

Extraordinary Swelling Behavior of Poly(AMPS) Organogel in Solvent/DMSO Binary Mixed Media

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ABSTRACT: The present article deals with super-swelling behavior of crosslinked homopolymer of 2-acrylamido-2-methylpropane sulfonic acid, poly(AMPS), in binary mixtures of dimethyl sulfoxide (DMSO) and various polar solvents including water, mono-, and polyhydric alcohols, and amide solvents such as *N*-methyl pyrrolidone. Extraordinary phase transition sequences including a new unusual swelling phenomenon, referred to as “overentrant” swelling, was observed for this polymeric organogel in the solvent/DMSO mixtures. The swelling behaviors were preliminarily explained based on the major interactions involved in the solvation process and dielectric constant of the swelling media. It was established that the “overentrant” region of the swelling profiles was progressed with the increase of dielectric constant of the mixed solvent media. The overen-

trant region was disappeared with partial replacement of AMPS units with acrylic acid. This was taken as an additional practical evidence for a major role of the sulfonic acid as the main interactive group involved in the solvation process. The unusual phase transitions were also explained via a semiquantitative approach based on the Gutmann’s acceptor number and donor number values to emphasis on the key effect of dissociation degree of the sulfonic acid group (as a function of the solvent type and composition) on the swelling behaviors. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 1127–1136, 2010

Key words: 2-acrylamido-2-methylpropane sulfonic acid; dimethyl sulfoxide; organogel; mixed organic solvent; volume phase transition

INTRODUCTION

Polymer gels swell in suitable solvents but cannot dissolve because of their network structure. Therefore, they are fascinating materials for a wide variety of applications. In particular, the hydrophilic gels (hydrogels) such as superabsorbents are used in wide variety of applications ranged from hygienic (e.g., baby diapers) to agriculture (as miniature water reservoirs in soil).¹

On the other hand, according to the critical review of Vintitoiu and Leroux,² organogels can be distinguished from hydrogels mainly by their organic continuous phase and can be further subdivided based on the nature of the gelling structure; polymeric or low molecular weight organogels (LMWO). The polymeric organogels (known also as oil-absorbents if the imbibed solvent is nonpolar) are crosslinked macromolecules prepared via polymerization of organophilic monomers such as long-chain alkyl acrylates³ or via modification of rubber compounds

such as polybutadiene, EPDM or styrene-butadiene rubber.^{4,6} These systems may be designed to uptake hydrocarbons particularly for decontaminating oil spills. Polyelectrolyte networks with lipophilic nature are also reported as super-absorbing polymers for nonpolar organic solvents.⁷ In recent years, nevertheless, a number of nonpolymeric organic compounds have been found to be effective LMWO for organic solvents. In organic solution, they have generally self-assembled into elongated fiber-like structures through specific intermolecular interactions. These fibers in turn form a three-dimensional network encapsulating the solvent.⁸ The use of organogels in controlled drug delivery has been reviewed recently.²

Among variety of hydrophilic monomers such as acrylamide, acrylic acid and its salts used for production of commercial hydrogels,¹ 2-acrylamido-2-methylpropane sulfonic acid (AMPS) is an inexpensive monomer with a special interest because it is quite hydrolytically stable and bears a strong organic acid functionality. AMPS applications include various hydrogels with nearly pH-independent swelling behavior.^{9–11} In the hydrated state, the AMPS homo- and copolymers exhibit high proton conductivity and have been used as components to prepare ion-conducting membranes^{12,13}

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Polymer gels, as organic solvent absorbents, possess promising applications due to super-swelling capacities; nevertheless, only scattered studies have been reported on the syntheses and characterization of the organogels prepared for superabsorbing applications.¹ In this relation, AMPS-based polymers have shown super-swelling behavior in organic media as effectively as their similar behavior in water. We recently prepared homopoly(AMPS) hydrogels and some particular nanocomposites and studied their solvent-, saline-, and pH-specific swelling behaviors.¹¹ In addition, some super-alcogels (super alcohol-absorbing gels) composing acrylic acid and AMPS were prepared and investigated by the authors.¹⁴

Dimethyl sulfoxide (DMSO) is a very common, nontoxic, highly polar organic fluid. It exhibits strange properties via formation of $m\text{DMSO}\cdot n\text{H}_2\text{O}$ clusters. This is why many basic researches have been carried out to disclose the secrets of DMSO and its mixture with water.¹⁵⁻¹⁷ It is an aprotic liquid with widespread uses from solvent to chemical intermediate. Among the widespread organic gels reported in the literature, gels of DMSO are of especial interest due to their use in numerous medical functions such as anti-inflammatory, anticancer, anti-oxidant, and analgesic activities.¹⁸ DMSO is totally miscible with water and many organic solvents.

The present article deals with swelling of a poly(AMPS) organogel in binary mixture media composing DMSO and numerous polar solvents. Super-swelling properties in DMSO and mixtures of solvent/DMSO, particularly above 60% DMSO, have been observed in most cases. In addition, extraordinary swelling behavior of the gel was observed and investigated in some details.

EXPERIMENTAL

Materials

2-Acrylamido-2-methylpropane sulfonic acid (AMPS, Merck), ammonium persulfate (APS, Merck), polyethyleneglycol dimethacrylate (PEGDMA 330, Aldrich), and solvents (all from Merck) were used as received.

Synthesis

The poly(AMPS) gel was prepared using a procedure reported elsewhere.¹⁹ Briefly, AMPS (30.0 g) was dissolved in 30.0 mL distilled water, and PEGDMA (0.065 mM) and the APS (0.32 mM) solutions were then added to the monomer solution. After heating at 70°C and gelation, the elastic samples were removed from the reactor, cut to small pieces, dried at 60°C in a forced draft oven, ground by a

mini-grinder to sugar-like particles, and kept in a dry place.

Swelling measurements

A 0.20 g sample of dried polymer (mesh 35–100) was dispersed in 100 mL of a desired medium and allowed to completely swell for 1 h to reach equilibrium swelling. Each dispersion was filtered through a polyester gauze to remove the excess water. Then, swollen gels were weighed. Swelling capacity (g/g) was calculated by dividing the weight of swollen gel by the weight of the initial dried sample.

RESULTS AND DISCUSSION

Crosslinked homopolymer of AMPS was prepared via a solution polymerization in the presence of a macromolecular water-soluble crosslinker, PEGDMA.¹⁹ The swelling behaviors of the gels were then investigated in different binary DMSO/solvent mixtures.

Generally, when a polymer gel is placed in an organic medium composing two miscible solvents, several phenomena may be observed depending on the polymer characteristics, nature, and composition of the solvents, etc. Different behaviors of polymer gels in the media²⁰⁻²⁶ are summarized in Table I. Straightforward swelling and collapsing are the most usual behaviors, while cosolvency, co-nonsolvency, and reentrant phenomena are moderately rare. In cosolvency, a mixture of two nonsolvents or a solvent–nonsolvent mixture forms a good solvent for a polymer. For instance, although either water or methanol are nonsolvents of poly(methyl methacrylate), a range of methanol/water mixture can dissolve this polymer.²⁰ The opposite phenomenon is known as co-nonsolvency in which a mixture of two good solvents for a polymer forms a nonsolvent. In this case, few examples including poly(*N*-isopropylacrylamide) in methanol/water have been mentioned by Winnik et al.^{21,22}

Reentrant is referred to an unusual swelling transition (volume phase transition; VPT) in which the gel first collapses then reswells when a particular external parameter such as an organic solvent or a linear polymer concentration is continuously varied. It was observed in hydrophobically modified hydrogels in aqueous solutions of organic solvent or linear polymer. Some examples of the reentrant transition, including poly(*N,N*-dimethylacrylamide), are mentioned by Okay and Orakdogan.²⁶

Poly(AMPS) gel in DMSO/water mixture

In a previous paper,¹¹ we reported VPT behaviors for a poly(AMPS) hydrogel and its chitosan-

TABLE I
Different Behaviors of Polymer Gels in Binary Mixed Solvents^a

Entry	Binary mixed solvent		Gel properties observed			
	Solvent A	Solvent B	Behavior	Phenomenon	Example	Ref.
1	+	+	Swelling	Complete solvency	PVP in water/methanol	23
2	+	+	Swelling	Solvency and VPT	Poly(AMPS) in water/ethanol	11
3	+	+	Collapsing	Co-nonsolvency	P(NIPAM) in water/methanol	21,22
4	+	-	Swelling	Co-solvency	PAM in DMSO/water	24
5	+	-	Partially swelling	Nonsolvency and VPT	P(NaAA) in water/acetone	25
6	+	-	Collapsing then reswelling	Reentrant	P(NDMAM) in water/organic solvents	26
7	-	-	Swelling	Co-solvency	PMMA in water/2-propanol	20
8	+	+	Swelling higher than that in single solvent	Overentrant	Poly(AMPS) in DMSO/water or glycerol/DMSO	This work
9	+	-	Swelling higher than that in single solvent	Overentrant	Poly(AMPS) in acetone/DMSO or acetonitrile/DMSO	This work

^a +, good solvent; -, poor solvent (nonsolvent). PVP, poly(*N*-vinyl pyrrolidone); P(NIPAM), poly(*N*-isopropyl acrylamide); PAM, poly(acrylamide); P(NaAA), poly(sodium acrylate); P(NDMAM), poly(*N,N*-dimethyl acrylamide); PMMA, poly(methyl methacrylate); VPT, volume phase transition.

modified nanoclay in aqueous solutions of various organic solvents. During the experiments, we realized a strange swelling behavior of the gel in some DMSO/water mixtures. In most of the mixtures, the hydrogels not only did not collapse, but also surprisingly exhibited the highest swelling; even more than that in pure water (Fig. 1). We name this extraordinary phenomenon as "overentrant" swelling, and this is a main objective of the present report. Such unusual phase transition in water-alcohol mixtures was also reported for a different gel based on *N*-acryloyl-L-proline methyl ester.²⁷

The swelling capacity of poly(AMPS) gel was ~ 170 g/g in pure water. According to Figure 1, when the gel was immersed in aqueous DMSO, it was decreased to around 150 g/g (the first gel collapse, *c*) in lieu of increasing DMSO fraction. In DMSO fraction of ~ 0.2 to ~ 0.4, it was elevated (reentrant region, *r*) and then, from the DMSO/water volume ratio of about 0.4–0.7, the swelling capacity was developed up to 180 g/g (i.e., even higher than that in pure water). This is the region we referred to as "overentrant" (abbreviated as *o*). More DMSO fraction led to loss of swelling (the second gel collapse, *c*). Thus, we term this unusual succession as *c-r-o-c* sequence.

Here we tried to present some preliminary explanations for each transition in the *c-r-o-c* sequence. To make sure the abnormal behavior, we repeated the swelling experiments and rechecked the results several times. The unusual behavior of the poly(AMPS) gels was found to be reproducible; it exhibited the highest swelling capacities in DMSO/water mixtures even more than that in pure water. Researchers have

reported some unexpected observations in nearly all polymer gels dealing with aqueous DMSO.^{28,29} For example, in DMSO/water mixtures, dissimilar to many aqueous solvents, both cationic gels of poly(allylamine)²⁸ and anionic gels of poly(styrene sulfonate)²⁹ did not show considerable VPT. Satoh et al.^{25,28,29} partially attributed the lack of gel-collapse to high dielectric constant, ϵ , of DMSO (47.24).

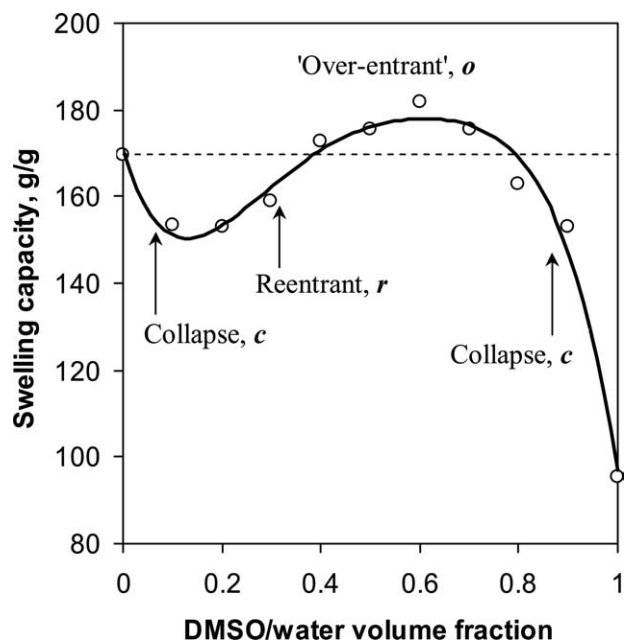


Figure 1 The unusual behavior (overentrant) in company with collapse and reentrant observed for the swelling of poly(AMPS) gel in water and DMSO/water mixtures with various compositions.

Expectedly, once ϵ becomes lower than a certain value (ϵ_{cr}), the sulfonic acid group on the chain cannot be dissociated, resulting in the collapse transition. They suggested that the ϵ around polymer charges (local ϵ) was not lowered enough, even in pure DMSO, to reach to the minimum ϵ required for the gel de-swelling (ϵ_{cr}). This reasoning has also been given for peculiar swelling behavior of *N,N'*-dimethylacryamide hydrogels in aqueous acetone (>80% acetone).⁹ However, higher swelling of the poly(AMPS) hydrogels in the mixed solvent rather than in water cannot be rationalized by such reason.

To explain the strange behavior, we have to preliminarily focus on DMSO and its properties in aqueous medium. DMSO is a simple highly polar molecule with a S=O group and two hydrophobic CH₃ groups [Fig. 2(a)].

Its polar sites are expected to interact with water to form strong hydrogen bonds. Its nonpolar sites may cause effects of hydrophobic hydration and hydrophobic dissociation of DMSO molecules.³⁰ Many fundamental researches have been conducted to disclose the secrets of DMSO and its mixture with water.¹⁵⁻¹⁷ Different associations of *m*DMSO-*n*H₂O (*m* = 1,2 and *n* = 1-3) have been recognized as complex clusters in the mixture.

Poly(AMPS) is a highly polar macromolecule with a high potential to be solvated in polar solvents. Based on the chemical principles, possible interactions involved in systems containing poly(AMPS) in water, DMSO and DMSO/water binary mixtures should be taken into consideration.¹¹ Among many polymer-solvent interactions engaged here, those involved with the sulfonic acid group are major. A very significant ionic interaction is sulfonate-sulfonate ionic repulsive forces between the polymer chains leading to the gel network expansion [Fig. 2(b)]. In absence of water (in pure DMSO), the sulfonic acid groups cannot probably be well-dissociated³¹ so these major ionic forces are mainly removed and the gel cannot be expanded extremely. However, dipole-dipole interactions of sulfonic acid-sulfoxide groups and O-H...O hydrogen bonding interactions are yet enough to cause swelling as high as 100 g/g (Fig. 1).

As the number of major polymer-solvent interactions can preliminarily give a rough prediction about the swelling extent¹⁴ considering additional C-H...O hydrogen bonding interactions in DMSO may lead us to order of DMSO/water mixture > water > DMSO, which is in agreement with the experimental results (Fig. 1). To roughly illustrate the solvent specificity, we employed a simple solvation model²⁷ of poly(AMPS) sites shown in Figure 2(b). Meanwhile, it seems that even solvent-solvent interactions, particularly well-known C-H...O hydrogen bonding, are not ineffective in the solvation promotion.

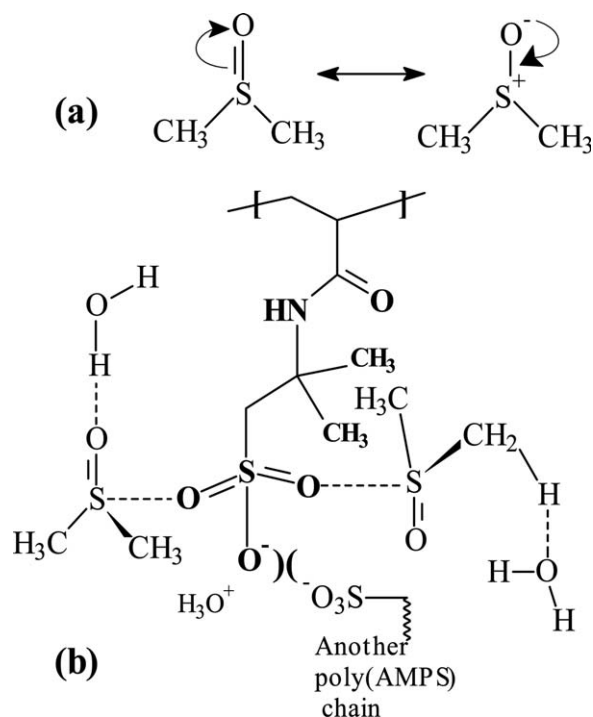


Figure 2 (a) DMSO dipole structure and resonance forms from charge delocalization. (b) A simple illustrative model of the major interactions involved in solvation of poly(AMPS) gel in DMSO/water mixture.

Finally, as a practical evidence for the role of sulfonic acid as an interactive group involved strongly in the solvation, we carried out an additional preliminary study. The AMPS units were partially replaced with acrylic acid (AA) in the polymer to prepare poly(AA-AMPS) copolymer networks under similar synthetic conditions. Figure 3 shows the relationship between AMPS comonomer content and the aqueous DMSO absorptiveness of the copolymeric gels. The overall swelling capacity of the sample having higher amount of AMPS was diminished considerably. In addition, an overentrant region (as an *o-c* sequence) was observed in the swelling profile of the high-AMPS sample composing 41 mol % of AMPS (i.e., S41). However, the overentrant phenomenon was disappeared when the comonomer incorporated was as low as 6 mol % (Sample S6), and, approximately, a DMSO concentration independency was observed for the swelling particularly at the range of 20-80 v/v% of the DMSO/water mixture. This can be taken as a preliminary experience confirming the key role of the sulfonic acid group and involvement of SO₃H-DMSO interaction in the solvation taken place in the mixed media.

Hiroki et al.²⁷ reported such swelling behavior (as *c-r-o-c* sequence) in water-alcohol mixtures for poly(acryloyl-L-proline methyl ester) gel. They explained the unusual phase transition using the dynamic hydration numbers as a parameter of the hydrophobicity of the alcohols.

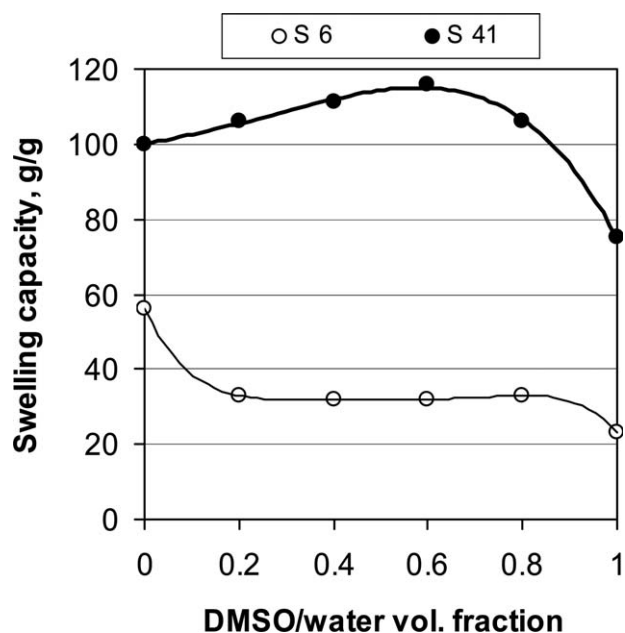


Figure 3 Swelling capacity of poly(acrylic acid-AMPS) gel samples in DMSO/water mixtures. Samples S6 and S41 are composed 6 and 41 mol % of AMPS units, respectively.

Poly(AMPS) gel in alcohol/DMSO mixtures

Does the aforementioned extraordinary phenomenon survive in the binary mixture of DMSO with other solvents excluding water? We experienced that poly(AMPS) gel swelling capability was preserved even in pure alcohols, so the gel swelling was exam-

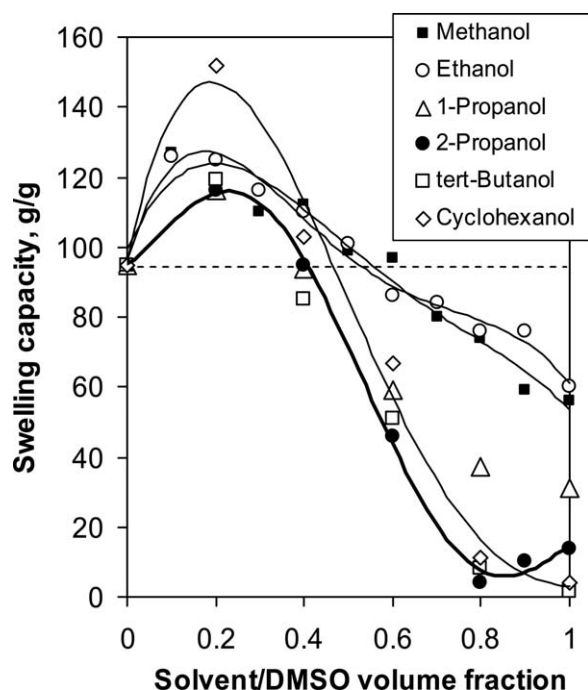


Figure 4 Variation of swelling capacity of poly(AMPS) gel in binary solvents of DMSO/monohydric alcohol.

ined in binary mixtures of DMSO with various alcohols. Figure 4 shows the swelling capacity changes in various alcoholic DMSO media. Since the gel swelling in pure DMSO was higher than that of the pure solvents used, the left-hand vertical axis of the plots was traditionally allocated to DMSO.

In DMSO mixtures with alcohols, no gel collapse was firstly observed in lieu of increasing fractions of the desired alcohol in the binary mixture. Instead, an overentrant transition was observed at the range of solvent/DMSO ratio of ~ 0.1 – 0.2 and a collapse was then occurred steadily (an *o-c* sequence).

The smallest amounts of swelling capacities in nearly all alcohol/DMSO compositions were recorded in the case of 2-propanol and *tert*-butanol (Fig. 4). The difference is originated mainly from their structural difference and steric effects. 2-Propanol and *tert*-butanol are secondary and tertiary alcohols having two and three CH_3 groups in their OH surrounding area, respectively. Therefore, the steric hindrance of the methyl groups disfavors the hydrogen bonding formation with the polymer. 1-Propanol, however, is a primary alcohol; so it can form H-bonding more freely to imbibe higher volume of solvent particularly in high solvent/DMSO ratios (Figs. 4 and 5a–5c). Actually, a similar truth is the reason why the boiling point of 1-propanol (97°C) is higher than that of its isomer, 2-propanol (82°C).³²

In the case of 2-propanol/DMSO, a reentrant transition was exceptionally observed around the alcohol fraction of 0.8 (an *o-c-r* sequence). In addition, according to Figure 4, the gel absorbed and retained

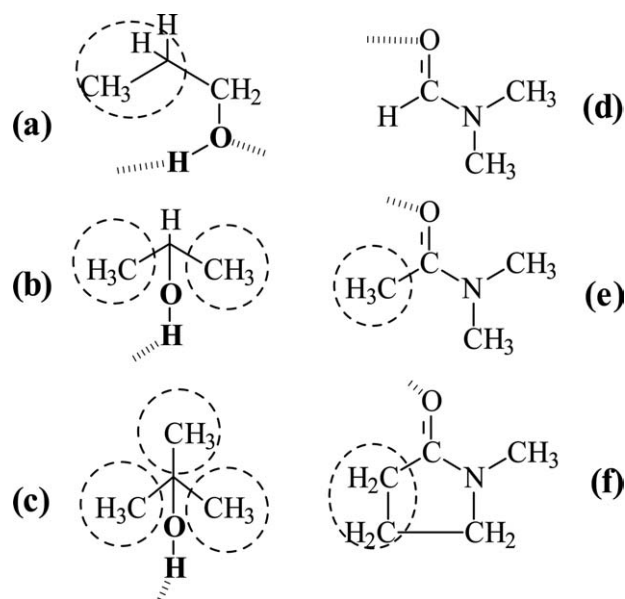


Figure 5 Steric hindrance of the neighboring groups in opposition to hydrogen bonding and/or dipole-dipole interactions of polar groups involved in solvation. (a) 1-propanol, (b) 2-propanol, (c) *tert*-butanol, (d) DMF, (e) DMAc, and (f) NMP.

TABLE II
Physical Constants and Values of Acceptor Number (AN) and Donor Number (DN) for the Solvents Used in the Present Work

Solvent	Dielectric constant, ϵ	Viscosity, mPa s	AN	DN
Water	80.10	0.89	54.8	18.0
Methanol	33.0	0.544	41.3	19.0
Ethanol	25.3	1.074	37.1	20.0
1-Propanol	20.8	1.945	–	–
2-Propanol	20.18	2.04	33.5	–
<i>tert</i> -Butanol	12.47	4.31	–	–
Cyclohexanol	16.4	57.5	–	–
Ethylene glycol	41.4	16.03	–	–
Glycerol	46.53	934.0	–	–
THF ^a	7.52	0.456	8.0	20.0
Acetone	21.03	0.306	12.5	17.0
MEK ^b	18.56	0.405	–	–
Acetonitrile	36.64	0.369	18.9	14.1
NMP ^c	32.55	1.7	13.3	27.3
DMF ^d	38.25	0.794	16.0	26.6
DMAc ^e	38.85	0.927	13.6	27.8
DMSO	47.24	1.987	19.3	29.8
Toluene	2.38	0.560	–	–

^a Tetrahydrofurane.

^b Methyl ethyl ketone.

^c *N*-Methyl pyrrolidone.

^d Dimethyl formamide.

^e Dimethyl acetamide.

remarkable amounts of pure alcohols, particularly ethanol and methanol. Cyclohexanol with the highest C/OH ratio (maximum organophilicity among the monohydric alcohols here) exhibited the largest overentrant. However, its swelling became near zero at high solvent/DMSO fraction due to either its high viscosity or low dielectric constant, ϵ (Table II).^{33,34} High viscosity limits the solvent diffusion through the gel network. Similarly, low ϵ is a major reason for the similar collapsing behavior of the gelator in media with high values of *tert*-butanol/DMSO (>0.8).

The swelling of poly(AMPS) gel in binary DMSO mixtures of polyhydric alcohols were also examined (Fig. 6). An *o-c* sequence was observed as well, however, the overentrant region was more extensive in comparison with those of the monohydric alcohols (Fig. 4). The overentrant transition was ranged from the solvent/DMSO \sim 0.1–0.8 and \sim 0.1–0.7 for ethylene glycol and glycerol, respectively. Afterward, the swelling was diminished sharply with increasing the polyol/DMSO ratio. However, the network absorbs significant amounts of the polyols of the pure state.

The wide-ranged overentrant behavior of poly(AMPS) gel may be explained by the solvent capability to form hydrogel bonding with the solute and the scheme of its swelling in aqueous DMSO media given in Figure 2. Glycerol possesses three OH groups, so it has great capability for hydrogen bond-

ing. If the water molecules are replaced with the polyhydric alcohols in the figure, we can expect extensive SO₃H-alcohol hydrogen bonding interactions led to absorption of the binary solvent in wide range of the solvent composition. Meanwhile, the swelling loss after the overentrant region is occurred at lower solvent/DMSO fractions when the solvent was glycerol. Glycerol possesses the highest hydroxyl group functionality (i.e., 3); however, its very high viscosity (Table II) highly restricts the diffusion of the solvent into the gel network. Yet, poly(AMPS) gel imbibe pure glycerol as high as 53 g/g. Pure ethylene glycol with OH functionality of two can be absorbed and retained by the gel in a greater extent (101 g/g) due to its lower viscosity and much higher dielectric constant (Table II).

Swelling in mixtures of DMSO and other polar solvents

Figure 7 shows variation of swelling capacity of poly(AMPS) gel in binary solvents of DMSO and selected polar solvents. Again, *o-c* patterns were observed here. Acetonitrile, as the solvent with the high dielectric constant after DMSO (Table II), exhibited a wide overentrant region. None of the solvents in the pure state could be absorbed by the gel. As far as related to dielectric constant (ϵ), the intensive collapse may be attributed to low values of ϵ . In addition, dissociation of the sulfonic acid group in each pure solvent will be more limited in comparison with the corresponding media containing

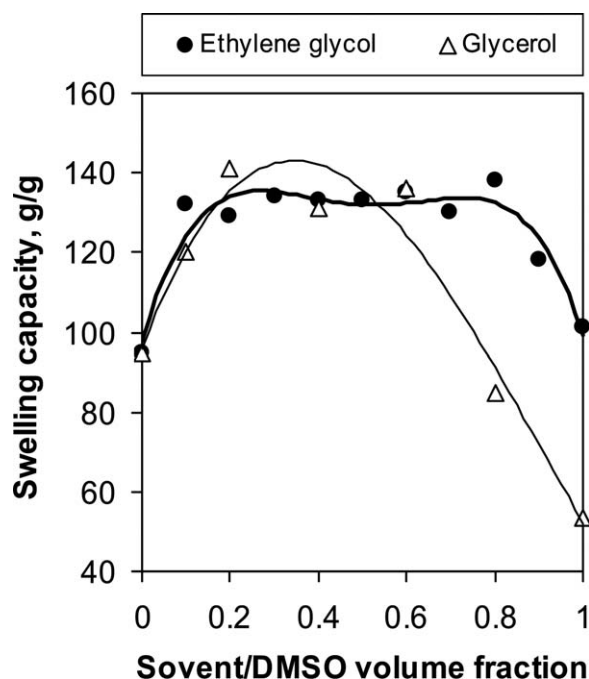


Figure 6 Variation of swelling capacity of poly(AMPS) gel in binary solvents of DMSO/polyhydric alcohols.

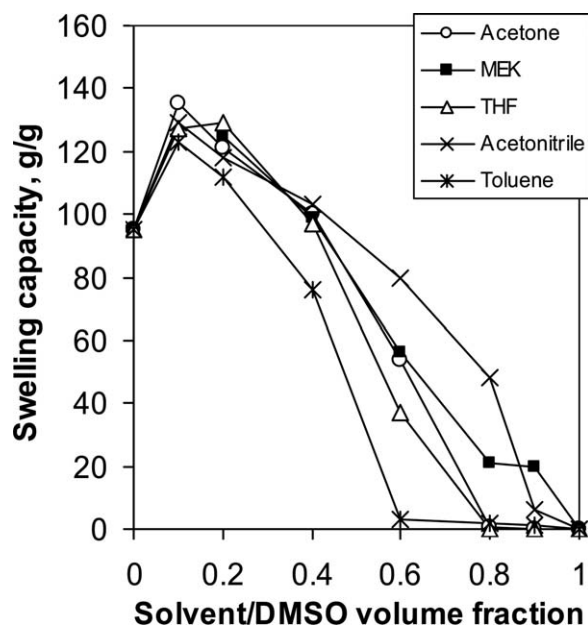


Figure 7 Variation of swelling capacity of poly(AMPS) gel in binary solvents of DMSO and selected polar solvents in comparison with toluene as a typical nonpolar solvent.

DMSO. Therefore, a significant factor for the swelling driving force, i.e., sulfonate-sulfonate repulsion, will be absent in these solvents in their pure state.

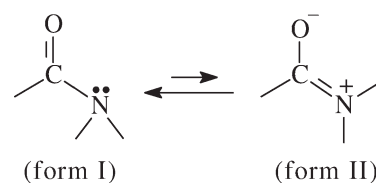
Meanwhile, toluene as a typical nonpolar solvent with minimum values dielectric constant was also examined. The swelling capacity in toluene/DMSO media passed a narrow overentrant region to collapse very intensively in the solvent/DMSO fraction of around 0.3.

Variation of swelling capacity of poly(AMPS) gel in binary solvents containing DMSO and solvents containing amide group was also examined (Fig. 8). In dimethylformamide (DMF)/DMSO, an *o-c* pattern was observed, while *o-c-r* sequences were monitored in the case of dimethylacetamide (DMAc)/DMSO and *N*-methyl pyrrolidone (NMP)/DMSO mixtures. This dissimilarity has to be somehow related to the chemical structure difference of the solvents, for example those concerning with the hydrogen bonding. Meanwhile, the absorbency of the pure solvent for DMF (80 g/g) is higher than that of DMAc (70 g/g) and NMP (45 g/g).

As the carbonyl of amide group of these solvents possesses the key role in the solvation, steric effects are also seemed to be involved in the amide solvent differentiation here. The surrounding area of the carbonyl group of DMF molecule is relatively more deserted than that of DMAc and NMP (Figs. 4d–4f). Therefore, the swelling behavior discrimination in DMF/DMSO in Figure 8 is well harmonized with its structural difference comparing to the other two amide solvents.

In the solvent/DMSO fractions less than ~ 0.7 (the overentrant region), however, the swelling values

and variations are similar. The very high swelling capacities either in the overentrant region (100–130 g/g) or in the pure amide solvents (45–80 g/g) can partially be attributed to the media with high dielectric constant and, therefore, high capability for dissociating the sulfonic acid group. This capability may be originated from the well-known polarizability of the amide bond of the solvent molecule via resonance formation³²:



DMF favors the resonance form II while NMP does not it, because form II intends to have a planar structure with ideal bond angle of 120° . In NMP, bond angles are restricted due to internal strain of the lactam ring. Therefore, form II will be thermodynamically disfavored; the circumstance leads to reduced dielectric constant of NMP in comparison with those of the noncyclic amide solvents DMAc and DMF.

Finally, an overall comparative re-consideration of Figures 4 and 6–8 may give us additional interesting results. Assuming a simple additive function of the concentration of solvents, the common method for calculating the dielectric constant of mixed solvents

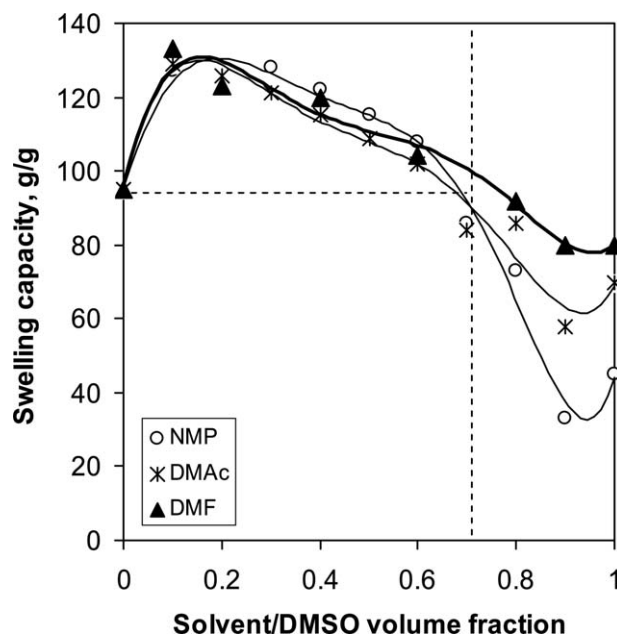


Figure 8 Variation of swelling capacity of poly(AMPS) gel in binary solvents containing DMSO and solvents containing amide group, i.e., dimethylformamide (DMF), dimethylacetamide (DMAc), and *N*-methyl pyrrolidone (NMP).

(ϵ_{mix}) based on the weighted average of the mixture components is written as eq. (1).³⁵

$$\epsilon_{\text{mix}} = \phi_s \epsilon_s + \phi_{\text{DMSO}} \epsilon_{\text{DMSO}} \quad (1)$$

where ϵ_s and ϵ_{DMSO} are dielectric constants of the solvent and DMSO, respectively, and ϕ_s and ϕ_{DMSO} are the volume fractions of the solvent and DMSO, respectively.

This equation obviously describes ideal solvent mixtures where no intermolecular interactions are assumed. It has been shown that the overall average percentage deviation for a variety of binary solvent mixtures including aqueous alcohols, ethanol/DMSO and 1-propanol DMSO was 6.39 (± 5.49).³⁵ However, it can give a rough estimation of ϵ_{mix} having sufficient usefulness for a preliminary comparative study here.

For each solvent, the maximum ϕ_s located in the overentrant region ($\phi_{s(\text{over})}$) is first determined and its corresponding ϵ_{mix} ($\epsilon_{\text{mix}(\text{over})}$) was then calculated using the aforementioned equation. Then, the plot of $\phi_{s(\text{over})}$ versus $\epsilon_{\text{mix}(\text{over})}$ can be drawn as Figure 9.

According to Figure 9, the region of the "overentrant" extraordinary phenomenon is progressed when dielectric constant of the solvent mixture is increased. That is why the most extensive overentrant areas were observed in the case of binary mixtures of polyhydric alcohol/DMSO as well as amide solvent/DMSO (Figs. 6 and 8).

Swelling behavior interpretation using concepts of the Gutmann's acceptor number and donor number

As implied for explaining the aforementioned empirical observation, the polymer-solvent intermolecular interactions are not the only cause of the strange behavior. Actually, an important part of these swelling characteristics are originated from variation of the dissociation degree (ionization) of the sulfonic acid group as a function of the solvent type and composition. Although these complicated circumstances cannot be easily explained (mainly due to lack of the literature data for the SO_3H dissociation degree in DMSO and the binary solvent mixtures), scientists have tried to create and use some empirical parameters to explain such solvent effects.

Satoh and coworkers^{25,28,29} employed the Gutmann-Mayer's acceptor number (AN)³⁶ to discuss their results from several polymers with ion- and solvent-specific swelling behaviors. As no general relationship exists between solvent polarity (that is reflected in dielectric constant) and ionizing properties (ability of the solvent to heterolyse covalent bonds), AN values can provide semiquantitative means to evaluate the solvent influence on the reac-

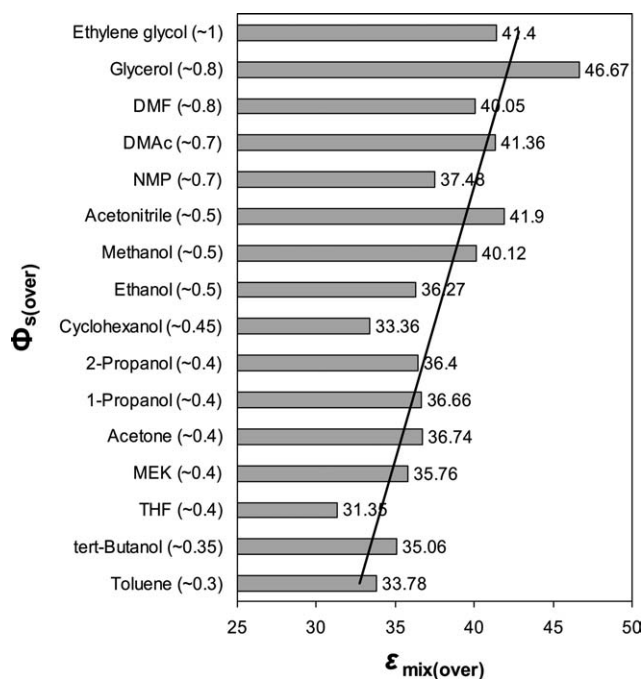
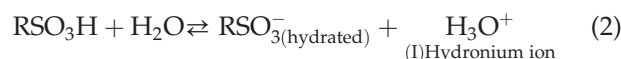
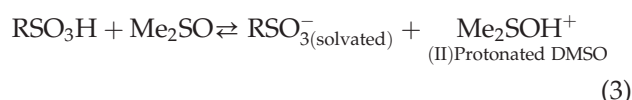


Figure 9 Plot of maximum ϕ_s located in the "overentrant" region ($\phi_{s(\text{over})}$) versus its corresponding ϵ_{mix} ($\epsilon_{\text{mix}(\text{over})}$) for the poly(AMPS) gel swollen in various solvent/DMSO binary mixtures. Approximate $\phi_{s(\text{over})}$ is written in the parentheses.

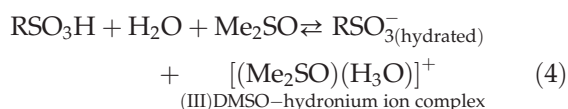
tions and solubility/swelling behavior of polymers. The AN values are dimensionless quantities (derived from ^{31}P -NMR measurements of triethylphosphine oxide (Et_3PO), a suitable model compound, dissolved in respective solvents) that represent a measure of the electrophilic properties of the solvents³⁶ (Table II). In fact, AN may be used as a measure of ability of solvation of anions, e.g., $-\text{SO}_3^-$. Namely, the higher the AN, the less favorable the contact ion-pair formation will be. Gutmann³⁷ has also quantified Lewis acidity and basicity using calorimetric measurements of interactions of a number of oxygen and nitrogen containing solvents (D) with SbCl_5 as a reference acceptor in dichloromethane. He defined the quantity $-\Delta H(\text{D}.\text{SbCl}_5)$ in kcal/mol to be the donor number (DN) of the solvent D (Table II).

According to AN and DN values given in Table II, the acceptor number of DMSO is lower than that of water (AN_{DMSO} 19.3 vs. AN_{water} 54.8). On the other hand, the donor number of DMSO is higher than that of water (DN_{DMSO} 29.8 vs. DN_{water} 18). It means that, in a pure solvent media, water favors the sulfonic acid dissociation (to give hydronium ion) more than what DMSO does [eqs. (2) and (3)]. It means that the dissociation capability of poly(AMPS) gel in DMSO is inferior than that in water.





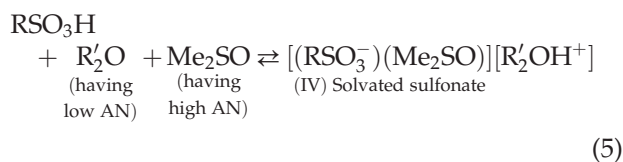
In the DMSO (Me₂SO)/H₂O mixed media, however, the organic solvent cause improved stability of the hydronium ion (I) and easy formation and stabilization of the sulfonate anion [eq. (4)]:



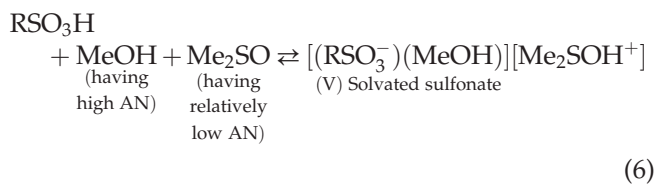
Here, DMSO interacts with the hydronium ion in special manner to form particular species assumed as complex (III), and therefore, favor the sulfonic acid dissociation more than that happened even in pure water. As a result, an overentrant swelling behavior is observed in DMSO/H₂O ratio of 0.4–0.7 (Fig. 1).

In media with very high DMSO fraction, the reaction (3) prevails over the system and leads to the partial collapse of gel. In media with very low DMSO (DMSO/H₂O ratio of 0–0.1; just before the re-entrant region), the small amount of DMSO cannot promote the reaction (4), and even probably interfere efficient sulfonic acid dissociation through hydration. Therefore, a partial swelling-loss is observed again. It should be pointed out that the supposing reactions here may not necessarily be written in a real stoichiometric manner, because the solvents quantity is very much higher than that of the polymer.

DMSO possesses the highest DN among the organic solvents used here. It means that DMSO has the most nucleophilic nature; but its tendency to accept electron (electrophilicity or AN value) is superior than that of solvents like THF and acetone, and inferior than that of solvents like methanol and ethanol (Table II). Therefore, for example in a THF (R'₂O)/water mixture [eq. (5)]:



With an assumption that the formation of complex (IV) favors highly the sulfonic acid dissociation, an overentrant swelling behavior is expected (Fig. 7, region of THF/DMSO ratio 0.1–0.4). Nevertheless, in methanol (MeOH)/DMSO mixture [eq. (6)]:

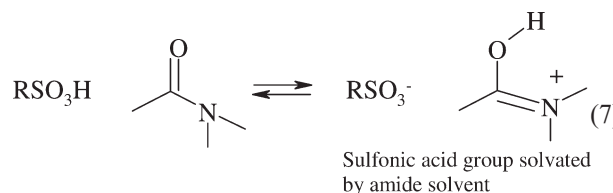


DMSO catches the proton of –SO₃H to protonate it. Then, with formation of the assuming complex (V), the solvation interactions highly favor the sulfonic acid dissociation resulted in an overentrant swelling behavior in MeOH/DMSO ratio of 0.1–0.4 as exhibited in Figure 4.

Ethanol, with a similar DN value of methanol, follows a similar manner lead to similar swelling behavior of the organogel in ethanol/DMSO mixtures (Fig. 4). However, 2-propanol with smaller AN value causes intense collapse in high ratio of alcohol/DMSO (e.g., pure 2-propanol), because it is a poorer solvent for the sulfonate anion and resulted in easier desolvation in comparison with methanol and ethanol (Fig. 4).

The overentrant swelling region is expanded when the OH functionality is increased (Fig. 6). The DN values are not reported for ethylene glycol and glycerol, however, DN values are expected to be higher than those of methanol and ethanol.³⁸ If so, the solvation interaction (6) will be logically promoted to the right side resulted in easier –SO₃H dissociation and wide-ranged overentrant behavior. However, this region for the triol is not as wide as the region of the diol (solvent/DMSO ratio of 0.1–0.6 vs. 0.1–0.9). In addition to the previously mentioned cause regarding viscosity, one reason may be related to the nature of DN values. The DN values reflect only enthalpic aspects of the solvation interactions. The solvation of glycerol may be disfavored entropically because of the triple OH functionality of this polyol.²⁸

The poly(AMPS) gel show similar swelling behavior and wide-ranged overentrant regions when put in DMSO binary mixtures containing amide solvents with similar DN values (DN 26–28) (Fig. 8). Since AN of DMSO (i.e., 19.3) is more than those of the amide solvents (i.e., 13–16), the solvation process is similar to what written for the reaction (5). As expected for the pure solvents (without DMSO), the organogel uptakes more volume of the solvent having higher AN, because such solvent is a good solvent for the sulfonate anion and can highly favors its solvation due to easy proton capture by the amide solvent [eq. (7)].



Overall, it seems that the unusual improvement of the swelling in this study, particularly the overentrant phenomenon, is even more than sum of all the interactive effects mentioned here; and a kind of synergism may be concerned. Deeper works are in progress to explain such complicated swelling behaviors in more details.

CONCLUSIONS

Swelling behavior of poly(AMPS) in different solvent/DMSO mixtures were studied. The main conclusions are as follows:

A new peculiar phenomenon, i.e., “overentrant” swelling, was observed for this gel in various solvent/DMSO mixtures. This behavior was attributed to strong polymer–solvent interactions involving the sulfonic acid group. Decreasing AMPS content (as poly(AA-AMPS) gels) caused disappearance of the overentrant swelling which practically confirmed the major role of sulfonic acid groups in the swelling phenomenon.

It should be considered that this behavior was not observed for poly(APMS) in DMSO-free solvent mixtures. Conventional continuous VPT had already been observed for poly(AMPS) in different water–solvent mixtures. This also indicated the importance of polymer–solvent interactions for poly(AMPS) in DMSO–solvent mixtures [Fig. 2(b)].

The “overentrant” behavior was observed for alcohol/DMSO mixtures as well (Fig. 4). The phase transitions of poly(AMPS) gel in these mixtures were explained based on parameters such as dielectric constant of alcohol, the alcohol viscosity and steric hindrance in the vicinity of the alcohol OH group. A reentrant behavior was observed for 2-propanol/DMSO mixture with alcohol fraction of around 0.8.

In amide solvent/DMSO mixtures, the “overentrant” and reentrant were observed for the poly(AMPS) organogel. Swelling capacity was higher in DMF/DMSO and DMAc/DMSO comparing with NMP/DMSO which was attributed to higher dielectric constant of DMF and DMAc. Finally, the “overentrant” region was found to be progressed with increase of dielectric constant of the solvent mixture.

To emphasis on the key effect of variation of the dissociation degree of the sulfonic acid group (as a function of the solvent type and composition) on the swelling behaviors, the swelling behaviors were also explained via a semiquantitative approach based on the Gutmann’s AN and DN values. Overall, the unusual swelling improvement in the overentrant region may also be attributed to some synergistic effects in the solvation processes involved in the DMSO contained media.

This article reflects just a preliminary report of some early observations of a number of extraordinary phenomena already reported very rarely. Deeper interpretation for the unusual VPT sequences and, particularly, the “overentrant” phenomenon need further investigations.

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