

# Alcoholphilic Gels: Polymeric Organogels Composing Carboxylic and Sulfonic Acid Groups

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**ABSTRACT:** Polymeric organogels based on acrylic acid (AA) and sodium allyl sulfonate (SAS) were prepared through solution polymerization using a persulfate initiator and a polyethylene glycol diacrylate (PEGDA) cross-linker. FTIR spectroscopy, elemental, and rheological analyses were used for a preliminary characterization. Thermo-mechanical analysis was also carried out for characterizing samples. Glass transition temperature ( $T_g$ ) of copolymer was decreased after acid treatment which could be attributed to detachment of ion pairs during the post-treatment. Due to counterion binding of  $\text{Na}^+$  to form ionomer, the poly(AA-SAS) gels showed no polyelectrolyte behavior to have high swelling capacity in conventional alcohols, i.e., ethanol and methanol. It was postulated that modification via removing  $\text{Na}^+$  could help breaking ion pair aggregates which leads to swelling enhancement.

Thus, poly(AA-SAS) was treated with hydrochloric acid to remove ( $\text{Na}^+$ ) counterions. This modification led to the gel transform from ionomer regime to a polyelectrolyte regime in which free mobile ions were existed in the network. The gel swelling capacity was increased due to raise of mobile ions after the treatment. It was found that both of the acid concentration and treatment time had constructive influence on the gel alcoholphilicity. The acid-treated samples could imbibe ethanol and methanol as high as 25.8 and 39.5 g/g, respectively. They may be superior candidates for applications such as pharmaceuticals gels and fire starters. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 3350–3356, 2011

**Key words:** organogel; acrylic acid; sodium allyl sulfonate; alcohol absorbent; swelling

## INTRODUCTION

Gels can be classified into two main groups: hydrogels and organogels.<sup>1</sup> Organogels can be based on low molecular weight materials or polymeric materials.<sup>1</sup> Polymeric materials also can be divided into physical and chemical organogels.<sup>1</sup> Chemical polymeric organogels are three-dimensional polymeric networks which have ability to absorb and retain large amounts of organic solvents.<sup>1</sup>

There has been a considerable raise of interest during the last few years in synthesis and characterization of organogels.<sup>2,3</sup> Organogels can be used in controlled release of fragrance, drugs and antigens,<sup>2,4</sup> engineered fuels,<sup>2</sup> surfactant industries, military applications,<sup>5</sup> hand sanitizers, fire starters,<sup>6</sup> and enzyme immobilization.<sup>7</sup> Gelation of organic solvents reduces risk of their explosion or fire instigation.<sup>5</sup>

There are a lot of researches on organogels based on low molecular weight materials<sup>1</sup> but fewer studies has been carried out about chemical polymeric organogels. Sada prepared lipophilic gels based on tetra-alkylam-

mounium tetraphenylborate and octadecyl acrylate for absorbing nonpolar solvents such as  $\text{CCl}_4$ , dichloromethane, THF, chloroform and toluene. This superabsorbent gel had ability to absorb nonpolar solvents even more than 100 g/g in, for example, dichloromethane and THF, but it could not imbibe polar solvents such as methanol.<sup>8</sup> Zhao employed free radical solution polymerization using  $\gamma$  rays and cations ( $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Ni}^{2+}$ ) to prepare an acrylic acid (AA)-based organogel for absorbing ethanol.<sup>9</sup> These superabsorbents can considerably absorb ethanol up to 159 g/g.<sup>9</sup> Xie prepared gels of copolymer (2-acrylamido-2-methylpropane sulfonic acid (AMPS) and acrylamide (AM)) which could absorb ethanol and methanol as high as 24 and 32 g/g, respectively.<sup>10</sup> Yang reported the preparation of gels based on poly(*N*-isopropylacrylamide- $\text{NaAMPS}$ ) (97 : 3) which can absorb ethanol up to 70 g/g.<sup>11</sup> Ishihara prepared poly(2-methyl acryloxyethyl phosphorycholine) gels having high absorbency in ethanol.<sup>12</sup> Wudl synthesized cross-linked poly(ortho-carbonate) for absorbing solvents such as acetone and dichloroethane. The polymer possessed low ability for absorption (<3 g/g).

There are several articles on volume phase transition of polymers in different water/solvent mixtures to achieve polymeric organogels which have ability to

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absorb pure organic solvents, particularly alcohols.<sup>13</sup> It can be deduced by reviewing these articles that polymers with sulfonated groups in their structure are appropriate for alcohol absorbency. For instance, poly(styrene sulfonate),<sup>13</sup> poly(*N*-*t*-butylacrylamide-*co*-AMPS),<sup>14</sup> poly(*N*-isopropylacrylamide-*Na*AMPS)<sup>11</sup> and poly(AM-AMPS) have shown absorbency in ethanol or methanol.<sup>15</sup> In addition to the sulfonated monomers, AA and its copolymers have potential for alcohol absorbency, i.e., its copolymer with 16-acryloylhexadecanoic acid could absorb ethanol up to 10 g/g.<sup>16</sup>

As cross-linked poly(AA) itself (known typically under a commercial name of Carbopol), has potential means for alcohol absorbency; we have focused on the AA copolymers with sulfonic acid monomers. In our previous work, alcohol absorbent gels based on poly(AA-AMPS) were prepared.<sup>6</sup> The copolymer having 41 mol % AMPS content could imbibe methanol and ethanol up to 58 and 65 g/g, respectively. In this article, a chemical polymeric organogel were synthesized from AA and sodium allyl sulfonate (SAS). FTIR, DMTA and rheological methods were employed for the sample analysis.

## EXPERIMENTAL

### Materials

SAS (Asahi Chemical), polyethylene glycol diacrylate (PEGDA 400, Rahn) and ammonium persulfate (APS, Merck) were used as received. AA (Sasol) was distilled under reduced pressure before use.

### Synthesis

After SAS dissolution in distilled water, AA and PEGDA were added to it so that the total monomer concentration was 50 wt %. The mixture was heated at 60°C. APS (0.100 g in 2.0 mL H<sub>2</sub>O) was then added to the solution for initiating the polymerization. After the gel point (1–7 min, Table I), the obtained product was cut into small pieces, dried in a forced draft oven (100°C, 6 h) and ground by a mini-grinder to sugar-like particles (mesh 35–100, i.e., 150–430 μ).

For acid treatment, the product was immersed in 0.1–0.5M HCl for 1–5 h. Acid-treated product was washed thoroughly with water, dried (100°C, 4 h), and ground by a mini-grinder to sugar-like particles with size range of 150–430 μ (mesh 35–100). Two samples (i.e., S25 and S50) were prepared. After separation of the soluble fraction via exhaustive extraction with water (0.200 g sample, 300 mL distilled water, 72 h), the gel content was measured (Table I).

**TABLE I**  
The Gelation Time of the Polymerization Reactions Conducted for Preparing Cross-Linked Poly(AA-SAS) Products and the Gel Content of the Samples

Sample code <sup>a</sup>	PEGDA (mmol)	Gelation time (s)	Gel content (wt %)
A1	0.02	180	20
A2	0.04	120	25
A3	0.08	60	45
A4	0.11	60	50
A5	0.15	48	50
A6	0.20	30	60
B1	0.04	420	10
B2	0.05	450	25
B3	0.06	180	25
B4	0.08	150	30
B5	0.10	120	35

<sup>a</sup> The mole percentages of SAS in proportion to total monomer feed of the polymerization reaction for preparing sample series A and B was 25 and 50 mol %, respectively (For A series: 40 mmol SAS, 80 mmol AA; for B series: 46 mmol SAS, 46 mmol AA).

### Swelling measurements

A 0.100-g sample was dispersed in 50 mL of solvent and allowed to swell for 2 h to reach equilibrium swelling (maximum water uptake). Each dispersion was filtered through a polyester gauze to remove the excess solvent. Then, hydrated gels were weighted. Swelling capacity (g/g) was calculated by dividing the weight of swollen gel to the weight of dried gel.

### Instrumental analysis

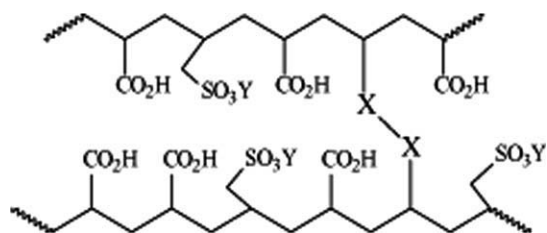
Fourier transform infrared (FTIR) spectra of dried samples as KBr tablets were recorded by an ABB-Bomem MB-100 FT-IR spectrophotometer. Elemental analysis was performed with a CHNOS elemental analyzer, Elementar VarioEL III. Rheological measurements of the water-swollen gels (0.500 g sample in 30.0 mL distilled water) were performed using a Paar-Physica oscillatory rheometer (MCR300, Germany) at 25°C with parallel plate geometry (plate diameter of 25 mm, gap of 3 mm). The detailed procedure was previously reported.<sup>17</sup>

Dynamic mechanical thermal analysis (DMTA) was performed employing a Polymer Laboratories (PL) instrument. The analyses of dried samples were carried out in the temperature range of 80–160°C, heating rate 20°C/min and frequency 1 Hz.

## RESULTS AND DISCUSSION

### The gel preparation and brief characterization

In the present work, solution copolymerization of AA and SAS was carried out in water using a



**Scheme 1** General structure of the alcoholophilic gels. The symbol X-X stands for the poly(ethyleneglycol) crosslink between the polymer chains. X-X:  $\text{COO}(\text{CH}_2\text{CH}_2\text{O})_n\text{CO}$ , Y: H, Na.

persulfate initiation. The copolymer structure is shown in Scheme 1.

A water-soluble macromolecular crosslinking agent, polyethylene glycol diacrylate (PEGDA 400), was used to prepare two series of lightly crosslinked poly(AA-SAS) gels differed from the amounts of SAS and the crosslinker (Table I). The gelation time and gel content of the samples are given in Table I. Elemental analysis-based values of the sulfonated monomer content in the copolymer structure of typical samples A2 and B2 were measured to be 11 and 33 mol %, respectively. It means that the reactivity of SAS toward free radical copolymerization is much lower than that of AA. The gelation time was increased with AA content increase. This may be attributed preliminarily to higher reactivity of AA rather than SAS in the copolymerization system. This was reconfirmed by gel content measurement (Table I). For series B the gel content was much lower than that for the series A (10–35 wt % versus 20–60 wt %).

Two representative samples (i.e., A2 and B1) having equal amount of the initial crosslinker PEGDA were post-treated with hydrochloric acid under different concentration of the acid (Table II) and treatment time (Table III). Alcohol absorption capacity of the acid treated samples was also investigated.

Meanwhile, a preliminary rheological measurement of the acid treated A2 and B1 showed that the storage modulus of the water-swollen sample B1 (the sample

**TABLE II**  
Effect of the Time of Acid Treatment on Alcohol Absorption Capacity of Typical Samples A2 and B1

Time of acid treatment (h)	Alcohol absorbency (g/g) of sample A2		Alcohol absorbency (g/g) of sample B1	
	Ethanol	Methanol	Ethanol	Methanol
0	6.3	11.5	4.5	10.5
2	8.8	21.8	10.8	17.9
3	29.6	30.8	13.2	36.1
5	27.4	29.5	12.3	32.0
24	28.1	33.7	16.5	39.1
48	25.8	35.2	21.1	39.5

[HCl] 0.10 mol/L. See Table 1 for the sample code.

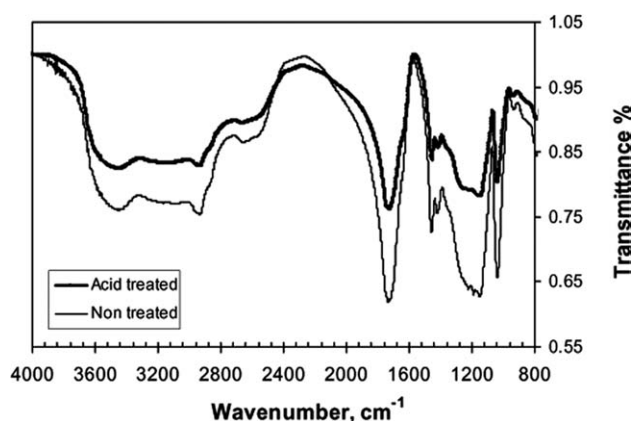
**TABLE III**  
Effect of the Hydrochloric Acid Concentration (Treatment Time 2 h) on Alcohol Absorption Capacity of the Acid-Treated Samples A2 and B1

[HCl] (mol/L)	Alcohol absorbency (g/g) of the acid-treated sample A2		Alcohol absorbency (g/g) of the acid-treated sample B1	
	Ethanol	Methanol	Ethanol	Methanol
0.10	8.8	21.8	10.8	17.9
0.30	22.1	24.9	18.0	21.1
0.50	25.9	27.5	19.2	23.4

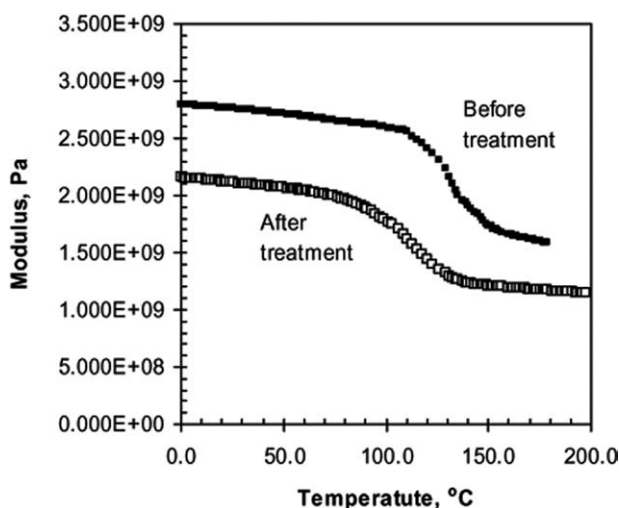
See Table 1 for the sample code.

with higher content of the initial sulfonated monomer, SAS) was much lower than that of acid treated sample A2 measured under the same conditions. For instance, as recorded at angular frequency  $40 \text{ s}^{-1}$ , the acid-treated B1 and the acid-treated A2 exhibited modulus values of  $\sim 500$  and  $\sim 3000$  Pa, respectively. Since the modulus is inversely proportional to the average molecular weight between crosslinks,  $M_c$ ,<sup>18</sup> it implies that SAS monomer possesses lower reactivity in comparison with AA in their competitive reaction with the crosslinker. This is in agreement with the above-mentioned conclusion resulted from the elemental analysis-based copolymer composition determination, gelation time and gel content. As a result, when higher quantity of SAS was charged (samples of series B), the crosslink densities of samples will be lower. Therefore, the swollen gels of series B will be mechanically softer than those of their counterparts of series A.

Representative gel samples were also characterized preliminarily by infrared spectroscopy. Figure 1 shows assignments for poly(AA-SAS) before and after acid treatment. There are some peaks to proof copolymerization of AA with SAS, i.e., C–S stretching at  $607\text{--}608 \text{ cm}^{-1}$  or O=S=O symmetrical stretching appeared at  $1147\text{--}1154 \text{ cm}^{-1}$ .



**Figure 1** Representative FTIR spectra for a poly(AA-SAS) gel, sample B1 (AA:SAS mole ratio of 1 : 1), before and after acid treatment.



**Figure 2** Storage modulus from DMTA analysis for a typical sample, A2, before and after acid treatment.

Acid treatment caused a little shift of O=S=O stretching from 1151 to 1147 for  $\text{cm}^{-1}$  as representatively shown for sample B2. It was attributed to different ionic interactions in  $\text{SO}_3^- \text{Na}^+$  and  $\text{SO}_3^- \text{H}^+$ . Increase degree of neutralization (DN) increased formation of clusters and multiplets.<sup>19,20</sup> These multiplets can act as ionic crosslinks in the polymer structure. There are few carboxylate groups at low degrees of neutralization, ion pairs can be increased with increase of DN causing formation of multiplets and clusters.<sup>20</sup> The wave number of absorption peak is related to force constant of the bond that is increased with enhancing additional ionic crosslinks.<sup>20</sup> Monerio observed that C=O symmetrical stretching was increased with enhancing DN for poly(methyl methacrylate-methacrylic acid).<sup>19</sup> Therefore, shifting O=S=O peak to lower wave number in acidic treated poly(AA-SAS) can be attributed to reduction of clusters and multiplets in the polymer network.

### Thermomechanical analysis

Figure 2 shows DMTA thermogram of sample A2 before and after acidic treatment. The acid-treated sample has distinctive differences with the non-treated one. Modulus was considerably decreased after acid treatment which indicated reduction of crosslink density after treatment.<sup>21</sup> For instance, modulus at 50°C was decreased from  $2.55 \times 10^9$  to  $2.065 \times 10^9$  Pa after acid treatment. Based on eq. (1), modulus ( $G'$ ) has direct relationship with crosslink density ( $\nu_c$ ).<sup>22</sup>

$$G' = \nu_c RT \quad (1)$$

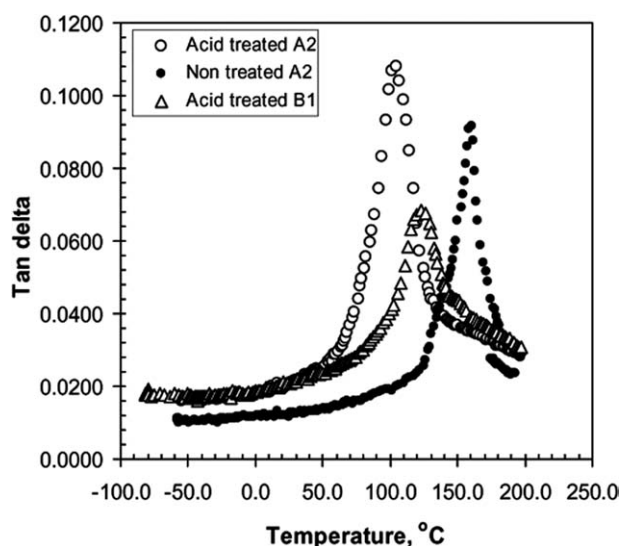
According to the Khokhlov group,<sup>23</sup> some multiplets may be formed through aggregation of the ion

pairs in the ion-containing polymers. These multiplets could act as crosslink points which enhance the crosslink density. Higher density of crosslinking ( $\nu_c$ ) leads to improved  $G'$ . When the multiplets are destroyed through removing  $\text{Na}^+$  from the gel by means of acid treatment, the crosslink density is decreased and results in a diminution of modulus.

Figure 3 shows variation of  $\text{Tan } \delta$  versus temperature for sample A2. The glass transition temperature ( $T_g$ ) was recorded to be 160.2 and 104.3°C for the nontreated and acid-treated A2 samples, respectively. The result showed that acid treatment had considerable influence on gel structure which leads to a significant loss of  $T_{g'}$  i.e.,  $\sim 56^\circ\text{C}$ . It is known that several factors have influence on  $T_g$  of polymer networks. Main chain rigidity and crosslink density are the most important factors.<sup>24</sup> Multiplet formation due via aggregation of ionomers causes a crosslink density enhancement. Increase of the crosslink density restricts chain movements leading to increased  $T_g$ .<sup>25</sup>

The value of  $\text{Tan } \delta$  is a sensitive indicator of crosslinking. Above  $T_g$  damping decreases with increasing degree of crosslinking.<sup>26</sup> Chain motions are highly restricted with increase of crosslink density and lead to diminution of the relaxation intensity.<sup>24</sup> Crosslink density of poly(AA-SAS) was decreased through destroying multiplets during exchange reaction which caused to increase chain movements.<sup>24</sup> Therefore chains could dissipate energy easier which caused to increase  $\text{Tan } \delta$ .

Figure 3 also shows  $\text{Tan } \delta$  for after-treated sample B1. As mentioned in the experimental section, the sulfonated monomer content in the copolymer structure of samples A and B series were measured to be  $\sim 10$  and  $\sim 30$  mol %, respectively. Here, as



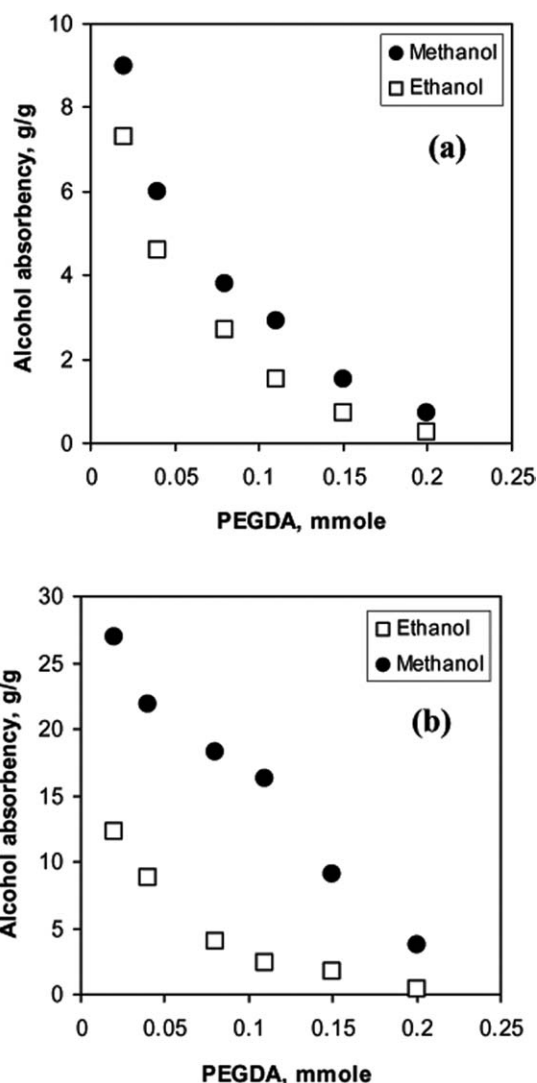
**Figure 3**  $\text{Tan } \delta$  from DMTA analysis of nontreated and acid-treated sample A2. The third curve (symbol triangle) is due to the acid treated sample B1.

observed for the acid-treated A2 and B1, it is obvious that higher sulfonated monomer increases  $T_g$  and decreases  $\tan \delta$ . This can be ascribed to increase chain rigidity with increase of sulfonated monomer.<sup>25</sup> Sulfonate groups can increase chain rigidity rather than the carboxylic acid groups. This may be attributed to stronger inter- and intra-molecular interaction between sulfonic acid groups rather than carboxylic acid groups. Decreasing or removing multiplets is another factor which causes to observe higher  $\tan \delta$ , decreased elastic properties, with decrease of sulfonated monomer.

### Swelling studies

Two series of poly(AA-SAS) gels were synthesized using different crosslinker amounts (Table I). Surprisingly, swelling capacity was very low in ethanol and methanol. Figure 4 shows alcohol absorbency of the sample series A in ethanol and methanol. The alcohol absorbency of was less than 10 g/g before acid treatment [Fig. 4(a)]. Similar behavior was observed for the nontreated sample series B (not shown). We had previously observed that poly(AA-AMPS) had considerable alcohol absorbency up to 65 g/g<sup>5</sup> and the swelling capacity was changed directly with AMPS content. Here, SAS, not only could not improve the alcohol absorbency, but also got worse the absorption capacity in comparison with pure poly(AA) having ethanol absorbency of 27 g/g.<sup>5</sup>

SAS is an ionic monomer which can easily dissociate in swelling media to produce mobile ions. Mobile ions create an osmotic pressure difference between gel phase and solvent phase which lead to swelling enhancement. This behavior has been known as polyelectrolyte effect.<sup>27</sup> SAS is a sodium salt of allyl sulfonic acid which belongs to the family of strong electrolytes. It was expected that SAS units in poly(AA-SAS) gel could be easily dissociated in polar solvents such as ethanol and methanol which causes to swelling enhancement. The abnormal low swelling capacity of poly(AA-SAS) can be attributed to ion pair and multiplet formation.<sup>23</sup> Philippova et al. investigated effect of ionization degree on swelling properties of poly(methacrylic acid), poly(MAA), gels in methanol/water mixtures. They observed two distinctive behavior for the swelling of poly(MAA) gels. Swelling capacity was increased with increase of the polyacid dissociation degree ( $\alpha$ ) in the methanol/water mixture with up to 65% methanol. At higher methanol content, a second swelling region was observed. At first, swelling capacity was increased with rising  $\alpha$  then a gel collapse was observed. The second behavior was named as the ionomer behavior.<sup>23</sup> This behavior was ascribed to the binding of dissociating cations to car-



**Figure 4** Alcohol absorbency versus crosslinker dosage for the series A of (a) nontreated and (b) acid-treated poly(AA-SAS) samples with a AA:SAS mole ratio of 3 : 1 (see Table I).

boxylate groups in polymer chain to form ion pair species. Only mobile counter ions can create osmotic pressure difference between the gel and solvent phase.<sup>28,29</sup> Omitting the polyelectrolyte effect caused the considerable loss of swelling. The second reason involved in the swelling reduction is aggregation of ion pairs with formation of multiplets due to dipole-dipole attraction.<sup>28,29</sup> Ion pair formation is energetically favored with increased ionization degree of gel. Polymer chains undergo a conformational transition to compact form in the collapsed state.<sup>30</sup>

Ion pairs can join to form multiplets which can act as a crosslink point. In another word, crosslink density in gel phase was increased due to aggregation of ionomers results in swelling reduction.<sup>27</sup>

The counterion binding ( $\theta$ ) based on Osawa-Manning theory is written as follows:<sup>31</sup>

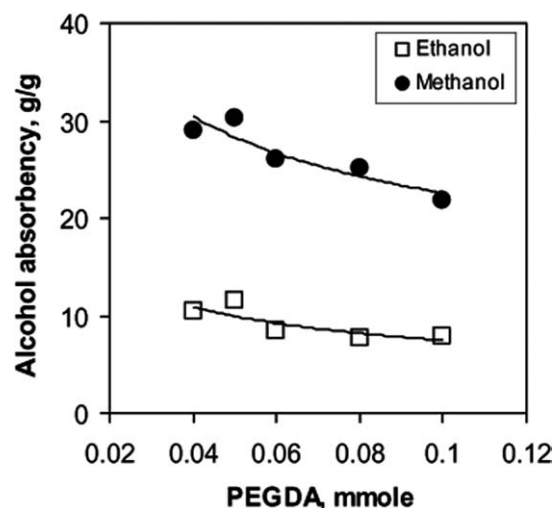
$$\theta = 1 - DkTb/e^2 \quad (2)$$

where  $e$  is the electrical charge,  $D$  is the dielectric constant of solvent, and  $b$  is the charge spacing. It is observed that counterion binding is increased with  $D$  reduction or charge density enhancement.<sup>31</sup>

These essential requirements for counterion binding were existed for our poly(AA-SAS) gels. They had charge density due to former neutralization of SAS and dielectric constant of alcohols ( $D$ : 32.6 and 24.6 for methanol and ethanol, respectively) were considerable less than that of water ( $D$ : 78.3). Swelling capacity of poly(AA-SAS) in distilled water was 60.4 g/g. This significant ability shows polyelectrolyte behavior of gel in water. SAS units could be easily dissociated in water causing an osmotic pressure difference between solvent and gel phase. As a result, the gel can swell in good solvents such as water. Probability of formation of counterion binding was considerably enhanced with reducing dielectric constant from water to ethanol or methanol based on eq. (2).

As our goal was preparation of alcohol absorbent gels, therefore, we had to find a way to lower the tendency of the sodium sulfonate regions to form ionomers (counterion binding). As a result, poly(AA-SAS) samples were treated with acid solution to replace counterion  $\text{Na}^+$  with  $\text{H}^+$ . Zhai was made similar procedure to convert poly(sodium styrene sulfonate) to poly(styrene sulfonic acid).<sup>32</sup> Figure 4(b) shows absorbency in ethanol and methanol versus crosslinker concentration for the acid treated samples A. After the acid treatment, the gel maximum swelling in ethanol and methanol was considerably increased to 10.4 and 27 g/g, respectively. Due to lower dielectric constant of ethanol rather than methanol, higher tendency to counterion binding in ethanol caused to from additional ionic crosslink leading to a decreased swelling.<sup>28</sup>

This preliminary result showed that acid treatment was effective to increase alcohol absorbency. Therefore, effect of two possible parameters on swelling properties (i.e., the acid treatment time and concentration) was investigated. Table II gives the effect of the time of acid treatment on the alcohol absorbency. It was measured to be 6.3 and 11.5 g/g nontreated for the nontreated sample A2 swollen in ethanol and methanol, respectively. After acidic treatment for 2 h, it was increased to 18.5 and 22.4 g/g in ethanol and methanol. Longer treatment time resulted in the alcohol absorbency enhancement. These experiments practically implied that the overall replacement of  $\text{Na}^+$  with  $\text{H}^+$  occurred gradually. Although this reaction instantly carried out in the solution phase or gel surface, however diffusion of acid molecules in to the gel bulk is a time consum-



**Figure 5** Alcohol absorbency versus crosslinker quantity for series B of acid-treated poly(AA-SAS) samples (see Table I).

ing process. As a result, possibility of the exchange reaction was increased with enhancing the treatment time. Afterward, the collapse tendency of the gel was converted to swelling enhancement.

Table III shows effect of acid concentration on alcohol absorbency. Increase of the acid molarity had considerable influence on the alcohol absorbency increasing. For example, after 2 h of acid treatment, swelling capacity was increased from 8.8 to 22.1 g/g in ethanol with increase of  $[\text{HCl}]$  from 0.10 to 0.30 mol/L. In more acidic reaction media, further diffusion of acid molecules into the gel bulk improves the exchange reaction of  $\text{Na}^+$  with  $\text{H}^+$ . In the alcohol swelling media, decreased density of counterion  $\text{Na}^+$  favors a polyelectrolyte rather than an ionomer regime.

Figure 5 shows alcohol absorbency versus crosslinker concentration for the acid treated samples B having a AA:SAS mole ratio of 1 : 1. Alcohol absorbency was higher in both ethanol and methanol in comparison with the copolymers with lower content of the sulfonated monomer [Fig. 4(b)]. For instance, methanol absorbency for acid treated samples prepared using a fixed amount of crosslinker (e.g., 0.05 mmol) was measured to be 21.8 g/g (for the sample with initial AA:SAS mole ratio of 3 : 1) and 30.3 g/g (for the sample with initial AA:SAS mole ratio of 1 : 1).

Poly(AA) itself can absorb alcohol due to hydrogen bond formation between carboxylate group and alcoholic hydroxyl group.<sup>27</sup> Dissociation of poly(AA) can not be occurred in alcohol because its essential characteristic is belong to weak polyelectrolytes.<sup>23</sup> In our work, upon acid treatment, poly(AA-SAS) is converted to poly(AA-SAS-ASA) in which ASA is allyl sulfonic acid. As explained above, extent of transformation of SAS to ASA depends on the acid

concentration and treatment time. Ionic dissociation can be occurred in polar protic or aprotic solvents such as dimethylformamide, dimethylsulfoxide, or alcohols with  $D$  ranged 20–50.<sup>33</sup> Poly(ASA) can be dissociated in polar swelling media such as ethanol and methanol to produce  $H^+$  because sulfonic acid group belongs to strong polyelectrolyte family. On the other hand,  $D$  values of the swelling media are sufficiently high (i.e., 24–33) to favor highly swelling behavior of the gels.

### CONCLUSION

Lightly cross-linked polymeric organogels composing AA and SAS were prepared characterized and modified via acid treatment. Limitation of the gel swelling in alcohols was attributed to some multiplets formed through ionomer aggregations ( $SO_3^-Na^+$ ). The gels exhibited high alcohol absorbency after the acid treatment through removing of  $Na^+$  cations from the network. It was found that both of the acid concentration and the treatment time had positive influence on improvement of alcoholophilicity. The higher the exchange of  $Na^+$  with  $H^+$ , the higher the alcohol absorbency will be. These organogels could absorb ethanol and methanol as high as 29 and 36 g/g, respectively. They can be good candidates for using in applications such as pharmaceuticals gels and fire starters.

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