraction of acetone in the solvent phase after equilibration with the gel. $V°$, V^{out}, and V^{in} represent the volume of the solvent mixture initially added, that remaining after equilibration, and that absorbed by the network, respectively. The assumption of no volume change upon mixing was made, such that $V° = V^{out} + V^{in}$.

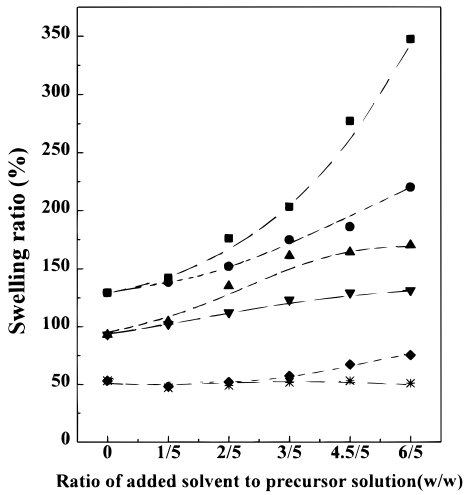

Figure 2. Swelling ratio (swollen weight /dry weight) of UAA networks in pure organic solvents vs the amount of solvent (water or dioxane) in the network preparation: (−■−) UAAG5-5 in DMSO; (−●−) UADG5-5 in DMSO, (−▲−) UADG5-5 in dioxane; (−▼−) UAAG5-5 in dioxane; (−◆−) UADG5-5 in acetone; (−∗−) UAAG5-5 in acetone.

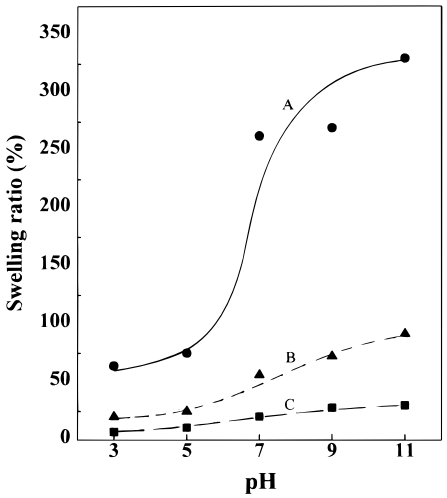

Figure 3. Swelling ratio of UAA networks prepared at different conditions as a function of buffer pH: (curve A, UAAG5-5; curve B, UADG5-5; curve C, UADG5-0).

Mechanical 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 temperature range 25−175 °C. A differential scanning calorimeter (Perkin-Elmer DSC 7c) was used at a heating rate of 1 °C/min to obtain thermograms in the same temperature range.

Results and Discussion

Swelling of UAA Networks in Pure Organic Solvents. 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 three organic solvents is shown in Figure 2. The swelling ratio of both types of networks is largest for DMSO, followed by dioxane and then acetone. In Figure 2 and all subsequent figures, the lines through the data are guides to the eye.

UAAG networks show nearly constant swelling ratio in acetone and a slight swelling enhancement in dioxane with increase in the amount of water in the preparation formulation. UADG networks swell more in acetone and in dioxane than the corresponding UAAG gels. One interpretation of this result is that cluster formation induced in UAAG networks brings about trapped entanglements that limit the swelling of UAAG networks in these solvents. Such an argument has been advanced by Visser and Cooper[25] for the interpretation of modulus enhancement in un-cross-linked polyurethane ionomers. The swelling results are reversed in DMSO where UAAG networks swell a lot more than the corresponding UADG networks. The special behavior of the highly polar DMSO has been documented in ionomer solutions. High dielectric constant solvents such as DMSO (see Table 2) are able to solvate the counterions and disperse ion pairs and multiplets present in an ionomer solution or network.[26,27] Since water in the formulation will increase microphase separation and lead to larger ionic clusters in the dried UAAG networks, these networks exhibit very large swelling increases in DMSO as a function of the water content in the formulation (Figure 2).

Table 2. Dielectric Constants and Dipole Moments of Organic Solvents Used in the Swelling Measurements[31]

solvent	dielectric constant (ϵ)	dipole moment (μ_D), D
acetone	20.70	8D
dioxane	2.209	0 D
DMSO	46.7	3.9D

The extent of swelling in dioxane for any network is intermediate between that of DMSO and that of acetone despite its very low dielectric constant. This is due to the better solvent quality of dioxane over acetone for the UAA hydrophobic backbone, to be discussed later in conjunction with the mechanical properties of the networks and their interaction parameters with the solvents.

pH Sensitivity and Hydrophilicity of UAA Gels. Figure 3 shows the equilibrium swelling behavior for UAAG5-5 and UADG5-5 gels prepared using the largest amount of solvent in the formulation (Table 1), measured as a function of pH at 37 °C. For the UADG5-5 gel (Curve B) prepared with dioxane, the swelling ratio is only slightly pH dependent. The UAAG5-5 gel (Curve A), however, exhibits higher swelling ratio and a much larger pH sensitivity with an apparent transition around pH 6 or 7. Although the two kinds of UAA gels are prepared with the same UAA precursor chains and in the same total amount of solvent (water or dioxane), these gels show quite different swelling behaviors due to the difference in the microstructure between UAAG5-5 and UADG5-5 in the pre-cross-linked formulations.

Whereas dioxane is absorbed homogeneously by the precursor and the solution is clear, the water is preferentially absorbed by the ionic clusters present forming a strongly scattering emulsion mixture. The water-in-UAA emulsification is caused by the microphase separation between hydrophilic segments (carboxylate anions) and the hydrophobic segments of the chains. The carboxylate anions orient toward the water phase to form ionic domains in a continuous hydrophobic phase. The dried UAA networks prepared here do not exhibit in their DSC thermograms between 25 and 175 °C the high-temperature glass transition which has been observed in high molecular weight polyurethanes that microphase separate into soft and hard segments.[28] The relative high cross-link density and the smallness of the chains have been known to inhibit a microphase separation of the chain backbone.[29,30]

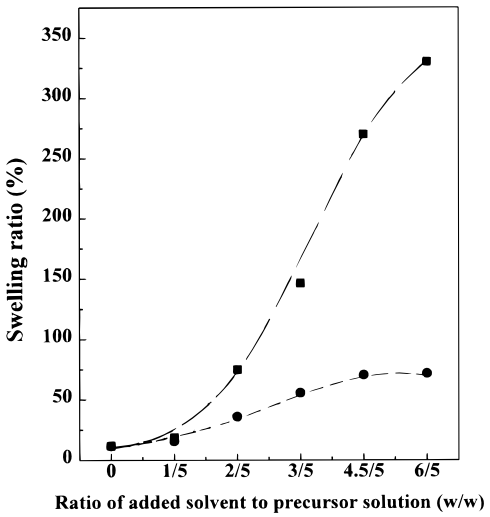

Figure 4. Swelling ratio of UAA networks in pH 11 vs the amount of water or dioxane in the preparation of networks: (−■−) UAAG gel; (−●−) UADG gel.

When the gelation of the UAA water-in-oil emulsion is carried out with KPS, initiator radicals probably first formed in the aqueous phase penetrate into the oil phase to initiate the cross-linking reaction between vinyl end groups. The hydrophilic−hydrophobic microphase-separated structure of this emulsion is locked-in by the cross-linking reaction. Once the networks are dried, the water droplets collapse to form ionic clusters. These clusters act as superabsorbent centers under appropriate external pH conditions, and a large volume change occurs. The larger the microphase separation between the hydrophilic moieties and hydrophobic backbone, the larger the ensuing hydrophilicity of the UAAG networks is. This microphase separation increases with the amount of water in the preparation mixture. In the preparation of UADG5-5 gel in dioxane, the degree of hydrophilic/hydrophobic microphase separation is negligible because the low dielectric constant of dioxane (see Table 2) is unable to solvate the ionic clusters to any large extent. Since dioxane turns out to be a good solvent for the hydrophobic UAA backbone, the dioxane−UAA solution is homogeneous. Although the amount of solvent in the preparation of the networks leading to the swelling curves A and B in Figure 3 is the same, the swelling properties of the networks in buffer solution are drastically different. Curve C in Figure 3 represents the swelling ratio of the UADG5-0 networks synthesized with no additional solvent. The difference between curves B and C can be interpreted as due to the decrease in chain overlap with addition of dioxane allowing for slightly larger swelling.

In Figure 4, the swelling ratio of UAAG and UADG gels in pH 11 buffer solution is plotted as a function of the amount of solvent (water or dioxane) used in the preparation of the networks. The swelling ratio of UAAG gels in pH 11 increased dramatically with the increase in the amount of water used in the preparation of UAAG. For UADG gels, however, the increase in the swelling ratio with the amount of dioxane used is much smaller and can be interpreted as due to the dispersion of the chains in fairly homogeneous preparation mixtures. For UAAG gels, on the other hand, 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 hydrophilic domains in the gel matrix. This is illustrated schematically in Figure 5. Once the networks are dried, the hydrophilic domains can be viewed as superelastic[32] leading to the large solvent absorption observed. The maximum possible swelling achieved is limited by the maximum amount of water-in-oil (UAA precursor) possible before a phase inversion occurs. Beyond this point, no wall-to-wall network formation is possible.

The difference in swelling behavior between UAAG and UADG networks is due to the extent of hydrophilic/hydrophobic phase separation in the samples. Although the initiators in the two types of networks are different, the radicals formed are likely to initiate the reaction at the vinyl termination of the chains with little difference on the ensuing chemical structure. This is supported by the fact that at small added solvent (water or dioxane using KPS or AIBN, respectively), the difference in swelling behavior between the two types of networks is negligible (see Figures 2 and 4).

Swelling of UAA Networks in Acetone/Water Mixtures. The degree of swelling of UADG5-5 and UAAG5-5 networks in large excess of solvent mixture is plotted as function of volume fraction of pH 11 buffer solution ($V°_b$) in acetone in Figures 6 and 7, respectively. In both cases, the swelling in intermediate solvent compositions is greater than that in either pure solvent and the swelling curves exhibit a maximum. The swelling ratios of UADG gels are smaller than those of UAAG gels, but these gels show a sharper maximum in intermediate concentrations (between $V°_b = 0.2$ and 0.4).

Two arguments can be advanced to explain qualitatively the above results: (1) the change of water−water, water−acetone, and acetone−acetone interaction with composition; (2) the difference in microstructure between UAAG and UADG gels.

Several reports have been made regarding the convex re-entrant swelling behaviors and maximum swelling at intermediate solvent composition of poly (isopropyl acrylamide) (PIPAAm) networks in water−aprotic solvent mixtures.[33−35] Swelling results in tetrahydrofuran, dioxane, and acetonitrile−water mixtures were interpreted in term of the change of the interactions between solvents as a function of concentration. The degree of PIPAAm network swelling in these solvent mixtures was shown to vary with the strength of the interaction between water and the aprotic solvent. Thus, Mukae et al.[35] interpret their swelling results in term of the variation of the Kirkwood−Buff parameter to represent the varying solvent−solvent interactions.

Recently, a more quantitative approach using a lattice fluid hydrogen bond theory has been successful in interpreting some of the swelling data of PIPAAm in mixed solvents.[36,37] The parameters of this model are not known for our UAA systems. Therefore, it is only possible here to qualitatively interpret the results of the UADG gels in Figure 6 in term of the variation of the solvent−solvent interactions as function of solvent composition.[38] Matteoli and Lepori[39] reported values of the Kirkwood−Buff parameter (G_{ij}) for the water−acetone mixture. G_{ij} is defined as

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

where $g_{ij}(r)$ is the radial distribution function between species i and j. Representing water by (1) and acetone by (2), G_{11}, and G_{22} exhibit a maximum (strong attrac-

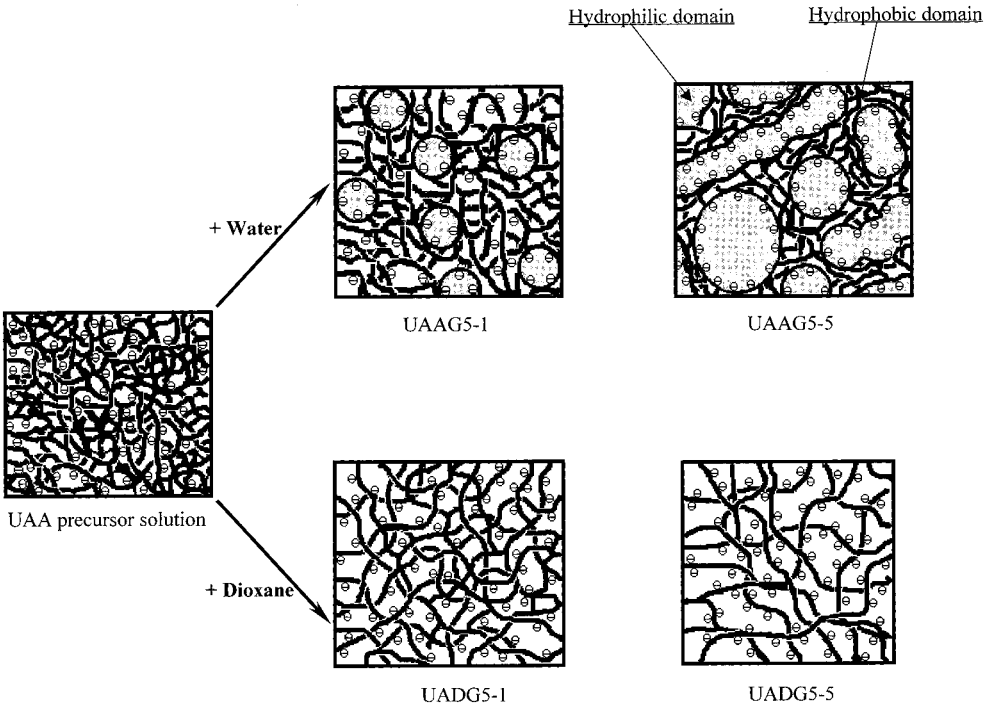

Figure 5. Schematic figure of structure of UAA solutions with addition of solvent (water or dioxane). The dioxane mixture remains homogeneous whereas the water mixture is inhomogeneous

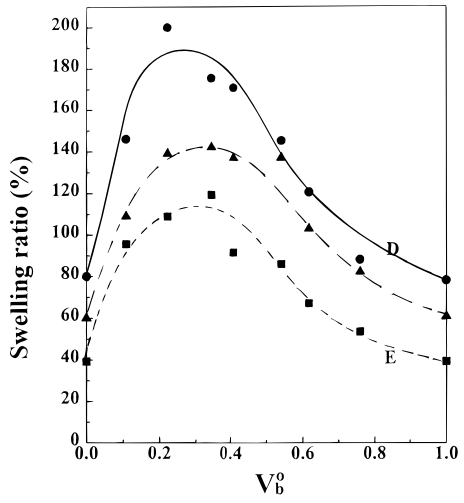

Figure 6. Swelling ratio of UADG networks in pH 11 buffer/ acetone mixtures as a function of the volume fraction of buffer: (−●−) UADG5-5; (−▲−) UADG5-3; (−■−) UADG5-1.

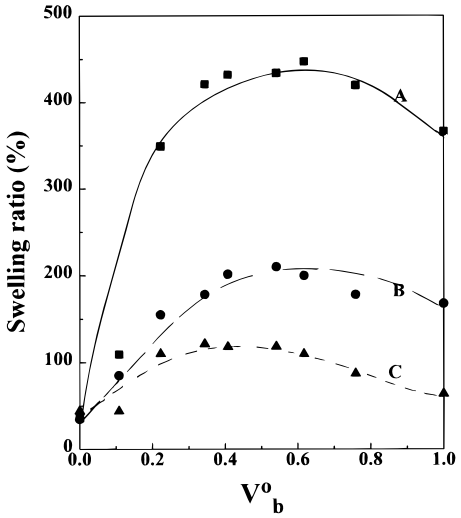

Figure 7. Swelling of UAAG networks in pH 11 buffer/ acetone mixtures as a function of volume fraction of buffer (−■−) UAAG5-5; (−●−) UAAG5-3; (−▲−) UAAG5-1.

tive interaction) and G_{12} exhibits a corresponding minimum around a water volume fraction of 0.4.[39] The sharply convex swelling results of Figure 6 occurring around this composition may thus be interpreted as due to the weaker water−acetone attractive interaction in this range of solvent composition. At higher water concentration, the water−acetone interaction increases and, as a consequence, decreases the ability of the mixture to swell the networks.

The swelling results of three of the UAAG networks examined are reported in Figure 7. These results are not as simply interpreted as for the UADG networks. Here, the swelling in acetone−water mixtures decreases only slightly after reaching a maximum despite the appreciable increase in the water−acetone interaction discussed above. Another factor must be playing an important role in the swelling of UAAG networks. This factor becomes evident when one considers the swelling of UAAG networks in pure acetone and pure pH 11 buffer solution. Whereas, there is no measurable difference in the extent of swelling in pure acetone, there is an order of magnitude difference in swelling in pure buffer solution ($V^o_b = 1.0$) (Figure 7). This large difference is most likely due to the different degree of microphase separation in the prepared networks caused by the different amounts of water used in the preparation. The larger the amount of water in the preparation (UAAG5-5), the larger the degree of microphase separation between ionic groups and the polymer backbone will be. This, in turn, induces a higher degree of hydrophilicity in the dried network. This change in microstructure, however, has little or no effect on the absorption of pure acetone which predominantly swells the backbone polymer (i.e., the continuous hydrophobic phase of the formed structures).

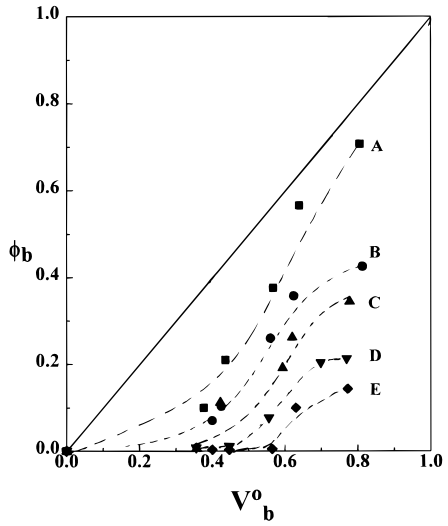

Figure 8. Volume fraction of water inside of gels equilibrated in water/acetone mixture as a function of volume fraction of water outside the gels obtained by UV spectrometry: (−■−) UAAG5-5; (−●−) UAAG5-3; (−▲−) UAAG5-1; (−▼−) UADG5-5; (−◆−) UADG5-1.

The improved hydrophilicity of UAAG networks as a function of water in the network preparation also allows more acetone to be absorbed since the good miscibility of acetone in water allows acetone to penetrate into the hydrophilic pockets formed during the preparation. This leads to the near flat dependence of swelling on solvent composition in Figure 7, once the maximum is reached. For the UADG networks, on the other hand, we expect their structure to be relatively uniform as they are prepared from homogeneous UAA solution comprised of UAA, NMP and dioxane. This is evident from the transparency of the prepared UADG networks as opposed to the opacity of the prepared UAAG networks. UAAG networks become transparent upon drying as the water pockets collapse and the polymer chains interdisperse to fill the void created. However, these shrunken interdisperse polymer domains act superelastically[32] and reswell in the presence of water or water−acetone solution to opaque gels.

Amphiphilic networks are known to exhibit strong preferential absorption with potential applications in separations. In Figure 8, we report results on preferential acetone absorption for some of the UAAG and UADG networks examined by plotting the volume fraction of water in the solvent mixture inside the gel versus the volume fraction of water outside the gel. Curves D and E obtained for UADG5-5 and UADG5-1, respectively, indicate that these networks take up only a small amount of water from the solvent mixture until about $V°_b = 0.5$. At higher external water concentration, relatively more water is absorbed but the total amount of solvent absorbed is decreasing (Figure 6).

Similar trends are observed for the UAAG networks (curves A, B, and C), but the increased hydrophilicity of these networks leads to relatively more water (pH 11 buffer solution) uptake and a much larger extent of overall swelling (Figure 6). Furthermore, as the UAAG networks are made more hydrophilic by increasing the amount of water in their preparation step, the larger amount of absorbed water entrains a larger amount of acetone. Thus, curve A now approaches the diagonal line (Figure 8) indicating that the network is losing its acetone selectivity at the high external water concentration ($V_b \geq 0.6$). Although the total extent of swelling of this network, UAAG5-5, is practically constant over the water concentration region from 0.3 to 0.8 (curve A in Figure 7), the concentration of water inside the gel varies dramatically as shown by curve A in Figure 8. Therefore, such networks can be made to be both absorbent and fairly selective by tuning the preparation conditions.

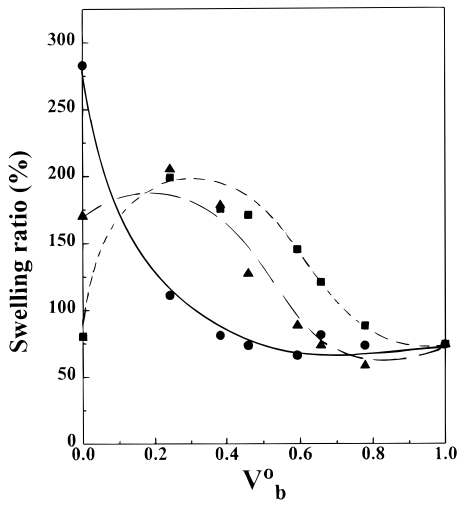

Figure 9. Swelling ratio of UADG5-5 gel in buffer/organic solvent mixtures vs the volume fraction of buffer solvent in solvent mixtures: (−■−) buffer/acetone; (−●−) buffer/DMSO; (−▲−) buffer/dioxane.

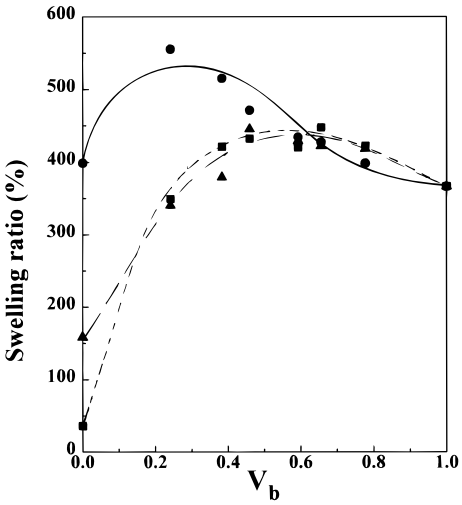

Figure 10. Swelling ratio of UAAG5-5 gel in buffer/organic solvent mixtures vs the volume fraction of the buffer solvent in solvent mixtures: (−■−) buffer/acetone; (−●−) buffer/DMSO; (−▲−) buffer/dioxane.

Swelling of UAA Networks in Organic Solvent/Water Mixtures. The swelling behavior of UADG5-5 and UAAG5-5 networks in mixtures of a polar solvent (dioxane, acetone, or DMSO) and pH 11 buffer solution as a function of solvent composition is shown in Figures 9 and 10, respectively. The swelling of the UADG networks in dioxane/buffer mixture still exhibits the convex maximum observed for the acetone/buffer mixture although the maximum is less accentuated (Figure 9). The results for the DMSO/buffer mixture are quite different as the swelling in DMSO dramatically decreases with the addition of water in the solvent mixtures and quickly levels off to its value for the pure buffer (Figure 9).

These results can again be interpreted qualitatively in term of the strength of the solvent−solvent interactions as embodied in the Kirkwood−Buff parameters G_{ij}. Whereas the changes of G_{ij} in water/acetone and water/dioxane mixture as a function of water concentration are quite similar, these changes are very different in water/DMSO mixtures.[39] Because the two hydrophilic methyl groups in DMSO reinforce the water structure, strong hydrogen-bonding formation between DMSO and water molecules occurs at intermediate concentrations.[40,41] This leads to more extensive water−DMSO coupling (increase in G_{12}) in contrast to the minimum in G_{12} observed in water−dioxane and water−acetone mixtures and a sharp decrease in the swelling ability of the mixture. The large swelling ability of pure DMSO as compared to dioxane and acetone can also be explained by the highly polar nature of the DMSO molecule (Table 2) and its ability to solvate the counterions ($(C_2H_5)_3NH^+$) of carboxylic acid segments in the networks. The unique solvent behavior of DMSO in ionomer solutions has been well documented.[26,42−44]

The swelling results for the UAAG networks in Figure 10 show a similar trend for DMSO mixtures as for dioxane and acetone mixtures. This similarity is in sharp contrast to the very different trend observed for DMSO mixtures in UADG. We postulate that this difference is again due to the microphase separated strongly hydrophilic ionic domains that have been captured in the cross-linking of UAAG networks. Here, the interactions between water and these hydrophilic domains are stronger than the water−DMSO interaction and lead to an increase in swelling as water is added to DMSO in the mixture. Above a certain water concentration in the bath, the swelling decreases as the strong DMSO−water interaction restricts the uptake of DMSO by the network.

Amphiphilic Biphasic Swelling Behavior of UAA Networks. We have considered above the swelling behavior of UAA networks in organic solvents and in organic solvent/water mixtures for solvents that are miscible with water. The UAA networks could also have applications in the removal of organic solvents that are immiscible or sparingly miscible in water. We report in this section the swelling of UAA networks in methylene chloride (MC) and in pH 11 buffer solution. MC is not miscible with water, but it dissolves the UAA precursor chains. Thus, we expect the UAA network to take-up pH 11 buffer solution in its hydrophilic domains and methylene chloride in the hydrophobic matrix. In Figure 11, we show the swelling results of various UADG networks as a function of the amount of dioxane in the preparation mixture of the network. Curve A reproduces the swelling ratio of UADG networks in buffer solution as a function of dioxane in the preparation mixture. When these networks swollen in buffer solution are placed in methylene chloride, they take up very large amounts of MC due to the hydrophobic UAA matrix. The results are represented by curve C. UADG networks swollen in neat MC yield the results presented by curve B.

The results for UAAG networks are shown in Figure 12. Curve A reproduces the large increase in pH 11 buffer solution as a function of the amount of water in the preparation of the network discussed earlier. In MC, the dry UAAG networks show practically constant swelling (Curve B). This can be explained by the fact that MC swells the hydrophobic matrix of the UAAG

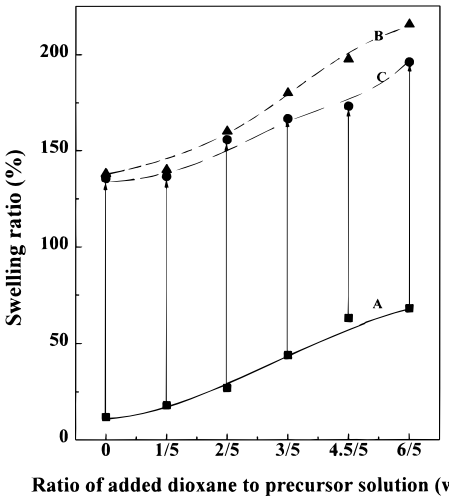

Figure 11. Swelling ratio of UADG networks in pH 11 buffer solution (curve A) and subsequently in methylene chloride (curve C) vs the amount of dioxane in the preparation of UADG networks. Curve B represents swelling in pure methylene chloride.

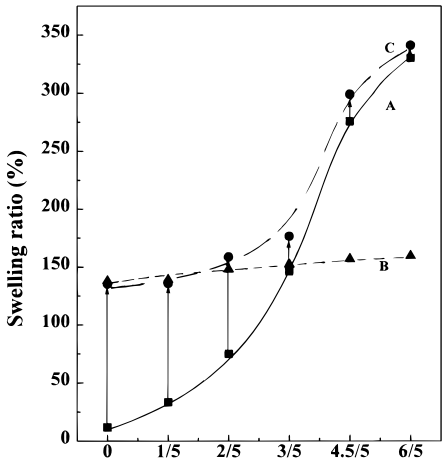

Figure 12. Swelling ratio of UAAG networks in pH 11 buffer solution (curve A) and subsequently in methylene chloride (curve C) vs the amount of water in the preparation of UAAG networks. Curve B represents swelling in pure methylene chloride.

networks, which remains essentially unmodified by the presence of water in the preparation of the networks. When the networks swollen in buffer solution are placed in MC, only those which have taken up small amounts of water because of their lower hydrophilicity (UAAG5-0 to UAAG5-2) are then able to take up substantial amount of MC. The others (UAAG5-3 to UAAG5-5) hardly take up any MC due to the osmotic pressure exerted by the highly swollen hydrophilic domains on the hydrophobic matrix. This pressure prevents the network from taking up any appreciable MC despite the favorable interaction of MC with the UAA polymer backbone.

Mechanical Property and Interaction Parameters of UAA Networks. It is well established that the aggregation of ionic groups into microdomains acting as physical cross-links gives rise to many of the unique properties of ionomers.[45−50] 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 were shown

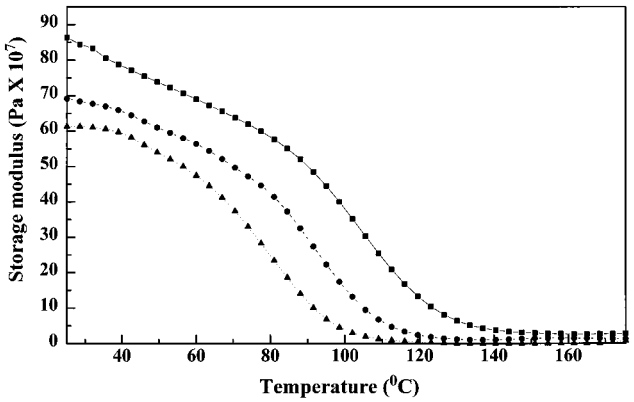

Figure 13. Storage modulus E' vs temperature curves measured at 1 Hz for UAA networks from different preparation conditions: (■) UAAG5-5; (●) UADG5-5; (▲) UADU5-5.

to increase with the increase in the ionic content of a sample in agreement with the expectation of an increase in ion clusters.

In this section, we report on the elastic modulus of several of the ionomer networks studied above using a Perkin-Elmer dynamic mechanical analyzer (DMA7e) in the extension mode. In Figure 13 we show the elongation modulus E' as a function of temperature for three networks: UAAG5-5, UADG5-5, and UADU5-5. All the networks were prepared in the same total amount of solvent. UAAG is prepared in water; UADG and UADU are prepared in dioxane. UAAG and UADG are prepared form the same UAA ionomer precursor whereas UADU is prepared from the un-neutralized carboxylic acid precursor chains (see Synthesis). The UAAG5-5 networks with the highest ion clustering due to the presence of water during its preparation has the highest modulus and the highest temperature transition to a rubbery plateau. This network, unlike the others, is quite brittle. We note that the un-neutralized network UADU has a fairly high room-temperature modulus due to extensive hydrogen bonding.[51−54] We noted earlier that DSC thermograms of these networks do not show a glass transition in the temperature range examined. This supports a one-phase morphology of the soft and hard segments of these UAA networks.

The higher modulus of UADG5-5 formed under identical conditions as the UADU network indicates some probable ion-clustering in these networks. Navratil and Eisenberg have reported[3] that un-neutralized carboxylic groups (−COOH) suppress ion clustering and decrease the role of ionic multiplets as effective cross-links. We tentatively conclude that the high modulus of the UADG5-5 networks at room temperature is due to a combination of hydrogen bonds, and ion clusters. The UADG5-0 networks prepared with no solvent other than the original 10% NMP in the UAA precursor solution exhibit a modulus (not shown) intermediate between the UAAG5-5 and the UADG5-5. The presence of dioxane in the network preparation of UADG5-5 decreases the modulus whereas the presence of water in the preparation of UAAG5-5 increases the modulus. Dioxane appears therefore to cause the dispersion of the backbone chains and possibly loosens ionic aggregates in the original UAA/NMP solution. Water, on the other hand, enhances ion-clustering and microphase domain formation.

To estimate the interaction between the different solvents used and the UAA backbone, we employ the

Table 3. χ_{12} Parameters of UADG5-0 and UADU5-0 Networks Swollen in Acetone, Dioxane, and DMSO

networks (M_c, g mol^{-1})	acetone	dioxane	DMSO
UADG5-0 (525)	0.63	0.44	0.15
UADU5-0 (610)	0.75	0.30	0.35

Flory−Rehner model with the swelling and mechanical measurements of the more homogeneous carboxylic (−COOH) based networks. We combine the value of the storage modulus E' at high temperature (~150 °C), which is past the H-bond transition of urethane linkages,[55−57] with the density ρ of the polymer to calculate an effective molecular weight (M_c) between cross-linking. We use[58]

$$M_c = 3\rho RT/E' \quad (3)$$

where R is the gas constant and T the absolute temperature.

The solvent−polymer interaction parameter χ_{12} can then be estimated using the Flory−Rehner expression for a phantom network,[59]

$$\chi_{12} = \{-[V_1/(2\nu_2 M_C)]\phi_2^{1/3} - \ln(1-\phi_2) - \phi_2\}/\phi_2^2 \quad (4)$$

where V_1 is the molar volume of the solvent and ϕ_2 is the volume fraction of polymer in the gel at swelling equilibrium. Also, ν_2 is the specific volume of the polymer.

An analysis using the above equations can only be applied to homogeneous networks as one can hope to obtain meaningful results only for such systems. Since the UAAG samples do not fall in this category, we are restricted to a comparison of the results from only a few samples. In Table 3, we compare the results for interaction parameters obtained using eqs 3 and 4 with the swelling results and modulus measurements of two networks: UADU5-0 and UADG5-0. The UADU5-0 networks allow calculations of interaction parameters for the un-neutralized carboxylic-group-based polymer minimizing any role of ion clustering.[56] The rubbery plateau modulus (E' at 150 °C) used in the calculations of χ_{12} appears to be the appropriate one to use assuming the internal hydrogen bonds of our networks are not effective cross-links and would break upon swelling. We can see from Table 3 that, under these assumptions, the values obtained for χ_{12} are reasonable. The solvent quality of acetone is better (lower χ_{12}) for UADG5-0 than for the neutral UADU5-0. This stems from the charges in UADG5-0 and the moderate dielectric constant of acetone. Dioxane and DMSO, with widely different dielectric constant, are comparable in solvent quality for the un-neutralized network. This shows the weak role the dielectric properties play in the swelling of the neutral network. On the other hand, for the ionomeric UADG5-0 network prepared in the absence of dioxane, DMSO with its high dielectric constant and strong ion-solvating power is by far the better solvent (lowest χ_{12}). Dioxane, with its low dielectric constant, is unable to solvate ion clusters which act as effective cross-links. Thus, dioxane appears as a poorer solvent (higher χ_{12}) than in the case with the un-neutralized UADU5-0.

The above results provide a qualitative explanation for the swelling behavior of UAAG and UADG networks in acetone, dioxane, and DMSO reported in Figure 2. This behavior exhibits the competing effects of the quality of the solvent toward the hydrophobic backbone

of the chains and the dielectric property of the solvent affecting the solvation of counterions of the side-chain carboxylic acid groups.

Conclusion

Amphiphilic ionomer networks have been synthesized from polyurethane acrylate anionomer precursors. The properties of these networks are very sensitive to the nature and amount of the solvent used during cross-linking. In the case of water as the solvent during network synthesis, the amount of water controls the degree of microphase separation present in the precursor chain dispersion before cross-linking. The equilibrium structures achieved in the dispersion are locked into the different network structures by an end-linking reaction. The degree of hydrophilic/hydrophobic balance in these networks, once dried, is then controlled by the degree of microphase separation that was present during their preparation.

The variety of network structures obtained by varying the nature of the solvent (water or dioxane) and its amount leads to very different swelling properties in buffer solutions, in pure organic solvents, and in mixed buffer/organic solvent mixtures. By tuning the preparation conditions, we show that these networks can be made to be both highly absorbent and fairly solvent selective, with potential application for separations.

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