

Poly(acrylic acid–sodium styrene sulfonate) Organogels: Preparation, Characterization, and Alcohol Superabsorbency

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ABSTRACT: Polymeric organogels based on acrylic acid and sodium styrene sulfonate (SSS) were synthesized and characterized by Fourier transform infrared spectroscopy, thermogravimetric analysis, dynamic mechanical thermal analysis (DMTA), and rheometrical analyses. The organogels exhibited medium alcohol absorbency because of counterion binding that formed in solvents with low dielectric constants. After acid treatment, the possibility of counterion binding was decreased, and the organogels achieved superabsorbency in alcohols, for example, about 80 and 50 g/g in methanol and ethanol, respectively. The superabsorbency was also measured in higher alcohols (i.e., *n*-propanol and isopropyl alcohol) and polyols (i.e., ethylene glycol, propylene glycol, 1,3-propanediol, and glycerol). The dielectric constant, viscosity, and structural features of the alcohols were investigated as important

parameters determining the alcohol superabsorbency. DMTA of dried samples showed two glass-transition temperatures (T_g 's), that is, the matrix T_g and the complex T_g , which increased with increasing SSS content. The $\tan \delta$ peak intensity increased after the acid treatment. With increasing SSS, the storage modulus of the dried gel increased; whereas that of the rheometrically measured hydrated gel decreased. $\tan \delta$ decreased with increasing SSS because of enhanced counterion binding. These alcohol-specific superabsorbing organogels are suggested as excellent candidates for the manufacture of products with high alcohol contents, such as hand sanitizers and fuel gels. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 2759–2769, 2011

Key words: gels; ionomers; swelling; synthesis

INTRODUCTION

Gels can be classified in two main groups: hydrogels and organogels.¹ Organogels can be based on low-molecular-weight materials such as 12-hydroxystearic acid² or polymeric materials. Polymeric organogels themselves are divided into two groups: physical and chemical organogels.¹ Intermolecular interactions, such as Van der Waals forces, hydrogen bonding, and electrostatic interactions, are the main forces that are involved in physical gelation.¹ Physical gelation is a thermoreversible process in which a phase transition from solid to liquid happens by heating. Heat obstructs solvent–polymer interactions, for example, hydrogen bonding.³ Chemical polymeric organogels may be composed of a linear or crosslinked structure, which can dissolve or swell in organic solvents, respectively. Crosslinked polymeric organogels can absorb organic solvents through a diffusion mechanism.

Organogels can be used in different areas, such as in the controlled release of drugs,¹ fragrances, and the surfactant industry.⁴ Alcohol-absorbent gels can be used as fuel gels, particularly in outdoor applications for warming, cooking, and boiling water. They can be used as fire starters⁵ or hand sanitizers. The latter is used for hand washing without water, which is so helpful in the prevention of diseases that can be transferred through contact with contaminated objects.

Conventional industrial crosslinked superabsorbent hydrogels, such as poly(sodium acrylate) or poly(acrylamide–potassium acrylate), are typically collapsed in organic solvents. Carbopols or carbomers are crosslinked poly(acrylic acid)s (PAAs) with ability to absorb organic solvents such as alcohols.

Recently, the preparation of polymeric organogels has attracted a lot of interest.^{6,7} There is growing attention to the preparation of novel polymeric networks with different chemical structures with the ability to absorb huge amounts of organic solvents. Sada et al.⁶ prepared copolymeric gels based on octadecylacrylate and an anionic comonomer for the absorption of nonpolar solvents. The gel could absorb nonpolar solvents, such as toluene and

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carbon tetrachloride.⁶ Zhao and Liu⁷ synthesized organogels based on crosslinked PAA using zinc or nickel oxide. The product had a high ethanol absorbency, up to 159 g/g. Sonmez and Wudl⁸ prepared crosslinked polyorthocarbonates that had low absorbency in solvents such as dichloroethane and tetrahydrofuran.

As *carbopols* (well-known commercial crosslinked PAA polymers) show the ability of alcohol absorption, we previously worked on a copolymeric alcohol absorbent based on acrylic acid (AA) and 2-acrylamido-2-methyl propane sulfonic acid (AMPS) prepared from solution polymerization with a macro-crosslinker.⁵ We found that the ionic monomer AMPS had a significant influence on the alcohol absorbency enhancement because of its high dissociation ability.⁵ What would happen to the swelling characteristics of the copolymeric organogel if just AMPS were replaced with a totally different sulfonated monomer, that is, sodium styrene sulfonate (SSS)?

This article is an attempt to find the answer. Thus, under similar conditions, poly(acrylic acid–sodium styrene sulfonate) [poly(AA–SSS)] networks were synthesized to be evaluated as alcohol-absorbing gels. The obtained organogels were also characterized through Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA), dynamic mechanical thermal analysis (DMTA), and rheology.

EXPERIMENTAL

Materials

SSS (Aldrich), poly(ethylene glycol) diacrylate (PEGDA 400; Rahn, Switzerland), and ammonium persulfate (APS; Merck) were used as received. AA (Sasol, South Africa) was distilled under reduced pressure before use. All alcohols, including ethanol, methanol, *n*-propanol, isopropyl alcohol, ethylene glycol, propylene glycol, 1,3-propanediol, and glycerol, were purchased from Merck.

Synthesis

Solution polymerization with the thermally induced initiator APS was used for the gel synthesis. After the dissolution of SSS (25–100 mol %) in water, AA and then PEGDA (molar fraction = 0.0125 in proportion to the total monomer) were added to the solution. The mixture was heated at 60°C. APS (0.100 g in 2.0 mL of H₂O) was then added to the solution to initiate the polymerization. After the gel point (8–17 min), the obtained product was cut into small pieces and dried at 100°C for 6 h in a forced-draft oven and ground by a minigrinder to sugarlike particles (mesh = 35–100, i.e., 150–430 μm). Four samples (encoded as S25, S50, S75, and S100) were pre-

TABLE I
Gel Content and Elemental-Analysis-Based Copolymer Composition of Poly(AA–SSS) Gel Samples

Sample code	Gel content (wt %)	Molar percentage of sulfonated monomer in the	
		Feed	Copolymer
S25	74.5	23.7	21
S50	75.5	48.7	40
S75	77.5	73.7	60
S100	73.0	98.7	98

pared. After the separation of the soluble fraction via exhaustive extraction with water (0.200 g of sample, 300 mL of distilled water, 72 h), the gel content was measured (Table I).

For the posttreatment, the dried sample was immersed in a hydrochloric acid (HCl) solution (0.5 M HCl) for 48 h. The acid-treated product was thoroughly washed with water and dried at 100°C for 4 h. The copolymer composition of the acid-treated samples was determined by elemental analysis (Table I).

Swelling measurements

A 0.100-g portion of dried sample was dispersed in 50 mL of the desired solvent and allowed to swell for 1 h to reach equilibrium swelling (the maximum absorbency) at room temperature (25–27°C). Each dispersion was filtered through polyester gauze to remove the excess solvent. Then, the hydrated gels were weighed. The swelling capacity (g/g) was calculated by division of the weight of the swollen gel by the weight of the dried gel.

Elemental analysis

Elemental analysis was performed with a CHNOS elemental analyzer (Elementar VarioEL III, Analysensysteme, Hanau, Germany).

FTIR spectroscopy

FTIR spectra of the dried samples as KBr tablets were recorded by an ABB-Bomem MB-100 FTIR spectrophotometer (Germany).

X-ray fluorescence (XRF) spectroscopy

A XRF instrument model Xepos, Spectro Co. (Germany) was used for the measurements. A dried sample (4.0 g) was mixed with 0.9 g of boric acid powder. The mixture was then compacted into standard discs for XRF analysis. The sodium content was measured with XRF for the copolymers before and after the acid treatment.

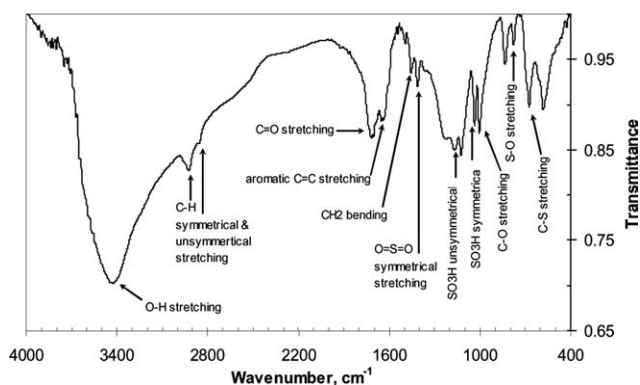


Figure 1 Representative FTIR spectra for the acid-treated poly(AA-SSS) gel as a typical sample with an AA:SSS molar ratio of 1 : 1.

DMTA

DMTA of the powdery sample was performed with a Polymer Laboratories instrument (England). The experiments were carried out in the temperature range 80–160°C at a heating rate of 10°C/min and a frequency of 1 Hz.

TGA

TGA of the dried samples were performed with a TGA Polymer Laboratories England instrument under a nitrogen atmosphere at a heating rate of 10°C/min.

Rheometry

The rheological measurements of the water-swollen gels (0.500 g of sample in 30.0 mL of distilled water) were performed with a Paar-Physica oscillatory rheometer (MCR300, Ostfildern, Germany) at 25°C with parallel-plate geometry (plate diameter = 25 mm, gap = 3 mm). The detailed procedure was reported previously.⁹

RESULTS AND DISCUSSION

Spectral characterization

Representative FTIR spectra for the acid-treated poly(AA-SSS), composed of 50 mol % SSS, are given in Figure 1.

The peak of S—O stretching (at $\sim 773\text{ cm}^{-1}$) or O=S=O symmetrical stretching (at $\sim 1411\text{ cm}^{-1}$) and the strong peak of the C=O stretching vibration at about 1710 cm^{-1} ¹⁰ verified that the copolymerization of AA with SSS was carried out successfully. The strong peak appearing at about 1630 cm^{-1} due to aromatic C=C stretching vibrations reconfirmed the copolymer structure. Similar peak assignments were reported for a blend of PAA and poly(sodium styrene sulfonate) (PSSS) homopolymers.¹¹ The other

infrared spectral band assignments are given in Figure 1. The FTIR spectra of all of the samples, except the homopolymeric samples, generally showed analogous peaks at similar wave numbers.

Thermal characterization

Figure 2 shows typical TGA thermograms of the dried organogels before and after the acid treatment.

The initial weight loss (IWL; the temperature at which the first major weight loss occurred) was attributed to the environmental moisture absorbed by the sample. The trend of these values was in agreement with that observed in the water-swelling capacities discussed in the Superswelling Properties section later. Therefore, similar causes were involved, as discussed in the previous section, to differentiate the hygroscopic characteristics of the samples.

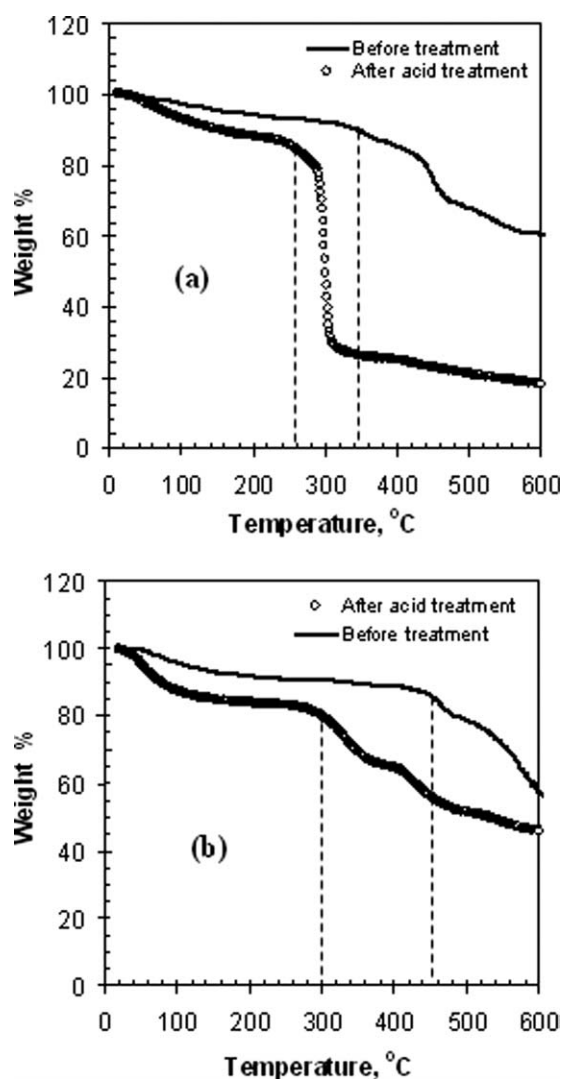


Figure 2 TGA thermograms for the poly(AA-SSS) before and after acid treatment of the sample with (a) 50 and (b) 100 mol % sulfonated comonomer.

TABLE II
Characteristic TGA Data for the Nontreated and Acid-Treated Poly(AA-SSS) Gel Samples

Sample	Posttreatment	IWL (wt %) ^a	IDT (°C)	AWL (wt %) ^b	Char yield at 600°C
S25	Nontreated	2.7	382.0	NO	33.0
	Acid-treated	1.4	221.8	28	27.5
S50	Nontreated	2.4	345.0	NO	60.6
	Acid-treated	6.8	260.0	50	18.0
S75	Nontreated	3.4	434.0	NO	67.6
	Acid-treated	7.1	282.2	73	49.3
S100	Nontreated	4.2	450.0	NO	59.3
	Acid-treated	12.6	300.0	NO	46.0

NO = no AWL was detected.

^a At 100°C.

^b AWL occurred around 300°C.

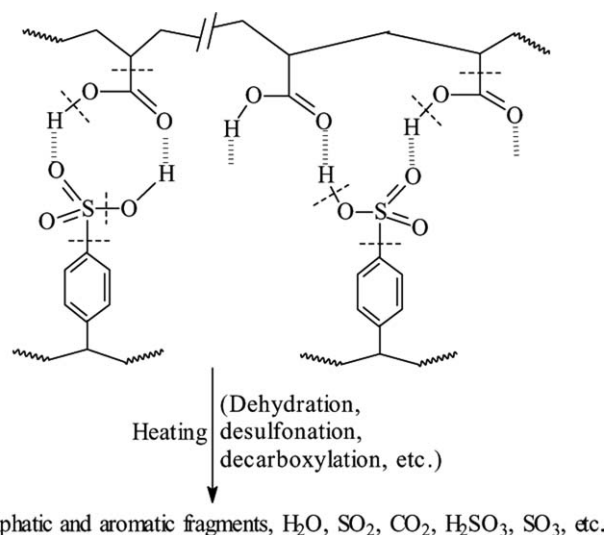
The acid treatment had an enormous effect on the thermal stability of the copolymeric network (Fig. 2). Before the posttreatment, the initial decomposition temperatures (IDTs) for poly(AA-SSS) samples with 50 and 100 mol % SSS were recorded to be 345 and 450°C, respectively. It is well known that the presence of aromatic groups in a polymer structure increases the thermal stability excessively. As a result, the higher the sulfonated monomer content is, the higher the thermal stability will be. Here, the incorporation of higher amounts of styrene sulfonic acid into the networks improved their thermal stability, as reflected in the IDT values given in Table II. The TGA data, particularly IDT and the char yield, obviously confirmed that the acid treatment did not favor the thermal stability of all of the samples.

PSSS after the acid treatment was converted to poly(styrene sulfonic acid) (PSSA). The first weight loss at 20–120°C was related to moisture removal, and the second weight loss at 280–360°C may have been due to the loss of sulfonic acid groups by desulfonation.¹² Shukla et al.¹² reported that the desulfonation of a 3 : 1 blend of poly(vinyl alcohol) and PSSA occurred at 180–420°C. For a 3 : 1 copolymeric counterpart, the transition observed between 250 and 420°C was attributed to decarboxylation and desulfonation.¹² During the thermal degradation of PSSA, small molecules, such as water, sulfur dioxide, ethylene, and carbon disulfide, were reported to be formed and released.¹³

In contrast to the SO₃Na group, SO₃H makes the polymer thermally vulnerable. The reason may be attributed to the easy formation and action of some small molecules produced upon thermal degradation around 300°C. In the initial stages of degradation, –SO₃H and –SO₃Na groups produce sodium sulfonate or sulfonic acid radicals, respectively. These radicals undergo a hydrogen abstraction reaction with the polymer chains to form NaHSO₃ or H₂SO₃, respectively. In this study, in the acid-treated samples, the acidic molecule (H₂SO₃) catalyzed thermal

degradation, which led to a remarkable decrease in the thermostability of, for example, PSSA, in comparison with PSSS [Fig. 2(b)].

In the TGA thermograms of the acid-treated copolymeric samples, a very characteristic weight loss was observed around 300°C [Fig. 2(a)]. A very intensive decomposition, a so-called abrupt weight loss (AWL), was detected neither in S100 nor in the PAA homopolymers. In fact, an AWL occurred only in the AA containing copolymers after the acid treatment, that is, in the acid-treated poly(AA-SSS) copolymeric samples. This may have been related to a concerted mechanism of degradation of some complexes formed between the carboxylic acid and sulfonic acid groups (Scheme 1). M'Bareck et al.¹¹ proposed similar interactions in PAA/PSSS physical blends studied by FTIR and DSC analyses. Thermogravimetry–mass spectroscopy was used by Yin et al.¹⁴ to investigate the thermal degradation of



Scheme 1 Assumptive COOH–SO₃H complexes in the acid-treated poly(AA-SSS) preliminarily suggested for its thermodegradation mechanism. The dashed lines stand for the concerted disconnections of bonds to release small gaseous species (e.g., H₂O, SO₂, CO₂).

TABLE III
Structural Features and Physical Constants of the Alcohols Used as the Swelling Media in This Study

Solvent	Structure	OH:C ratio	Viscosity (mPa s)	ϵ	Absorbency (g/g) of the acid-treated sample with an AA:SSS ratio of	
					3 : 1	1 : 3
Methanol	$\begin{array}{c} \text{CH}_3 \\ \\ \text{OH} \end{array}$	1	0.54	33	43.3	75.3
Ethanol	$\begin{array}{c} \text{CH}_2\text{-CH}_3 \\ \\ \text{OH} \end{array}$	0.5	1.07	25.3	33.1	46.4
<i>n</i> -Propanol	$\begin{array}{c} \text{CH}_2\text{-CH}_2\text{-CH}_3 \\ \\ \text{OH} \end{array}$	0.33	1.94	20.8	19.8	27.7
Isopropyl alcohol	$\begin{array}{c} \text{CH}_3\text{-CH-CH}_3 \\ \\ \text{OH} \end{array}$	0.33	2.04	20.18	15	19.2
Ethylene glycol	$\begin{array}{c} \text{CH}_2\text{-CH}_2 \\ \quad \\ \text{OH} \quad \text{OH} \end{array}$	1	16.03	41.4	67.9	100.7
Propylene glycol	$\begin{array}{c} \text{CH}_2\text{-CH-CH}_3 \\ \quad \\ \text{OH} \quad \text{OH} \end{array}$	0.66	40.4	27.5	30.3	44.3
1,3-Propanediol	$\begin{array}{c} \text{CH}_2\text{-CH}_2\text{-CH}_2 \\ \quad \quad \\ \text{OH} \quad \quad \text{OH} \end{array}$	0.66	56.0	35.1	54.4	89.2
Glycerol	$\begin{array}{c} \text{CH}_2\text{-CH-CH}_2 \\ \quad \quad \\ \text{OH} \quad \text{OH} \quad \text{OH} \end{array}$	1	934	46.53	43.6	58.1

The alcohol absorption capacities of the acid-treated poly(AA-SSS) organogels containing 25 and 75 mol % SSS are also given.

highly sulfonated polyimides from bis(3-sulfopropoxy)benzidine diamines. They attributed a major weight loss starting around 290°C to the decomposition of SO₂ accompanying other aliphatic fragments, including propene.

In addition, at high temperatures (>400°C), PSSS degradation results in carbonaceous foam and inorganic salts, which lead to an inhibited thermal degradation.¹⁵ An eightfold volume expansion at 400°C was reported for PSSS.¹³ The formation of inorganic salts, such as Na₂SO₄, during the degradation of sodium salts of sulfonated monomers was reported.¹³ Inorganic salt formation led to an increase in the thermal stability in comparison with its acidic counterpart. This was verified by the high char yield values of the nontreated samples (Table III).

The increase in sulfonated monomer caused a thermostability enhancement either before or after acid treatment. For instance, the weight losses at 600°C were 67 and 40.7% for the samples containing 25 and 100% sulfonated monomer before treatment (Table III). This trend was preserved after the acidic treatment as well; that is, the samples with higher sulfonated monomer contents exhibited higher ther-

mal stability. This was related to the chemical structure because of the presence of sulfonate or sulfonic acid groups. Strong interactions, particularly in the copolymers, improved the thermal stability. DMTA studies (discussed in the next section) showed that a kind of ion-pair formation occurred in the copolymers, particularly before the acid treatment. The aggregation of ionomers led to clusters, which could act as crosslink points.¹⁶ These additional crosslinks caused an increase in the thermal stability of the copolymers.

Similar reports are available in this field. For instance, Okamura et al.¹⁷ reported that the decomposition time of poly(styrene-sodium styrene sulfonate) copolymers was increased with decreasing SSS content. This was attributed to the catalytic action of sulfonic acid groups, which promoted the decomposition. An increase in the thermal stability of polyacrylamide with a sulfonated monomer was also reported.¹⁸

Thermomechanical characterization

Figure 3(a) shows the storage modulus of the post-treated dried gels versus temperature. It was clear

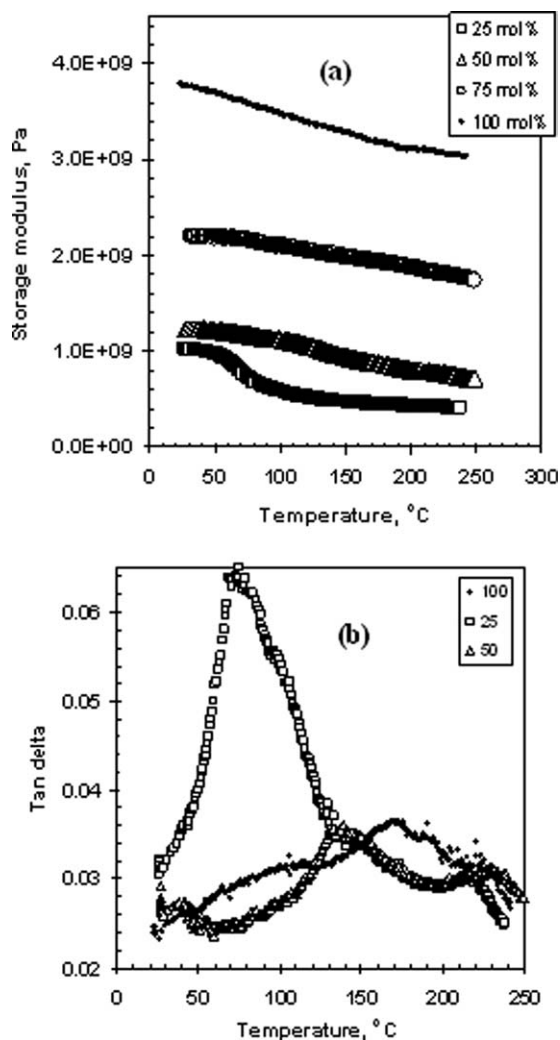


Figure 3 Effects of the (a) storage modulus and (b) $\tan \delta$ on the temperature as recorded in DMTA of the acid-treated poly(AA-SSS) gel samples with 25–100 mol % sulfonated comonomer.

that an increase in the sulfonated monomer led to a significant increase in the modulus. The sulfonated monomer had an aromatic structure, which could increase the stiffness of the polymer chains.

Figure 3(b) shows the $\tan \delta$ versus temperature for the treated gels. The samples exhibited two glass-transition temperature (T_g) values; the first appeared at 70–170°C, and the second appeared at 220–240°C. The first one [the matrix glass-transition temperature (T_{gm})] belonged to the copolymer matrix, which increased with increasing sulfonated monomer content. For example, it was enhanced from 75 to 138°C with an increase in the sulfonated monomer content from 25 to 50%. This was attributed to the chain stiffness, which improved with increasing aromatic group content in the polymer structure.

The second T_g [complex glass-transition temperature (T_{gc})] was attributed to the ionomer or interchain complexes, which can form in polymers hav-

ing sulfonic groups. Because T_{gc} increased with increasing sulfonated comonomer content, the probability of the formation of ion-pair or interchain complexes increased with increasing SSS content. A similar observation was reported for poly(styrene-sodium acrylate).¹⁹ So-called cluster T_g 's were observed at 191 and 274°C for the copolymers containing 6.5 and 24.7% sodium acrylate, respectively. The area under the $\tan \delta$ peak of the cluster region (y) was found to increase with increasing ionic content.²⁰ A linear relationship was also reported between y and the ionic content of poly(styrene-sodium acrylate).¹⁶

Figure 4 shows the T_{gm} and T_{gc} values for the acid-treated poly(AA-SSS) versus the ionic content from the sulfonated comonomer SSS. An increasing trend for both T_g values with increasing ionic content was clear. Both T_g values had a linear relationship with the sulfonated group molar percentage [X ; eqs. (1) and (2)]:

$$T_{gm} = 106 + 0.65X \quad (1)$$

$$T_{gc} = 220 + 0.40X \quad (2)$$

Another noticeable point in Figure 3(b) ($\tan \delta$ vs temperature) is the decreasing surface area of the matrix peak with increasing sulfonated monomer content. This shows that the ionomer-type phase increased with increasing sulfonate groups. The peak area of the $\tan \delta$ curve for the assuming complexes (clusters) was enhanced with increasing sulfonated monomer content from 25 to 50%. Such a $\tan \delta$ peak of the complexes was not observed when the sulfonated group content was 100%. This may have been due to the shifting of T_{gc} to temperatures

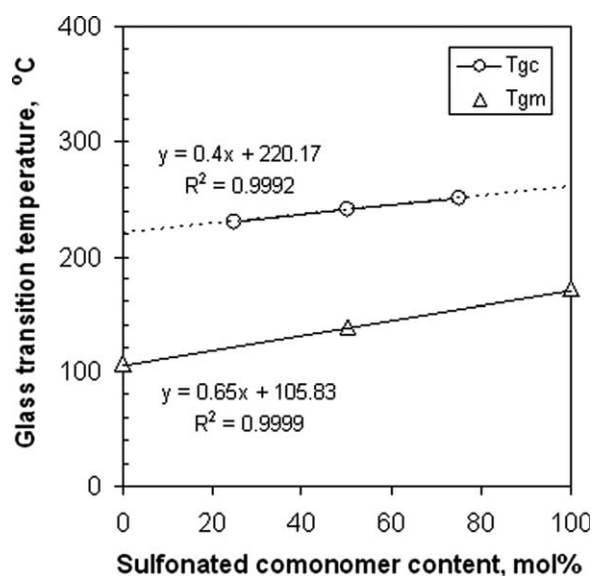


Figure 4 Variations of different T_g 's versus the sulfonated monomer content of the acid-treated poly(AA-SSS) gels.

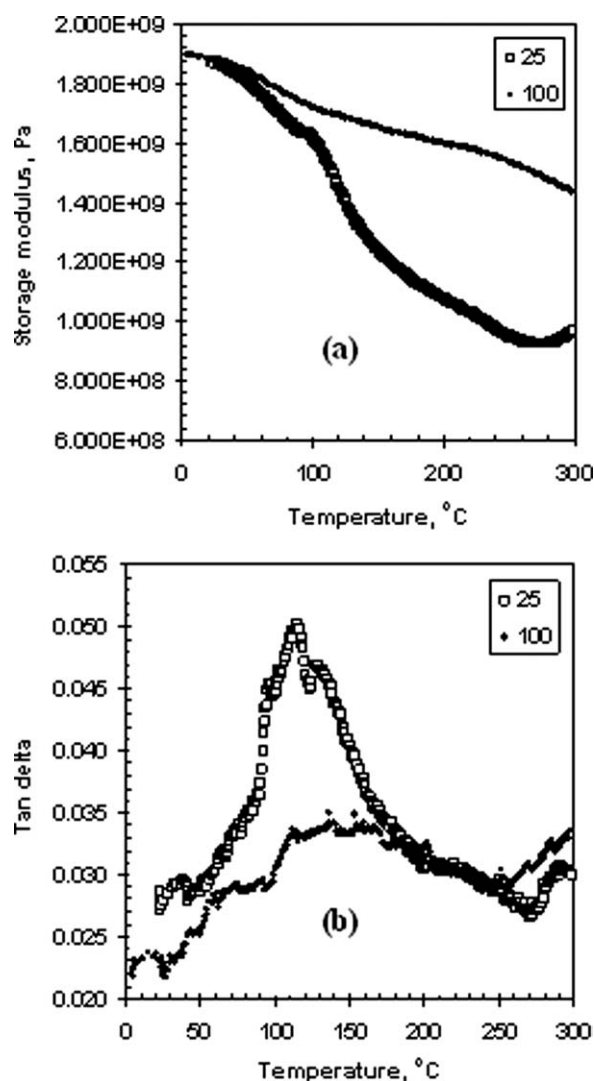


Figure 5 Effects of the (a) storage modulus and (b) $\tan \delta$ on the temperature as recorded in DMTA of the nontreated poly(AA-SSS) gel samples with 25 and 100 mol % sulfonated comonomer.

higher than that of the polymer decomposition temperature ($>250^{\circ}\text{C}$).¹⁶ Such a high T_{gc} detected for sulfonated polystyrene was attributed to strong interactions between metal sulfonate ion pairs.¹⁶ Ion-omer behavior has been reported to be different in various systems, depending on the size and mass of the repeating units.¹⁶

Figure 5(a) shows the storage modulus versus temperature for the nontreated samples containing 25 and 100% SSS. Clearly, an increase in the SSS content led to an increase in the modulus. This was attributed to two reasons: an increase in the chain stiffness due to an increase in aromatic structures in the polymer and an increase in ionic cluster formation due to an increase in the number of ionic groups in the gel structure.

Figure 5(b) shows $\tan \delta$ versus temperature for the gels containing 25 and 100% SSS before acid treat-

ment. Again two β transitions were observed for both samples; these could be ascribed to the matrix and ionic cluster. The T_{gm} values for the samples containing 25 and 100% sulfonated comonomer were recorded to be 115 and 147°C , respectively. The cluster T_g was found to be 293°C for the sample containing 25% SSS. It was not observed for the homopolymer of PSSS because this temperature was higher than the polymer decomposition temperature. Because the ionic interactions in the clusters became stronger with increasing SSS content in the gel structure, the cluster T_g shifted to higher temperatures. The intensity of the $\tan \delta$ peak in the matrix region decreased with increasing SSS content. This was attributed to the decreasing chain flexibility with an increase in the aromatic rings in the polymer chains.

A comparison between the $\tan \delta$ curves before and after the acid treatment for PSSS and PSSA containing 25% sulfonated monomer [Figs. 3(b) and 5(b)] indicated that the acidic treatment decreased T_{gm} . This showed that the ionic interactions in PSSS were considerably stronger than those in PSSA. The cluster T_g 's were 293 and 218 before and after treatment, respectively. This verified that the probability of ionic cluster formation was significantly reduced with changing counterion Na^+ with H^+ . The peak area under the matrix peak increased after the acid treatment; this showed a higher ability of chain movements due to weaker intermolecular or intramolecular interactions of PSSA rather than PSSS.

Superswelling properties

The swelling capacities of the poly(AA-SSS) organogels in methanol and ethanol are shown in Figure 6(a) as a function of SSS content. The gel containing 25 mol % sulfonated monomer had a 4.2 g/g absorbency in ethanol. An increase in the sulfonated monomer content caused an enhancement in the ethanol absorbency. It reached 14.8 g/g for the PSSS homopolymer. This enhancement was attributed to an increase in ionic groups in the chemical structure.

Ionic groups can dissociate in polar protic solvents such as alcohols to produce mobile ions.²¹ Dissociation can occur without consideration of the ionic content in the gel structure. The osmotic pressure difference between the gel and solvent phase leads to an enhancement of the swelling capacity. Because alcohols such as ethanol and methanol are poor solvents for the copolymer, the overall absorbency is not satisfactory. The polyelectrolyte chain in a poor solvent does not exist in an expanded coil state; instead, it is in an unperturbed coil or in the collapse state.²² The number of mobile ions decreases in the unperturbed coil state, but there are still some mobile ions that contribute to swelling. Therefore, poly(AA-SSS) was assumed to be in an unperturbed coil

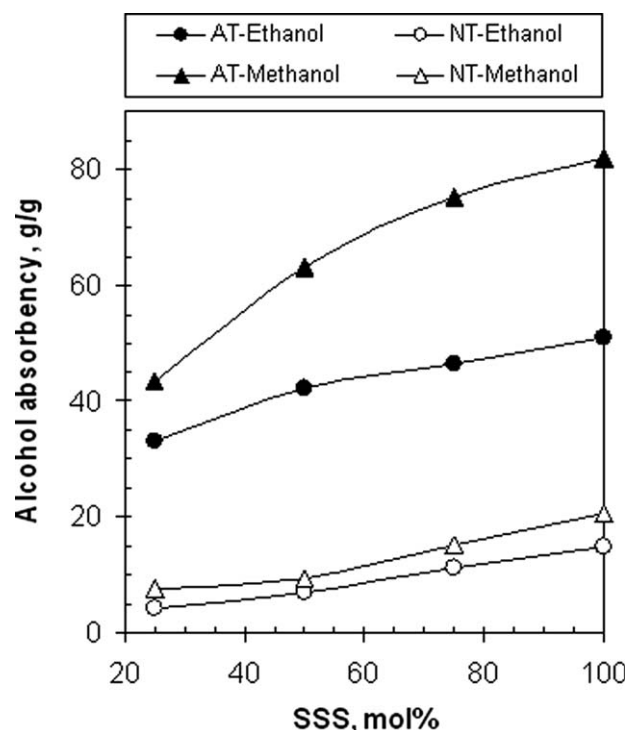


Figure 6 Absorption capacity of the nontreated (NT) and acid-treated (AT) poly(AA-SSS) organogels in methanol and ethanol versus the sulfonated comonomer content (SSS mol %) of the samples.

state when the swelling media was ethanol or methanol.

The tendency of the gel to collapse in alcohols increases with increasing degree of neutralization. Nishiyama and Satoh²³ reported that the swelling capacity of a PAA gel decreased with increasing pH [enhancing neutralization degree (ND)]. This fact encouraged us to carry out a deneutralization treatment to obtain gels with a higher alcohol absorbency. Therefore, synthesized samples were treated with HCl for to exchange the counterion Na^+ with H^+ . On the basis of XRF analysis, the sodium contents were determined to be 3.57 and 0% for the PSSS homopolymer before and after acid treatment, respectively. This showed that a treatment time of 48 h was high enough for the exchange reaction to be completed. The swelling capacity of the treated copolymers with HCl versus sulfonate monomer content is shown in Figure 6(b). The swelling capacity significantly increased after acid treatment. This showed that the replacement of the counterion Na^+ with H^+ was an efficient and successful treatment for increasing the alcohol absorbency. The swelling capacities were measured to be 4.2 and 32 g/g in ethanol for the sample containing 25% sulfonated monomer before and after acid treatment, respectively. The highest alcohol absorbency was achieved for the acid-treated PSSS homopolymer (i.e., PSSA). It could absorb ethanol and methanol

up to about 50 and 80 g/g, respectively. The absorbencies of the PSSS homopolymer before acid treatment were determined to be around 14 and 21 g/g when the sample swelling media were ethanol and methanol, respectively. These observations can be described with the Osawa–Maning theory [eq. (3)]:²⁴

$$\theta = 1 - (\varepsilon kTb/e^2) \quad (3)$$

where e is the electronic charge, ε is the dielectric constant of the solvent, b is the charge spacing, T is absolute temperature, k is Boltzman constant, and θ is the counterion binding. The theory indicates that counterion binding increases with decreasing ε of the swelling media and increasing ionic content. There are two reasons for the reduction in swelling capacity in solvents having low ε values. Because counterion binding reduces mobile ions, the swelling capacity is decreased because of a loss of osmotic pressure difference between the gel phase and the solvent phase. In addition, counterions can form clusters, which can act as crosslink points and lead to a reduction in swelling.^{25,26}

In addition to a change in the counterion, an increase in the sulfonated monomer content also led to an increase in the alcohol absorbency. For instance, the methanol absorbencies of the copolymers were 42 and 73 g/g after acid treatment for the samples containing 25 and 75 mol % sulfonated monomer, respectively. The greater the number of sulfonate groups in the organogel structure was, the greater the number of mobile ions was. Therefore, the swelling of the organogels increased because of a higher osmotic pressure difference between the gel and solvent phase.

Meanwhile, the absorption capacity of individual sample in methanol was higher than that of the sample swollen in ethanol (Fig. 6). The higher swelling capacity in methanol was attributed to the higher ε of methanol in comparison with that of ethanol (33 vs 25.3).²⁷ The dissociation degree of the sulfonate groups decreased with decreasing ε . As a result, the mobile ion density decreased with diminishing ε of the solvent; this led to a loss of swelling.

The Gutmann's donor number and acceptor number (AN) concepts can also be used to describe the swelling of gels in organic solvents.^{27,28} The ANs for methanol and ethanol are 41.3 and 37.1, respectively.²⁷ A higher AN of a solvent means that it has a higher tendency to accept electron pairs; this leads to a better dissociation of ionic groups in the organogel structure, which leads to an enhancement in swelling.²⁸

Satoh et al.²⁸ reported that an increased degree of sulfonation in sulfonated polystyrene led to a swelling diminution in water/organic solvent at lower solvent concentration (nearly <70%). An increase in the solvent composition in aqueous solvent mixtures

causes gel collapse. Gel collapse is also observed at lower solvent contents with increasing sulfonation degree.²⁸ This behavior is contrary to the polyelectrolyte behavior, in which the swelling capacity is enhanced with increasing ionic groups in the gel structure. Hydrogels, particularly those based on weak acids such as AA, are intentionally neutralized to increase their capability for water absorption originating from the dissociation of ionic groups.

Sulfonic acids such as AMPS are usually dissociated in water even without neutralization.²⁹ An increase in degree of neutralization has adverse effects on the swelling capacity in organic solvents. Figure 6 shows that the swelling capacity of the acid-treated sample was significantly lower than that of the sample before the acid treatment. The swelling capacities were 22 and 80 g/g in methanol before and after the acid treatment, respectively. The counterion type also had an influence on the swelling capacity so that a smaller counterion in an organic solvent increased the probability of counterion binding. Large cations had a lower tendency toward counterion binding because of steric hindrance.²⁸ This role is valid in poly(styrene sulfonate) (PSS); for instance, PSS–lithium had a higher tendency toward counterion binding than PSS–sodium (PSSS).²⁸ Earth-metal cations are mostly used to investigate the effect of counterions in counterion binding.²⁸ To our knowledge, an explicit opinion has not reported about the tendency toward counterion binding of H⁺. H⁺ has a smaller size than Na⁺; this should lead to increased counterion binding, but we observed that after acidic treatment for the removal of Na⁺, the swelling capacity of PSSS increased. In other words, the probability of counterion binding decreased in alcohols with the removal of Na⁺ and its replacement with H⁺. The reason for the opposite observation of reduced counterion binding with reduced counterion size for PSSS was unclear.

A swelling reduction of poly(SSS-*co*-*N*-vinylimidazole) in methanol with increasing sulfonated monomer content was reported by Valencia and Pierola.³⁰ They found that an increase in the ionic monomer content in the gel structure generally enhanced the swelling capacity. The swelling loss was attributed to the lower ϵ of methanol, but the effect of a counterion change on swelling was not studied.

The swelling capacity of the acid-treated organogels was measured in other low-molecular-weight alcohols with more carbon atoms (Table III). Different alcohol absorbencies were observed in different alcoholic media. This was attributed to several factors. The first factor was ϵ , as described earlier. An increase in the hydroxyl/carbon number ratio in alcohols generally has an increasing effect on ϵ . This also means that hydrogen-bond formation between

TABLE IV
Swelling Capacity in Distilled Water for the Nontreated and Acid-Treated Poly(AA-SSS) Gel Samples

Sample	Water-swelling capacity (g/g) of	
	Nontreated sample	Acid-treated sample
S25	158	93
S50	116	118
S75	110	138
S100	104	141

the polymer and alcohols increases, which causes an enhancement in swelling.

The second important factor on the alcohol absorbency of the gels may have been related to steric effects in the solvent structure. For example, *n*-propanol and isopropyl alcohol possess nearly identical ϵ 's, but the swelling capacity of the organogel in *n*-propanol was higher than that in isopropyl alcohol. This could be attributed to the position of the hydroxyl groups in the alcohol structure. Steric hindrance for hydrogen-binding formation is higher when the OH group is placed on the C2 carbon atom in isopropyl alcohol as a secondary alcohol. This causes a decrease in the extent of hydrogen bonding between the alcohol and the gel, which leads to a reduction in swelling. A similar trend was observed in propylene glycol and 1,3-propanediol (Table III).

The third effective factor in alcohol absorbency was viscosity. Glycerol and ethylene glycol had comparable ϵ values (46.5 vs 41.1). We expected that the swelling capacity in glycerol would be higher than, or at least equal to, that in ethylene glycol. Unexpectedly, glycerol exhibited a considerably lower alcohol absorbency than ethylene glycol. For instance, the absorbencies were measured to be 100.7 and 58.1 g/g when the acid-treated poly(AA-SSS) containing 75% sulfonated monomer was tested in ethylene glycol and glycerol, respectively. This significant swelling difference was attributed to the viscosity difference of the solvents. The viscosity of glycerol (934 mPa s) was much higher than that of ethylene glycol (16 mPa s). High viscosity in a thick liquid disfavors its facile diffusion through the gel network. Therefore, a swelling loss was observed when glycerol was used as the swelling medium.

The swelling capacities of nontreated and acid-treated copolymers with different sulfonated monomers in distilled water were also measured (Table IV). Before acid treatment, the water absorbency was diminished with increasing sulfonated comonomer content in the copolymer. This was in contrast to the reported behavior of the neutralization of weak acids such as carboxylic acid.³¹ It is well known that the swelling capacity increases with increasing ND of –COOH because of an increased density of pendant mobile ions (–COO[–]), which are responsible for the

network expansion. This behavior was observed up to an ND of 75%. Then, it was reported to decrease with ND enhancement because of the screening effect of the additional cations, for example, Na^+ .³¹ The swelling reduction in lieu of an ND enhancement in strong polyelectrolytes [e.g., poly(2-acrylamido-2-methyl propane sulfonic acid)] may be attributed to a tendency of mobile ions to form multiplets or ionomeric zones, even in good solvents. These multiplets can act as crosslink points in the gel network and increase the modulus.³²

After acid treatment, an opposite behavior was observed for the swelling capacity with increasing sulfonated comonomer content. The exchange of the counterion Na^+ with H^+ decreased the possibility of the formation of multiplets. H^+ does not have a tendency to form multiplets in alcohols or water. The increase in the swelling capacity of the acid-treated copolymers with increasing sulfonated monomer content was attributed to the increase in the ionic content and the density of the mobile ions of $-\text{SO}_3^-$.

Polyelectrolyte/ionomer behavior is mostly determined by ϵ of the medium. Philippova et al.³³ mentioned different regimes for swelling behavior of ionic gels, which were determined on the basis of ϵ of the swelling media. Swelling monotonically increases at high ϵ 's (first regime) with increasing ionization degree.³³ This behavior was observed for the copolymers after acid treatment, in which swelling capacity increased with an increase in the sulfonated comonomer content. In the second regime, at low ϵ , the swelling capacity decreased with increasing ionic content of the gel structure. Poly(AA-SSS) before acidic treatment showed such behavior. We concluded that movement from the first regime to the second one in poly(AA-SSS) gels was carried out through the cation-exchange reaction.

Swollen gel strength

From a practical viewpoint, one of the most important properties of a gel is its swelling capacity when it is under an external pressure or load. Therefore, the gel strength or stiffness in its swollen state can be taken as a measure of its absorbency under load. We showed that the swollen gel strength may be quantified by rheometrical analysis.⁹

Figure 7(a) shows the shear storage modulus of acid-treated samples in their hydrated form with a fixed water volume (lower than their maximum water content, given in Table IV). The hydrated gel modulus decreased significantly with increasing sulfonated monomer content. This observation was contradicted by the storage modulus obtained from the DMTA studies on the dried gels (see the Thermomechanical Characterization section).

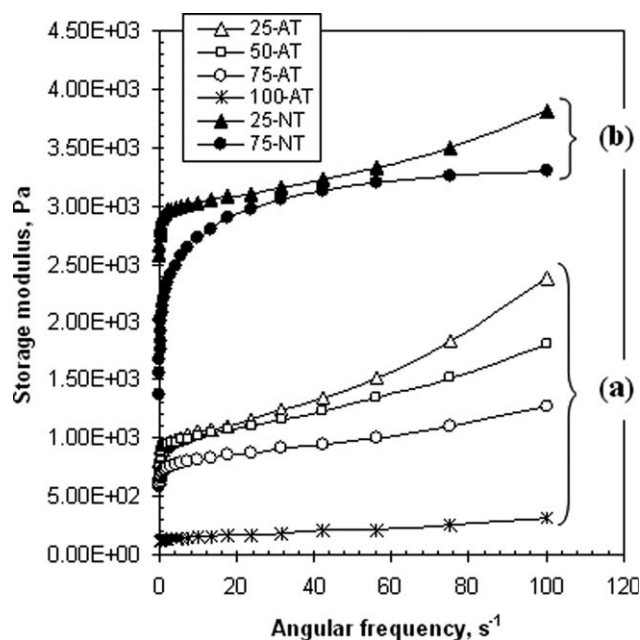


Figure 7 Rheological behavior of the poly(AA-SSS) gel samples with 25–100 mol % sulfonated comonomer: (a) acid-treated (AT) and (b) nontreated (NT) samples. The sample was hydrated by a fixed amount of water before measurements.

The hydrated gel modulus (G) is usually considered to be the swollen gel strength.^{9,34} It is inversely proportional to the average molecular weight between crosslinks [M_c ; eq. (4)]:^{9,34}

$$G = \rho RT/M_c \quad (4)$$

where ρ is the polymer density and R is the gas constant.

The loss of storage modulus of the hydrated gel with increasing sulfonated monomer (SSS) content was related to the decreased crosslink density. The loss of crosslink density with increasing SSS may have been due to the reactivity ratios of SSS and the macrocrosslinker PEGDA, which have not been reported in the literature. Most probably, in the copolymerization reaction, the nonacrylic monomer (i.e., SSS) had a lower tendency to react with PEGDA than with AA. Therefore, more crosslinker remained unreacted as the sulfonated monomer content increased. Therefore, the crosslink density decreased, and this led to a decrease in the modulus of the swollen gel. As shown in Figure 6, the swelling capacity improved with increasing sulfonated monomer content. As mentioned before, this was related to an increase in the ionic groups in the gel structure, which caused an increase in mobile ions. Another probable reason was the loss of crosslink density.

Figure 7(b) shows the storage modulus versus angular frequency for the copolymers before the acid treatment. A similar trend for storage modulus

was observed, as in the acid-treated copolymers. The storage modulus decreased with increasing sulfonated monomer content; this was attributed to the lower reactivity ratio of the sulfonated monomer with the macrocrosslinker.

CONCLUSIONS

Poly(AA-SSS) organogels were synthesized through solution polymerization with a PEG-based macrocrosslinker. The gels were characterized with FTIR, TGA, DMTA, and rheometry.

Poly(AA-SSS) gels showed low absorbencies in ethanol and methanol, even at high ionic contents; this was attributed to counterion binding. The alcohol absorbency of the samples significantly increased after posttreatment in HCl medium so that an acid-treated sample (e.g., the sample with an AA:SSS molar ratio of 1 : 3) absorbed methanol, ethanol, ethylene glycol, and glycerol as high as 75, 46, 100, and 58 g/g, respectively. On the other hand, samples with a higher sulfonated monomer contents exhibited higher alcohol absorbencies.

Despite the ability of SSS dissociation as an original reason for the alcohol absorbency, the counterion Na^+ had high potential to be aggregated (via the so-called process of counterion binding) in alcohols to limit the swelling capacity. This was why the required osmotic pressure difference between the gel and solvent phase for absorbing alcohols could not be supplied. Acidic treatment removed Na^+ from the gel network to prevent counterion binding.

The swelling capacity of the gels was evaluated in a series of important alcohols. It was found that the ϵ , steric hindrance, and viscosity of the alcohol were the most important factors affecting the alcohol superabsorbency.

These alcohol-specific superabsorbing organogels are suggested as outstanding candidates for the manufacture of products with high alcohol contents, such as hand-sanitizing agents and fuel gels.

References

- Vintiloiu, A.; Leroux, J. C. *J Controlled Release* 2008, 125, 179.
- Rogers, M. A.; Wright, A. J.; Marangoni, A. G. *Curr Opin Colloid Interface Sci* 2009, 14, 33.
- George, M.; Luo, C.; Wang, C.; Carretti, E.; Dei, L.; Weiss, R. *Macromol Symp* 2005, 227, 173.
- Markovic, N.; Ginic-Markovic, M.; Dutta, N. K. *Polym Int* 2003, 52, 1095.
- Kabiri, K.; Lashani, S.; Zohuriaan-Mehr, M. J.; Kheirabadi, M. *J Polym Res* 2010, in press. DOI 10.1007/s10965-010-9436-y.
- Ono, T.; Sugimoto, T.; Shinkai, S.; Sada, A. *Nat Mater* 2007, 6, 429.
- Zhao, Q.; Liu, C. *Polym Sci* 2007, 105, 3458.
- Sonmez, H.; Wudl, E. *Macromolecules* 2005, 38, 1623.
- Ramazani-Harandi, M. J.; Zohuriaan-Mehr, M. J.; Yousefi, A. A.; Ershad Langroudi, A.; Kabiri, K. *Polym Test* 2006, 25, 470.
- Kabiri, K.; Azizi, A.; Zohuriaan-Mehr, M. J.; Bagheri Marandi, G.; Bouhendi, H. *J Appl Polym Sci*, to appear.
- M'Bareck, C. O.; Nguyen, Q. T.; Metayer, M.; Saiter, J. M.; Garda, M. R. *Polymer* 2004, 45, 4181.
- Sahua, A. K.; Selvarania, G.; Bhat, S. D.; Pitchumani, S.; Sridhar, P.; Shukla, A. K.; Narayanan, N.; Banerjee, A.; Chandrakumar, N. *J Membr Sci* 2008, 319, 298.
- Jiang, D. D.; Yao, Q.; Mckinney, M. A.; Wilkie, C. A. *Polym Degrad Stab* 1999, 63, 423.
- Yin, Y.; Fang, J.; Watari, T.; Tanaka, K.; Kita, H.; Okamoto, K. *J Mater Chem* 2004, 14, 1062.
- Yao, Q.; Wilkie, C. A. *Polym Degrad Stab* 1999, 66, 379.
- Nishida, M.; Eisenberg, A. *Macromolecules* 1996, 29, 1507.
- Okamura, H.; Takatori, Y.; Tsunooka, M.; Shirai, M. *Polymer* 2002, 43, 3155.
- Audibert, A.; Argillier, J. F. Presented at the SPE International Symposium on Oilfield Chemistry, San Antonio, TX, Feb 1995.
- Kim, J. S.; Wu, G.; Eisenberg, A. *Macromolecules* 1994, 27, 814.
- Kim, J. S.; Yoshikawa, K.; Eisenberg, A. *Macromolecules* 1994, 27, 634.
- Jousset, S.; Bellissent, H.; Galin, J. *Macromolecules* 1998, 31, 4520.
- Loh, P.; RoshanDeen, G.; Vollmer, D.; Fischer, K.; Schmidt, M.; Kundagrami, A.; Muthukumar, M. *Macromolecules* 2008, 41, 9352.
- Nishiyama, Y.; Satoh, M. *Macromolecules* 2000, 21, 21174.
- Nishiyama, Y.; Satoh, M. *J Polym Sci Part B: Polym Phys* 2000, 38, 2791.
- Khokhlov, A. R.; Kramarenko, E. *Macromol Theory Simul* 1994, 3, 45.
- Khokhlov, A. R.; Kramarenko, E. *Macromolecules* 1996, 29, 681.
- Mayer, U.; Gutmann, V.; Gerger, W. *Monatshefte Chem* 1975, 106, 1235.
- Fukunaka, Y.; Hayashi, M.; Satoh, M. *J Polym Sci Part B: Polym Phys* 2007, 45, 1166.
- Kabiri, K.; Faraji-Dana, S.; Zohuriaan-Mehr, M. J. *Polym Adv Technol* 2005, 16, 659.
- Valencia, J.; Pierola, I. F. *Eur Polym J* 2001, 37, 2345.
- Chen, J.; Zhao, Y. *J Appl Polym Sci* 1999, 74, 119.
- Okay, O.; Durmaz, S. *Polymer* 2002, 43, 1215.
- Philippova, O. E.; Sitnikova, N. L.; Demidovich, G. B.; Khokhlov, A. R. *Mixed Macromol* 1996, 29, 4642.
- Ramazani-Harandi, M. J.; Zohuriaan-Mehr, M. J.; Yousefi, A. A.; Ershad-Langroudi, A.; Kabiri, K. *J Appl Polym Sci* 2009, 113, 3676.