ABSTRACT

PolymERIC organogels, macromolecular networks with ability to imbibe polar or non-polar organic solvents, have recently been attracted by both academy and industry. These materials (called also polymer organogelator) can convert an organic liquid to a solid gel. Alcohol specific super-swelling organogels (i.e., super-alcogels) can be used for various applications such as fuel gels or pharmaceutical formulations. In this paper, super-alcogels were synthesized using a macromonomer (macromer), polyethylene glycol methylether methacrylate (PEGMA), and an ionic monomer, 2-acrylamido-2-methylpropane sulphonic acid (AMPS), through solution polymerization using a persulphate initiator and a macromeric cross-linker (polyethylene glycol diacrylate). The copolymers exhibited very high absorbency of various monohydric and polyhydric alcohols including methanol, ethanol, n-propanol, iso-propanol, ethylene glycol, propylene glycol, 1,3-propane diol and glycerol. For example, a typical sample imbibed ethanol and methanol as high as 33 and 36 g/g, respectively. It was found that several parameters had influence on swelling of an organogel such as: dielectric constant of the solvent, the alcohol OH/C (as a simple measure of the hydrophyl/organophyl ratio) and the isomeric position of hydroxyl group in the alcohol chemical structure. The dissociating ability of the ionic groups (i.e., SO₃H groups) was recognized to be mainly affected by dielectric constant of the solvent. Higher AMPS content in the alcogel structure improved alcohol absorbency because of increased sulphonic acid mobile ions in the gel phase. Thermal and mechanical properties of these copolymers were also studied. Glass transition temperature of the copolymer was decreased with increase of the macromer and the samples with high macromeric content showed elastomeric behaviour at room temperature in dry state. Thermal stability was improved with lowering of AMPS content due to susceptibility of sulphonic acid group at lower temperatures.

INTRODUCTION

Organogels are materials which can solidify organic solvents; they may be composed of low molecular weight or polymeric materials [1]. Polymeric organogels itself can be classified into physical and chemical organogels. Chemical polymeric organogels are three-dimensional macromolecular networks which can absorb and retain organic solvents [1]. Many research works have been published on physical organic gelators particularly based on the low molecular weight materials [2,3]. There are few reports about polymeric network organogels prepared through solution cross-linking polymerization. Recently, some research works have been published on preparation
of cross-linked polymeric organogels [4,5]. Sada et al. prepared an organogel for super-absorbing non-polar solvents based on octadecyl acrylate and an anionic monomer [4]. The organogel absorbs tetrahydrofuran and non-polar solvents such as toluene and benzene. Cross-linked poly(acrylic acid) was prepared using zinc oxide or nickel oxide as cross-linker for obtaining ethanol absorbing gel. The products could absorb ethanol to a maximum of 159 g/g [5]. Copolymers of acrylic acid with 2-acrylamido-2-methylpropane sulphonic acid (AMPS) were prepared through solution polymerization and their alcohol absorbency was investigated in different low molecular weight alcohols [6].

Organogels can be used in controlled release of fragrance and drugs [7-9]. Organogels with super-absorbency of alcohols such as ethanol and methanol are used as fuel gels, fire starters, hand sanitizers, etc. [6,10].

Macromers are macromolecular monomers used for synthesizing special polymers. As poly(ethylene glycol) (PEG) is biocompatible, PEG-based macromers are frequently employed to prepare bioactive and compatible polymers. Belleney et al. investigated terpolymerization of methyl methacrylate methacrylic acid with macromers such as PEG methyl ether methacrylate or PEG ethyl ether methacrylate [11]. Freeman et al. studied gas permeability in cross-linked poly(ethylene glycol diacrylate) [12]. Zhang et al. synthesized terpolymer electrolytes to be used in new batteries based on acrylonitrile-methoxy PEG (350) monoacrylate-lithium acrylate [13].

In this paper, for the first time macromer based on PEG methyl ether methacrylate is used for preparation of elastomeric alcohol absorbent gels (super alcoho-philic gels, super-alcogels). The macromer iscopolymerized with AMPS through solution polymerization using thermal initiator and macromeric cross-linker (PEG diacrylate). Alcohol absorbency, thermal and mechanical properties of these copolymers are studied in detail.

EXPERIMENTAL

Materials
Polyethylene glycol methyl ether methacrylate 350 (PEGMA, Aldrich, Switzerland), 2-acrylamido-2-methylpropane sulphonic acid (AMPS, Fluka, Switzerland), polyethylene glycol diacrylate 400 (PEGDA, Rahn, Switzerland) and ammonium persulphate (APS, Merck, Germany) were used as received.

Synthesis of Alcogel Absorbent
Solution polymerization was used for preparation of super-alcogels. The AMPS was dissolved in distilled water followed by addition of PEGMA and PEGDA. Table 1 shows the quantitative amounts of ingredients in each experiment. The solution was stirred and heated to maximum 60°C, and finally APS was added to the solution to initiate polymerization. Gelation was observed in less than 5 min for all samples, and then elastic product was cut to small pieces and dried for 6 h at 100°C. The obtained samples showed different appearance after drying. The samples at high and low macromonomeric contents were transparent elastic and opaque glassy, respectively. Glassy copolymers were grinded with hammer type minigrinder and the elastic copolymers were cut to small pieces for characterizations.

Table 1. Quantity of reactants used for preparation of AMPS-PEGMA organogels.

<table>
<thead>
<tr>
<th>Poly(AMPS-PEGMA) gel products with mol% of AMPS</th>
<th>Weight of reactants (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMPS</td>
<td>PEGMA</td>
</tr>
<tr>
<td>100</td>
<td>10.0</td>
</tr>
<tr>
<td>75</td>
<td>8.0</td>
</tr>
<tr>
<td>50</td>
<td>3.0</td>
</tr>
<tr>
<td>25</td>
<td>1.2</td>
</tr>
<tr>
<td>0</td>
<td>0.0</td>
</tr>
</tbody>
</table>
Characterization

Swelling Measurements
An amount of 0.100 g sample of final dried polymer was dispersed in 50 mL of desired alcohol and allowed to swell for 1 h to reach equilibrium. Dispersions were filtered individually through polyester gauze to remove the excess solvent. Then, hydrated gels were weighed. Equilibrium swelling (ES, g/g) was calculated by the following relationship.

\[ ES = \frac{(Q_2 - Q_1)}{Q_1} \]  

where \( Q_2 \) and \( Q_1 \) are weights of hydrated gel and dry gel, respectively.

Dynamic Mechanical Thermal Analysis
Dynamic mechanical thermal analysis (DMTA) of the powdery sample (mesh 35-100) was performed using a Polymer Laboratories Instrument. The experiments were carried out in the temperature range of 20°C to 200°C, heating rate of 10°C/min and frequency of 1 Hz.

Rheometry
The rheological measurements of the water-swollen gels (1.00 g sample in 5.0 mL distilled water) were performed using a Paar-Physica Oscillatory Rheometer (MCR300, Germany) with parallel plate geometry (plate diameter of 25 mm, gap of 3 mm) at 25°C. The detailed procedure was previously reported [14,15].

Thermogravimetric Analysis
Thermogravimetric analyses (TGA) of dry samples were performed using a TGA-Polymer Laboratories, England, in nitrogen atmosphere with heating rate of 10°C/min.

RESULTS AND DISCUSSION

A PEG monoacrylate (PEGMA) was copolymerized with the sulphonated monomer AMPS in the presence of PEG diacrylate as a cross-linker, in aqueous solution to prepare the super-alcogel networks. The chemical structures of the monomers and cross-linker are shown in Scheme I.

The alcohol absorbing products were evaluated in variety of alcohols as swelling media and further characterized by thermal analysis and rheometrical technique.

Alcohol Absorbency
Figure 1 shows absorbency in ethanol, methanol and water versus AMPS content in gel structure. Poly(PEGMA) homopolymer has low alcohol absorbency either in ethanol, methanol or in water. It can only absorb 4.4 g/g ethanol and 6.3 g/g methanol. This gel is non-ionic, therefore polymer-solvent interaction is the major factor in swelling. Copolymers with AMPS in their structure possess higher absorbency capability. Swelling capacity of copolymer with AMPS content of 25 mol% is 7.1 g/g in ethanol and 8.2 g/g in methanol.

Increase of the AMPS content in the copolymers improves alcohol absorbency, it is increased to 22.3 g/g and 24.9 g/g when AMPS content is 75 mol%. Ionic forces are involved in swelling of the copolymers due to presence of an anionic comonomer (AMPS) in the gel structure. The AMPS is a strong organic acid with high ability to dissociate SO₃H to produce mobile ions -SO₃⁻ [16]. Dissociation ability of sulphonic acid group is decreased with diminution of dielectric constant. Dielectric constants of ethanol and methanol are 25.3 and 33, respectively, which are...
significantly lower than that of water (i.e., 78.3) [6]. That is why all the homo- and copolymers here absorb water more than the alcohols (Figure 1). Sulphonic acid group can be dissociated without any need for neutralization due to its strong acid nature [16]. Neutralization is an essential requirement for involving ionic interactions for swelling enhancement in weak acids such as acrylic acid [16]. Dissociation of sulphonic acid group not only occurs in a very good solvent such as water, it can also be completed in poor solvent such as alcohols which are mostly taken as non-solvent for majority of organic polymers. The existence of mobile ions creates an osmotic pressure difference between the gel and solvent phases which leads to swelling enhancement in comparison with non-ionic PEGMA homopolymer. Increase in the ionic content of copolymers to 100% increased mobile ion density resulting in swelling enhancement.

The results showed that counter-ion binding at high ionic content does not occur in alcohols or it might occur partially. There is no evidence for ion-pair formation based on swelling studies, although DMTA studies show that ion-pair can be formed in poly(PEGMA-AMPS). Alcohols are poor solvents for these hydrophilic polymers. Dielectric constants of ethanol (25.3) and methanol (33) are considerably lower than that of water (78.3) [6]. The possibility of counter-ion binding ($\theta$) is increased with lowering dielectric constant of the solvent based on Osawa-Maning theory (eqn 2) [17].

$$\theta = 1 - \frac{DkTb}{e^2}$$

where $e$ is the electronic charge, $D$ is the dielectric constant of solvent and $b$ is charge spacing.

The swelling studies empirically demonstrate that in spite of dielectric constant diminution, the counter-ion binding does not occur. This shows that $H^+$ counter-ion has no tendency to form ion pairs in poor solvents. In our previous report we noted that Na$^+$ counter-ions have high tendency to form ion pairs in copolymers of sodium allylsulphonate and acrylic acid in ethanol and methanol [18]. The reason can be attributed to smaller size of H$^+$ in comparison with the Na$^+$ metal cation leading to reduced feasibility of the ion pair formation.

![Figure 1. Alcohol absorbency versus AMPS content of poly(AMPS-PEGMA) organogels.](image)

<table>
<thead>
<tr>
<th>Polyhydric alcohols</th>
<th>Dielectric constant</th>
<th>Alcohol absorbency (g/g) for the copolymeric super-alcogels with mol% of AMPS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>iso-Propanol</td>
<td>20.2</td>
<td>2.3</td>
</tr>
<tr>
<td>n-Propanol</td>
<td>20.8</td>
<td>4.5</td>
</tr>
<tr>
<td>Propylene glycol (1,2-propanediol)</td>
<td>27.5</td>
<td>7.0</td>
</tr>
<tr>
<td>1,3-Propanediol</td>
<td>35.1</td>
<td>12.7</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>41.4</td>
<td>14.6</td>
</tr>
<tr>
<td>Glycerol (1,2,3-propanetriol)</td>
<td>46.5</td>
<td>16.5</td>
</tr>
</tbody>
</table>
Table 2 shows swelling capacity of the organogels in different mono- and polyhydric alcohols. Alcohol absorbency is increased in all alcohols with increase of the AMPS content due to higher ionic interactions. Distinct differences are observed in alcohol absorbency for one sample in different swelling media. This can be attributed to several parameters. The most important parameter is dielectric constant of the solvent. Frequently, the higher the dielectric constant, the higher would be the alcohol absorbency (Table 2) [6].

The absorbency in water is higher than that in alcohols (Figure 1) due to higher dielectric constant of water. There are some alcohols with nearly equal dielectric constant such as n-propanol and iso-propanol (20.8 and 20.18, respectively), but they have different alcohol absorbency. For instance, the alcohol absorbency for the organogel containing 75 mol% AMPS is 8.6 g/g in n-propanol and 4.2 g/g in iso-propanol. This difference is possibly related to polymer-solvent interactions particularly through hydrogen bonding (H-bonding). H-bonding formation is higher in the case of n-propanol rather than iso-propanol. The iso-propanol is a secondary alcohol having two CH3 groups in its OH vicinity. Therefore, the steric hindrance of two methyl groups disfavour the H-bonding formation with the polymer. The n-propanol, however, is a primary alcohol; so it can form H-bonding more freely to imbibe higher volume of solvent. Actually, for similar reason the boiling point of n-propanol (97°C) is higher than that of iso-propanol (82°C).

In polyhydric alcohols, the alcohol absorption capacity is increased with increase in polyol dielectric constant. For example, the sample with 75 mol% AMPS absorbs ethylene glycol (EG), propylene glycol and glycerol as high as 17.9, 12.6 and 28.8 g/g, respectively. In spite of the higher dielectric constant of EG compared to ethanol, swelling of the organogel in EG is less than that in ethanol (Table 2, Figure 1). This may be attributed to higher viscosity of the glycol (~16 mPa.s) in comparison to its mono-ol counterpart, ethanol (~1.1 mPa.s). This behaviour is comparable with the corresponding behaviour of poly(acrylic acid-AMPS) organogel [6].

Overall, it can be concluded that the major factor having the main influence on alcohol absorbency is the ionic interactions. Ionic interactions are directly related to dielectric constant of the solvent. Dissociations of SO3H groups are increased with increase in solvent's dielectric constant. It increases mobile ion density in the gel phase which in turn increases osmotic pressure difference between the phases of gel and of solvent leading to increased alcohol absorbency. The second important parameter in alcohol absorbency is capability of H-bond formation. The viscosity of the solvent may also have impact on the swellability of the organogel. In the case of glycerol (a triol), yet, the presence of the PEG long chains in the polymer structure compensates in some way the very high viscosity of glycerol (934 mPa.s). Thus, the sample with 75 mol% AMPS absorbs this solvent as much as ~29 g/g. This result is not in agreement with the result reported for poly(acrylic acid-AMPS) gel [6]. The dissimilarity can primarily be related to high potential of glycerol OH-PEG hydrogen bonding formation.

**DMTA Studies**

Figure 2 shows tan δ versus temperature for poly(PEGMA) and poly(PEGMA-AMPS) containing 50 mol% of AMPS.

Based on the DMTA patterns, the glass transition temperature (T_g) of poly(PEGMA) is -31.1°C. This gel displays elastomeric behaviour at room temperature in contrast to conventional hydrogels which are mainly glassy at room temperature. This special characteristic allows us to cut the gel into any
desirable shape and to use it in other applications such as sealing material. Incorporation of AMPS in copolymer increases \( T_g \), which would be for instance -7.7°C for the sample containing 50 mol% of AMPS. The reason can be attributed to higher stiffness of AMPS units in comparison with the PEGMA homopolymer. Poly(PEGMA) includes flexible polyoxyethylene pendant chains which can move easily, so it exists in a rubbery state at room temperature. In contrast, poly(PEGMA-AMPS) possesses \( \text{SO}_3\text{H} \) groups having tendency for inter- and intra-molecular interactions which restrict the chain movements.

Another peak in the \( \tan \delta \) curve (Figure 2) is observed at 92°C only for the PEGMA-AMPS copolymer. The second \( T_g \) can be attributed to the cluster \( T_g (T_{gc}) \) [19]. Multiplets can be formed due to aggregation of ion-pairs which leads to development of the second \( T_g \). The peak between 0-50°C and 50-100°C can be attributed to the multiplet formation. The difference can be attributed to cross-link density of the clusters. Clusters having lower cross-link density appear between 0-50°C while the major transition due to multiplet formation occurs at 92°C.

It is reported that the second \( T_g (T_{gc}) \) is increased with increased ionic monomer content in the gel structure [19]. In some cases, the second \( T_g \) cannot be detected because \( T_{ge} \) is higher than decomposition temperature of polymer [19].

\( \tan \delta \) value before \( T_g \) is considerably higher in poly(PEGMA) than poly(PEGMA-AMPS). This indicates that the energy dissipation ability is decreased with incorporation of AMPS units to the gel structure. The PEGMA is a macromonomer with high flexibility; chain movements of PEGMA units are significantly easier than those of AMPS units with strong interactions.

Figure 3 shows storage modulus versus temperature for poly(PEGMA) and poly(PEGMA-AMPS) (AMPS content 75%). Homopolymer of poly(AMPS) is in glassy state whereas, homopolymer of poly(PEGMA) is in rubbery state at room temperature. Therefore, increase of the AMPS content which has higher stiffness in comparison with PEGMA leads to enhanced storage modulus.

**Rheological Studies**

Figure 4 shows storage modulus of water-swollen gel with various AMPS contents. Storage modulus does not have a regular trend with increased AMPS content. It is expected that increase of the flexible monomer (PEGMA) decreases the modulus. Homopolymer of poly(PEGMA) is in rubbery state at room temperature, therefore, it should display the lowest storage modulus. Nevertheless, the results (Figure 4) show such postulated trend is not exhibited by the samples. The increase of AMPS content from 0 to 75 mol% decreases the modulus. This observation probably indicates that more than one factor is involved in the modulus and AMPS content relationship. Poly(AMPS) has higher storage modulus which can be attributed to its higher stiffness compared to poly(PEGMA) having long flexible PEG chains. Unexpectedly, storage modulus is not decreased with increase of PEGMA in the copolymers, e.g. the modulus of the copolymer containing 75 mol% AMPS is lower than that of the copolymer containing...
Figure 4. Storage modulus versus angular frequency for organogels with different AMPS contents.

25 mol% AMPS. This observation testifies that another parameter acts to make such considerable changes of modulus here. This may possibly be attributed to the cross-link density variation of the gel structure. Storage modulus ($G'$) has direct relationship with cross-link density ($\nu_c$) (eqn 3) [21].

$$G' = \nu_c RT$$  \hspace{1cm} (3)

As reactivity ratios of monomer AMPS and the PEG macromers, i.e. PEGMA and PEGDA, have not been reported in the literature, most probably PEGMA has higher tendency to react with PEGDA instead of AMPS. The reason is the structural similarity of the comonomer PEGMA and the cross-linker PEGDA (Scheme I). AMPS has an acrylamide-based structure while the PEG macromers possess (meth)acrylic esters with polyoxyethylene long chains. Therefore, in the polymerization feed with high amounts of AMPS, some portions of cross-linker are not involved in the cross-linking process. The cross-linker chemically favours to react with the monomer having a structure like itself. As a result, cross-link density ($\nu_c$) is decreased with higher AMPS content which lowers the storage modulus, $G'$.

Thermogravimetric Studies

Figure 5 shows TGA thermogram for poly(AMPS), poly(PEGMA) and poly(AMPS-PEGMA) containing 50 mol% AMPS.

Initial decomposition temperature (IDT) is improved with lower AMPS content. IDT is 184, 204 and 232°C for poly(AMPS), poly(AMPS-PEGMA) and poly(PEGMA), in the order given. It can be attributed to instability of sulphonic acid group which can be degraded to SO$_2$ or SO$_3$ [22]. Similar observation was reported for blends of poly(AMPS) with poly(vinyl alcohol) (PVA) and poly(vinyl pyrolidone) (PVP) [22]. The blends of PVP or PVA with poly(AMPS) have lower thermal stability than pristine PVP or PVA. According to Qiao et al. [22], weaker hydrogen-bond formation between PVP or PVA with poly(AMPS) decreases the thermal stability. A higher probability of hydrogen bonding with increase in AMPS content is also reported for poly(acrylic acid-AMPS) copolymerization [6]. The bulky pendant groups of AMPS would weaken the feasibility of H-bond formation between carboxylic groups of poly(acrylic acid) [6].

Char yield shows an inverse trend with increases in AMPS content. It is increased with increase of AMPS content. Poly(AMPS) demonstrates several decomposition stages while poly(PEGMA) exhibits a sharp transition in TGA thermogram (Figure 5). Strong H-bonding causes poly(PEGMA) to show thermal stability as high as 324°C. At higher temperature, however, the PEG polyacrylic structure...
is degraded to remove some species of oxyalkanes, CO₂, etc. The degradation of repeating unit which has a high weight percentage contribution of PEGMA results in sharp thermal transition.

CONCLUSION

The copolymers of AMPS and PEGMA are synthesized in this study. The main conclusions are as follows: The organogel has ability to absorb and retain variety of alcohols as high as 2 to 36 g/g depending on the copolymer composition. Increase in AMPS content enhances alcohol absorbency due to increased mobile ion density in alcohol medium. The sulphonated copolymeric networks have significant advantage over the gels containing sodium styrene sulphonate or sodium allyl sulphonate which have been reported before [18]. In the present work by using AMPS there would be no need to additional acid treatment; a process which was necessary for previously reported organogels having sodium sulphonate groups (as earlier gels had high potential for counter-ion binding in organic solvents and therefore, Na⁺ had to be removed through acid treatment from gel structure to achieve high alcohol absorbency).

Swelling measurements in other alcohols show that the ionization degree, dielectric constant and steric hindrance have influence on swelling capacity in alcohols. Swelling capacity is increased with enhancing dielectric constant of the solvent and increasing the ionic groups in organogel structure.

Elastomeric behaviour is observed for the samples with high PEGMA content. These gels can be proper candidates for sealing application like superabsorbent hydrogels [23,24] in addition to the organogel applications.

Storage modulus of the water-swollen samples shows an inverse trend with increase of AMPS content, which is attributed to either polymer structure or the cross-link density. Thermal stability of the copolymers is improved with decreases in AMPS content which is attributed to lowering H-bond formation due to bulky pendant group of AMPS.

Due to their ability for alcohol superabsorbency, these gels can be used as fuel gel for warming, cooking or boiling water. They can also be used for hygienic applications such as sanitizers and controlled release of fragrance and drugs.

REFERENCES


