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Cationic highly alcohol-swellaable gels: synthesis and characterization

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Abstract Cationic alcogels (alcohol-absorbing gels) based on acrylamide and methacrylamidopropyltrimethyl ammonium chloride (MAPTAC) were synthesized using solution polymerization in the presence of ammonium persulfate as an initiator and poly(ethylene glycol) diacrylate as a crosslinking agent. The swelling capacities of the gels in alcohols (i.e., methanol and ethanol) were investigated. The swelling capacities of the alcogels increased with increasing MAPTAC content, and the prepared gels had the ability to absorb up to 105.5 g/g methanol and 73.3 g/g ethanol, respectively. An ability to absorb more than 100 g/g of alcohol was only rarely observed. According to the results of rheological studies, the storage moduli of the ethanol-swollen gels were higher than those of the methanol-swollen gels, and enhancing the MAPTAC content caused the storage moduli of the gels to increase. Thermomechanical analysis was carried out to characterize the organogels. The values for the glass transition temperature (T_g) implied that the structural rigidity of the acrylamide homopolymer is higher than that of the poly(MAPTAC), which indicates that the presence of the MAPTAC units softens the system. The DMTA results showed that the intensity of the $\tan\delta$ peak in the matrix region decreased with increasing MAPTAC content. Thus, acrylamide units are better than MAPTAC units at damping dynamic forces, which can be attributed to the greater chain mobility of acrylamide.

Keywords Organogel · Alcogel · Acrylamide · Methacrylamidopropyltrimethyl ammonium chloride · Swelling

Introduction

A gel may be defined as a soft, solid-like material composed of solid and liquid components in which the solvent (liquid component) is immobilized within the three-dimensional solid network as a result of surface tension and capillary forces. Gels are commonly used in our daily lives and have a broad range of applications in food, medicine, biomaterials, separation, contact lenses, and cosmetics [1–3]. There are a variety of ways to classify a gel, based on its source, the nature of the solvent, the constitution of the gel, and the type of crosslinking that is present in the 3D network [4, 5]. Gels are separated into two categories according to the gel source: natural and synthetic gelators. Natural gelators are macromolecules such as gelatin, collagen, agar, and starch that form gels by physical crosslinking, whereas synthetic gelators are further subdivided into supramolecular and macromolecular gelators that form gels via physical interactions and chemical crosslinking, respectively. Physical gels are formed due to the presence of weak noncovalent interactions (hydrogen bonding, van der Waals forces, π – π stacking), and are thermoreversible: they can be transformed into fluids by heating. Chemical gels, on the other hand, are held together by covalent bonds, cannot be redissolved, and are thermally irreversible [6]. Gels can also be classified into organogels and hydrogels. Organogels, in contrast to hydrogels, utilize an organic solvent and are subdivided according to the nature of the gelling molecule into polymeric or low molecular weight organogelators (LMWO) [7]. Organogels are used in the controlled release of drugs [7], the surfactant industry [8], hand sanitizers, and fire starters [9]. There has been a lot of research into organogels based on low molecular weight organic gelators (molecules with molecular weights of <3,000 Da) [1, 2, 10–19], but few studies have focused on chemical polymeric organogels. For instance, syndiotactic polystyrenes form organogels in chloroform, carbon tetrachloride, and benzene [20]. Atactic polystyrene dissolves in organic solvents and

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does not exhibit organogel formation, while stereoregular polystyrenes show gelation in some organic solvents. In the same way, it has been reported that syndiotactic poly(methyl methacrylate) forms a thermoreversible organogel in bromobenzene, chlorobenzene, and toluene [21]. Also, the organogelation of poly(*N,N*-dimethylacrylamide) (PDMA) copolymers has been observed; the resulting organogel has dihydroperfluorodecanoyl pendant groups connected to the polymer backbone via poly(ethylene glycol) chains with 23–336 ethylene oxide units [22]. These copolymers form organogels in organic solvents such as benzene, dioxane, tetrahydrofuran, and methanol. Recently, some research into the preparation of crosslinked polymeric organogels with three-dimensional networks that can absorb and retain large amounts of organic solvents has been published. Rao et al. prepared elastic superhydrophobic silica aerogels synthesized using methyltrimethoxysilane (MTMS) as a precursor by a two-step sol–gel process followed by supercritical drying [23]. The aerogel absorbed nearly 15 times its own mass in organic liquids and oils such as toluene, xylene, octane, butanol, and diesel. Sonmez and Wudl prepared a series of crosslinked poly(orthocarbonate)s (CPOCs) through the condensation of tetraethyl orthocarbonate and different diol and triol monomers at moderately high temperatures [24]. All of the polymers were insoluble in organic solvents such as tetrahydrofuran, dichloromethane, and dichloroethane, but they rapidly absorbed large quantities of those fluids. Sada et al. synthesized lipophilic polyelectrolyte gels based on tetraalkylammonium tetraphenylborate (a lipophilic and bulky ionic group) and octadecyl acrylate, which were able to absorb nonpolar solvents such as dichloromethane, THF, chloroform, and chlorobenzene but not polar solvents such as methanol [25]. Among organogels, those with the ability to absorb alcohols (alcogels) have been a target for research in recent years. For example, several articles have reported that copolymers based on sulfonated monomers (anionic monomers) such as 2-acrylamido-2-methylpropane sulfonic acid (AMPS) [9, 26, 27], sodium allyl sulfonate (SAS) [28], and sodium styrene sulfonate (SSS) [29] have high potential for use as alcogels, and that alcohol is absorbed into such structures due to the dissociation of the ionic groups of the sulfonated monomers, while alcogels based on cationic monomers have only rarely been studied.

In the work described in the present article, acrylamide-based alcogels were synthesized through solution polymerization using methacrylamidopropyltrimethyl ammonium chloride (MAPTAC) as a cationic ionizable comonomer in the presence of poly(ethylene glycol) diacrylate (PEGDA 400) as a crosslinker and ammonium persulfate as an initiator. To the best of our knowledge, this is the first time that the synthesis and characterization of cationic alcogels have been reported. All previous reports in this field have focused on anionic or nonionic alcogels (Table 1). However, it should be noted that the swelling data are not necessarily comparable among alcogels

due to the utilization of different types of crosslinker and polymerization conditions, and (especially) the presence of different degrees of crosslinking in the alcogels (the degree of crosslinking mainly depends on the concentration and type of crosslinker as well as the reactivity ratio of the monomers).

Experimental

Materials

Methacrylamidopropyltrimethyl ammonium chloride (MAPTAC, Aldrich, St. Louis, MO, USA), acrylamide (AM, Merck, Darmstadt, Germany), ammonium persulfate (APS, Merck), poly(ethylene glycol) diacrylate (PEGDA 400, Rahn, Zurich, Switzerland), and water-miscible solvents (all from Merck) were used as received.

Synthesis of poly(AM-MAPTAC)

The solution polymerization reaction of acrylamide and MAPTAC was performed in a 100-mL glass reactor. The

Table 1 Comparison of the characteristics of the cationic alcogel prepared in the present work with those of previously reported anionic or nonionic alcogels

Polymer structure	Chemical nature	Maximum ethanol absorption (g/g)	Maximum methanol absorption (g/g)	Reference
AA ^a -AMPS	Anionic	58	65	[9]
AM-AMPS	Nonionic/anionic	24	32	[27]
AA-SAS	Anionic	25.8	39.5	[28]
AA-SSS	Anionic	46	75	[29]
AMPS-PEGMEMA ^b	Anionic/nonionic	33	36	[30]
VPA ^c -PEGMEMA	Anionic/nonionic	15.1	17.8	[31]
AA	Anionic	159	—	[32]
IPN ^d PAANA ^e -AMPS	Anionic	21	39	[33]
AM-MAPTAC	Nonionic/cationic	73.3	105.5	Present work

Dissimilar types of crosslinker, polymerization conditions, and degrees of crosslinking mean that the swelling data are actually not necessarily comparable, but a comparison of the results is generally informative

^a Acrylic acid

^b Poly(ethylene glycol methyl ether methacrylate)

^c Vinyl phosphonic acid

^d Interpenetrating polymer network

^e Poly(sodium acrylate)

Table 2 Amounts of monomers used in the polymerization and copolymerization reactions to prepare polymeric and copolymeric gel samples

MAPTAC (mol %)	AM (mol %)	MAPTAC (g)	AM (g)	Sample code
0	100	0	10.0	S1
20	80	6.0	8.0	S2
40	60	12.4	6.0	S3
60	40	18.5	4.0	S4
80	20	24.7	2.0	S5
100	0	30.9	0	S6

required proportions of these monomers were dissolved in water and the amounts of them used in each experiment are given in Table 2. Briefly, the crosslinker (0.10 g PEGDA 400 in 2.0 mL H₂O) along with the thermally induced initiator (0.10 g APS in 1.0 mL H₂O) were added to the monomer solution. In order to initiate the polymerization, we used a water bath (70 °C) and stirrer. After gelation, the obtained products were cut into small pieces and dried in a forced-draft oven at 50 °C for 4 h. The dried products were ground by a minigrinder and kept in a dry place. The structure of the copolymer is shown in Scheme 1.

Swelling measurements

A 0.10-g sample of the dried polymer (mesh 35–100, i.e., 150–430 μm) was dispersed in 50 mL of the desired medium and allowed to completely swell for 1 h and reach equilibrium swelling (the maximum absorbency) at room temperature. The swollen gels were then filtered through a polyester gauze to remove the excess solvent before they were weighed. The swelling capacity (g/g) was measured by dividing the weight of the swollen gel by the weight of the initial dried sample.

FTIR spectroscopy

Fourier transform infrared (FTIR) spectra of the dried samples in KBr pellets were recorded at room temperature (in the range 400–4,000 cm⁻¹) using an ABB Bomem (Zurich, Switzerland) MB-100 FTIR spectrophotometer.

DMTA

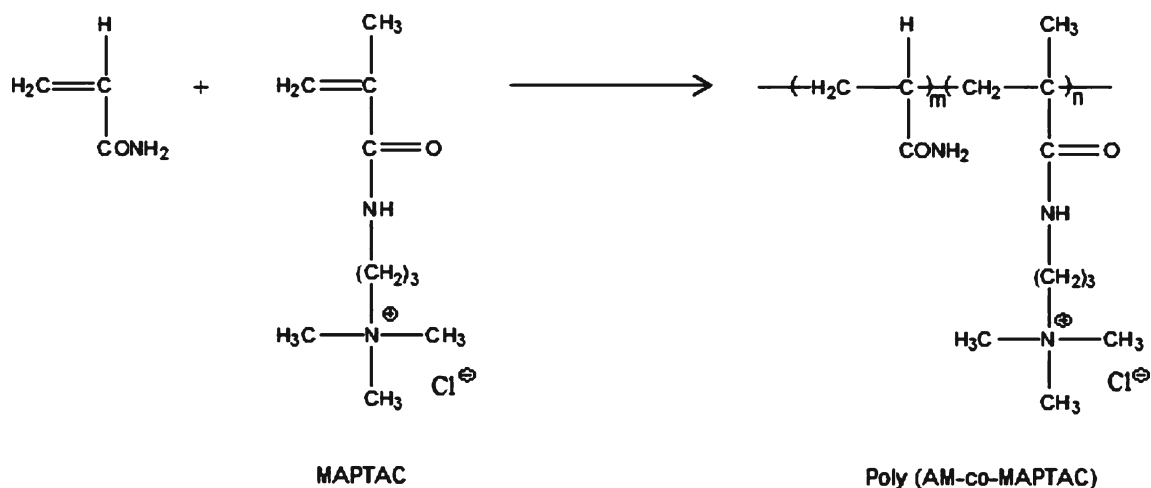
Dynamic mechanical thermal analysis of the dried powdery samples was performed using a Polymer Laboratories instrument (Palo Alto, CA, USA). The experiments were carried out at temperatures ranging from 10 to 250 °C, which were accessed at a heating rate of 10 °C/min, and a frequency of 1 Hz.

TGA

Thermogravimetric analyses of the dried samples were performed using a Polymer Laboratories PGA in the temperature range 25–600 °C under a nitrogen atmosphere, with heating performed at a rate of 10 °C/min.

Rheometry

The rheological measurements of the ethanol- and methanol-swollen gels (0.40 g sample in 2 mL ethanol and 0.20 g sample in 5.5 mL methanol) were performed with a Paar-Physica (Ashland, VA, USA) MCR300 oscillatory rheometer at 25 °C with a parallel plate geometry (plate diameter = 25 mm, gap = 3 mm). The detailed procedure was reported previously [34].

**Scheme 1** Structure of poly(AM-co-MAPTAC) alcogel

Results and discussion

Swelling studies

Figures 1 and 2 show the swelling capacities of the samples in ethanol, methanol, water, and salt solutions. As is expected, due to the high dielectric constant of water (78.3), synthesized polymers swell more in water than in methanol (33) and ethanol (25.3), due to the greater dissociation of the ionic groups of the synthesized polymers in water. Accordingly, dissociation ability decreases with decreasing dielectric constant. Generally, four factors (polymer–solvent, ionic, elastic, and electrostatic interactions) are involved in the swelling of the gels. Poly(AM) had the lowest absorbency in all of the swelling media because this gel does not contain any ionizable groups, so only elastic interactions and polymer–solvent interactions play major roles in its swelling. The most important influence on the absorption of the gel is the degree of dissociation of its ionic groups. The swelling capacity of the alcogel clearly increases with increasing MAPTAC content. MAPTAC is an ionic monomer that readily dissociates in swelling media, generating mobile ions. The existence of these mobile ions leads to an osmotic pressure difference between the gel and solvent, and the solvent has the ability to enter the gel, which leads to greater swelling than seen for a nonionic acrylamide homopolymer. This behavior is termed the polyelectrolyte effect [35].

In our study, gel collapse was not observed for the gels in methanol and ethanol. This meant that we achieved the goal of this work: to prepare alcohol-absorbing gels. Distinct variations in alcohol absorbency were observed for one sample in various swelling media, which can be attributed to the different dielectric constants of the solvents. Therefore, all of the samples can be expected to show more swelling with methanol than with ethanol. The alcohol absorbency increased in methanol and ethanol with increasing MAPTAC content due to enhanced ionic interactions. In anionic alcogels, the negative

charge tends to prompt ion exchange, which leads to increased gel stiffness. As a result, the absorbency of an anionic alcogel is low. In our cationic alcogel because of its bulkiness, the attraction between counterions of MAPTAC is weaker than anionic alcogels [36]. Hence, cationic alcogels show enhanced alcohol absorbency compared to anionic alcogels.

The second most important parameter in alcohol absorbency is the capacity to form hydrogen bonds. Hydrogen bonds between amide groups and hydroxyl groups of alcohols also contribute to alcogel swelling, although free ions are more important to the swelling process than hydrogen bonds are.

The swelling characteristics of superabsorbents are affected by the presence of ionic salts in aqueous solutions. The nature of the external solution in which the gel is swelled, the ionic strength of the solution, and the charge valence of the ions in the solution are reported to be the factors that influence the swelling characteristics to the greatest degree [37, 38]. Figure 2 shows the swelling capacities of the prepared samples in NaCl and CaCl₂ solutions. The ionic gels swelled less in saline solutions than in water [39], and enhanced absorbency in NaCl and CaCl₂ solutions was also observed when the MAPTAC content was increased from S1 to S6. In this study, the same salt concentration was chosen (0.15 M) but with different ionic strengths. The ionic strength of a salt can be calculated using the following equation:

$$I = \frac{1}{2} \sum_{i=1}^n c_i z_i^2, \quad (1)$$

where I is the ionic strength, c_i is the molar concentration of ion i , z_i is the charge on ion i , and the sum is performed over all ions in the solution. In solutions with high ionic strength (e.g., $I=0.45$ for CaCl₂ solution) as compared to those with low ionic strength (e.g., $I=0.15$ for NaCl solution), the osmotic pressure difference between the gel and the external solution is

Fig. 1 Effect of MAPTAC comonomer content on the pure ethanol and methanol absorption capacities of poly(AM-MAPTAC) organogels

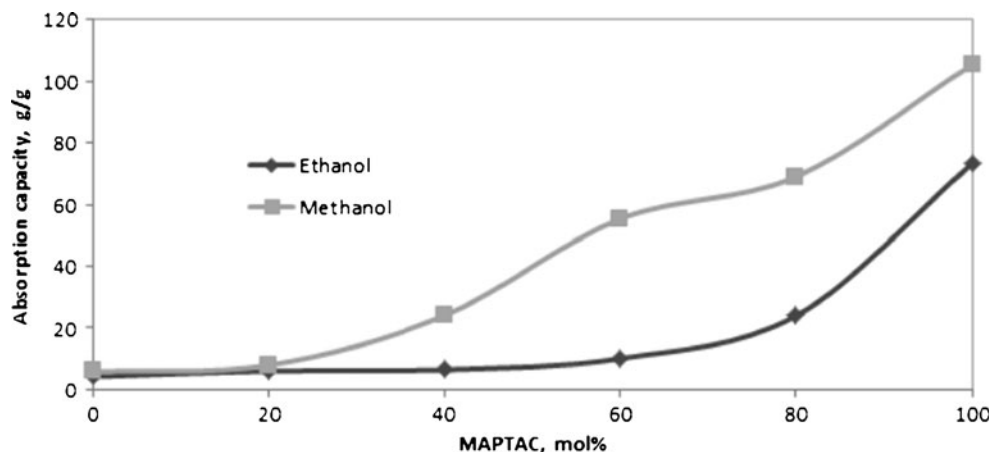
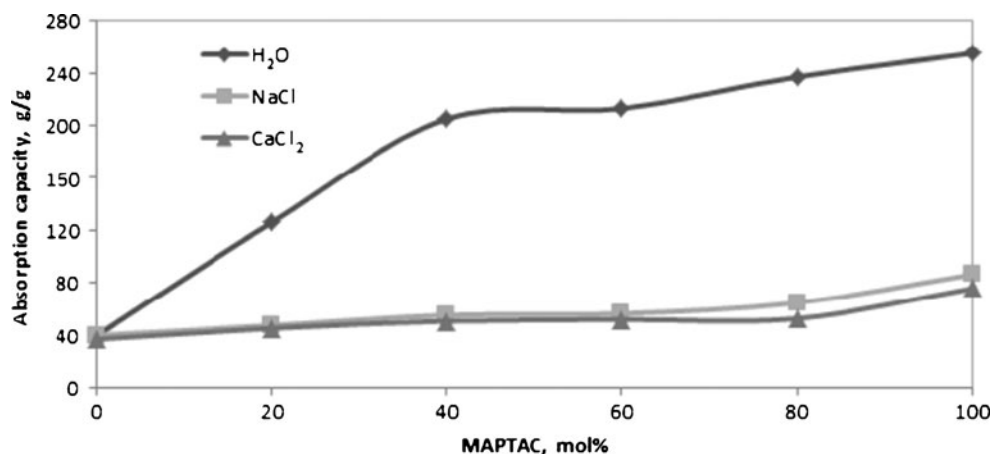


Fig. 2 Effect of MAPTAC comonomer content on the capacities of poly(AM-MAPTAC) organogels to absorb aqueous solutions (H_2O , 0.15 M NaCl, and 0.15 M CaCl_2)



lower, reducing the swelling. Also, in solutions with high ionic strength, ionic complexation reactions between the quaternary amino group of MAPTAC and the ion are more probable than in low ionic strength solutions, which increases the crosslink density. Thus, the final amount of swelling is less. However, in low ionic strength solutions, the repulsive electrostatic forces are exerted across a wider area, and the network expands to minimize the repulsive free energy [40].

Spectral characterization

The chemical structures of the gel samples were characterized by infrared spectroscopy. The FTIR spectra of the homopolymers (PMAPTAC and PAM) and a copolymer of AM-MAPTAC are shown in Fig. 3.

The IR spectrum of PMAPTAC showed a characteristic peak at $3,478\text{ cm}^{-1}$ corresponding to N–H stretching, a sharp absorbance at $1,656\text{ cm}^{-1}$ attributed to the carbonyl group of the MAPTAC unit, a peak at $1,546\text{ cm}^{-1}$ related to N–H bending, and a feature due to CH_3 bending at $1,400\text{ cm}^{-1}$. The IR spectrum of PAM showed strong peaks at $3,453$ and $3,303\text{ cm}^{-1}$ that can be attributed to NH_2 stretching, a strong

peak due to carbonyl stretching at $1,654\text{ cm}^{-1}$, and a peak due to CH_2 bending at $1,461\text{ cm}^{-1}$. Comparison of the IR spectra of the homopolymers with the IR spectrum of poly(AM-co-MAPTAC) showed that the characteristic absorption bands of both homopolymers appear in the spectrum of the AM-MAPTAC copolymer, indicating that the copolymerization reaction was carried out successfully.

Thermogravimetric analysis

TGA is a powerful technique for determining the thermally stable ranges of polymers and evaluating the conditions associated with polymer degradation. TGA thermograms of dried poly(AM), poly(MAPTAC), and poly(AM-MAPTAC) containing 60 mol% MAPTAC are shown in Fig. 4.

The thermogram of PAM showed three steps during its mass loss. The first weight loss, at $40\text{--}220^\circ\text{C}$, was related to moisture removal, with the sample losing 10.5 % of its weight. The second weight loss (the sample lost 19 % of its weight), at $220\text{--}350^\circ\text{C}$, was attributed to the thermal decomposition of the amide side groups, which leads to the release of ammonia and other gaseous species from the polyacrylonitrile structure

Fig. 3 FTIR spectra of poly(AM) (S1), poly(AM-co-MAPTAC) (S4), and poly(MAPTAC) (S6) gels

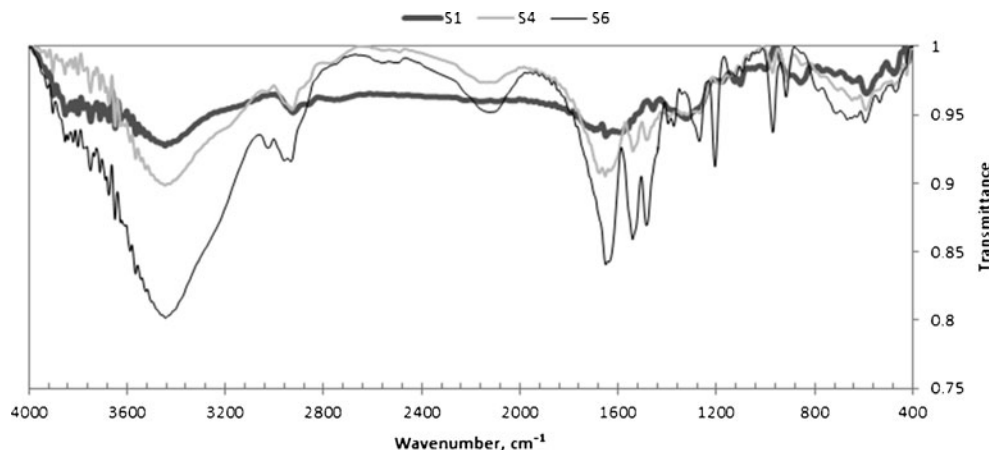
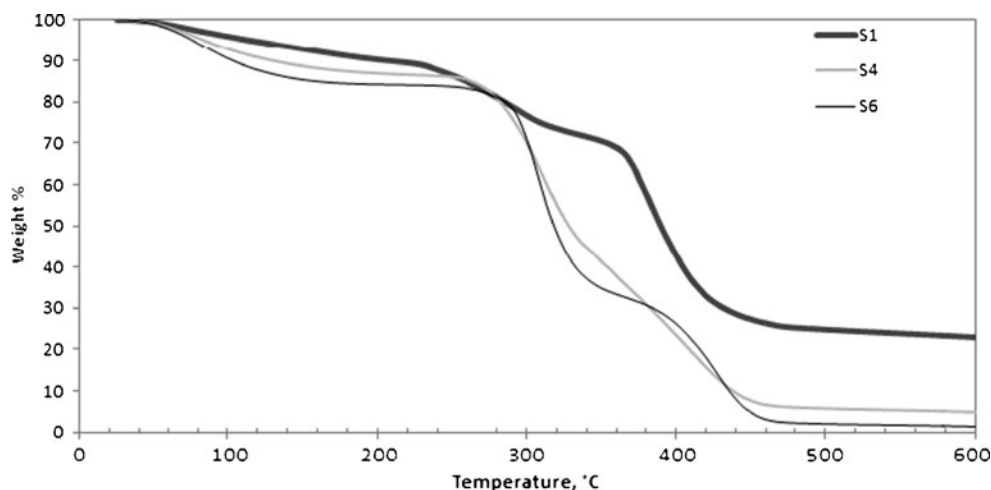


Fig. 4 TGA thermogram of a poly(AM-MAPTAC) sample with 60 mol % MAPTAC (S4) along with those for homopolymers of AM (S1) and MAPTAC (S6)



formed during the decomposition of PAM [41]. In the third step, a sharp weight loss (43.4 %) occurred at 350–450 °C, which may have been due to polymer backbone degradation, and the final decomposition temperature (FDT) was observed to be 460 °C. The thermogram of PMAPTAC showed that more weight was lost (15.6 %) in the temperature range 40–220 °C compared with that lost from PAM, which indicates that it had more bound water and a more hydrophilic polymer network [36]. Moreover, the sample lost 49.2 % and 30.1 % of its weight at 220–350 °C and 350–450 °C, respectively. The final decomposition temperature was also observed to occur at 460 °C. The thermal data shown in Fig. 4 are consistent with corresponding data reported in other papers [42]. Therefore, up to 350 °C, PAM lost 29.5 % of its weight, while PMAPTAC lost 64.8 % of its weight. On the other hand, PMAPTAC lost less weight than PAM at 350–450 °C, which suggests that its backbone is more thermally stable. The char yield of PMAPTAC was approximately zero, which can be ascribed to the absence of any mineral materials, while that of PAM was 23 %. The thermogram of the copolymer was located between those of its homopolymers, indicating somewhat intermediate thermal stability.

Thermomechanical analysis

DMTA tests were performed on the samples to investigate their glass transition temperatures (T_g) and storage moduli in the temperature range 0–250 °C. Typical storage moduli and $\tan\delta$ curves for PAM, PMAPTAC, and the copolymer of them in the solid state are presented in Figs. 5 and 6, respectively.

The maximum $\tan\delta$ is assumed to correspond to the glass transition temperature of the polymer [43]. PAM displayed two glass transition temperatures (T_g); the first appeared at 99 °C and the second at 244 °C. The first T_g corresponded to that of the polymer matrix (T_{gm}) and the second (the complex glass transition temperature, T_{gc}) can be attributed to the inter- and intrachain complexes that form due to hydrogen bonding. Two glass transition temperatures were also observed for PMAPTAC (see Fig. 6). The glass transition temperature of PMAPTAC was found to be 65 °C (T_{gm}), which was less than that of PAM. In PAM, amide groups are more able to form hydrogen bonds, which restrict chain movements and hence raise the glass transition temperature. There is another peak for poly(MAPTAC) at about 144 °C. The second T_g can be ascribed to the formation of clusters resulting from the

Fig. 5 Plot of storage modulus versus temperature from DMTA analysis for the PAM (S1), poly(AM-MAPTAC) with 60 mol % MAPTAC (S4), and PMAPTAC (S6) gels

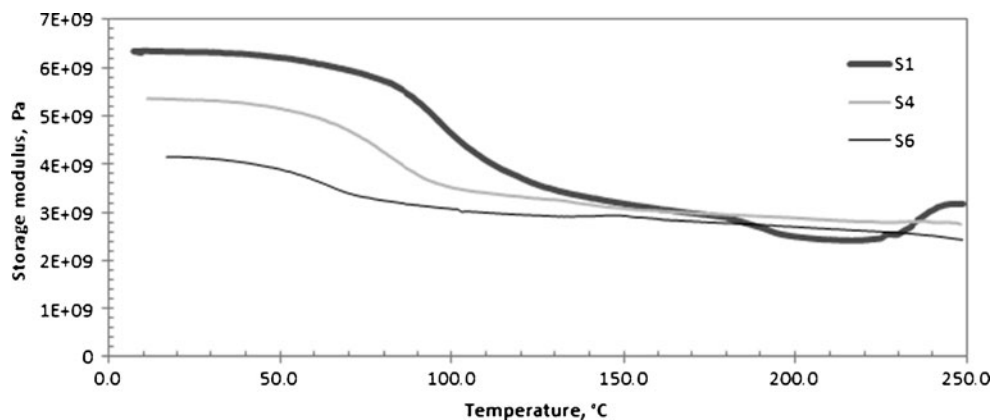
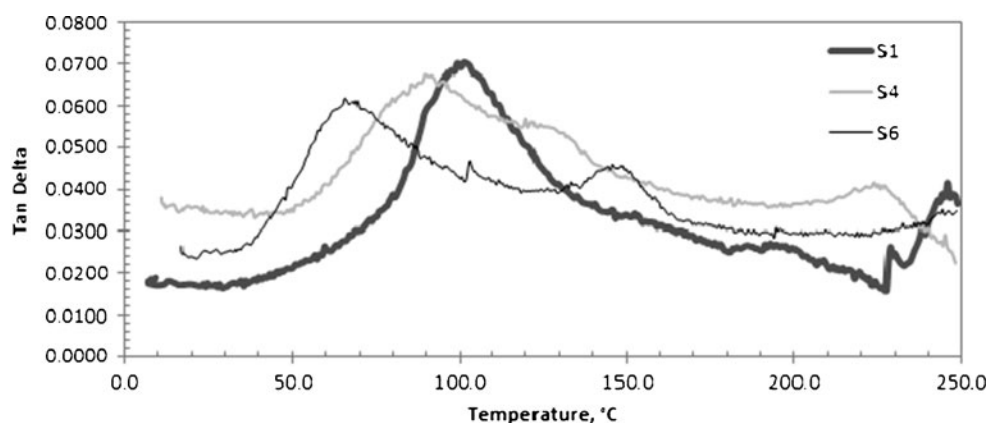


Fig. 6 Plot of $\tan\delta$ versus temperature for PAM (S1), poly(AM-MAPTAC) containing 60 mol % MAPTAC (S4), and PMAPTAC (S6)



association of ion pairs. The T_g due to clusters (T_{gc}) can be seen in polymers with ionic groups [44] and it increases with increasing ionic monomer content in the gel structure. In some cases a second T_g is not observed because T_{gc} is higher than the decomposition temperature of the polymer [45]. These T_g values insinuate that the structural rigidity of the acrylamide homopolymer is higher than that of PMAPTAC, which indicates that the inclusion of MAPTAC units softens the system. Maximum $\tan\delta$ values of 0.070, 0.065, and 0.060 were recorded for PAM, poly(AM-co-MAPTAC), and PMAPTAC, respectively. These results show that the intensity of the $\tan\delta$ peak in the matrix region decrease with increasing MAPTAC content. Acrylamide units are more able to damp dynamic forces than MAPTAC units are, which is due to the high chain mobility of acrylamide compared with the high steric hindrance of MAPTAC. The small values for the damping factor (0.060–0.070) can be attributed to crosslinking. Multiplet formation via the aggregation of ionomers leads to increased crosslink density [46]. Increasing the crosslink density further restricts the movements of the chains in the gel network and reduces its damping ability. The storage modulus for the copolymer decreases in a single-step pattern in Fig. 5, which shows that the copolymer has a random structure. A two-step decrease in storage modulus is often seen for block copolymers [47]. The increase in the storage modulus at 220–240 °C for

PAM is related to complex formation, which can increase crosslink density.

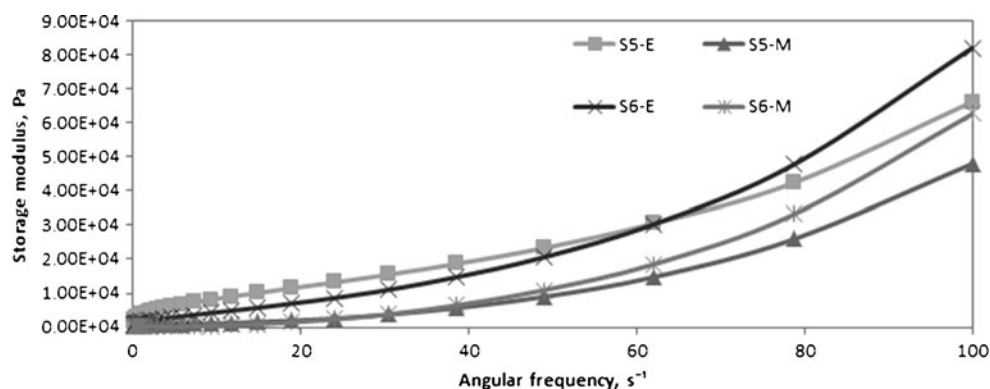
Rheological studies

The swelling capacity of the gel under an external load is one of the most important properties of gels. To evaluate the mechanical stiffnesses of the swollen gels and the effects of the MAPTAC content on them, the ethanol-swollen gel strength and methanol-swollen gel strength were investigated by rheometrical analysis. Figure 7 shows, for S5 and S6, the storage moduli of the swollen gel in ethanol and methanol versus the angular frequency.

The storage moduli of ethanol-swollen gels are higher than those of the corresponding methanol-swollen gels. Also, increasing the MAPTAC content enhances the storage moduli of the gels. It was expected that the more rigid sample (S5) would have a higher modulus than S6 due to its capacity for hydrogen bonding, but the results showed the opposite trend. Thus, it is anticipated that factors other than intermolecular interactions influence the storage modulus. These observations can be described using the Osawa–Maning theory [48]:

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

Fig. 7 Plots of hydrated storage modulus versus angular frequency for poly(AM-MAPTAC) containing 80 mol % MAPTAC (S5) and PMAPTAC (S6) in ethanol and methanol



where θ is the counterion binding, e is the electronic charge, D is the dielectric constant of the solvent, k is the Boltzmann constant, T is the absolute temperature, and b is the charge spacing. It is observed that counterion binding increases with decreasing dielectric constant of the swelling medium or increasing ionic content (charge density). Counterions form clusters that can act as crosslinking points and thus enhance gel strength because the storage modulus (G') is directly related to the crosslink density (ν_c) according to the following equation [49]:

$$G' = \nu_c RT, \quad (3)$$

where T is the temperature and R is the gas constant. Therefore, PMAPTAC, which has the highest charge density of all the samples, has the highest storage modulus and gel strength in ethanol (which possesses a lower dielectric constant than methanol). The modulus increases with increasing angular frequency due to the relaxation of the polymer chains that occurs upon applying stress. When the angular frequency is increased the polymer chains do not have the opportunity to rest, so an increase in the storage modulus is observed.

Conclusion

Cationic alcogels based on acrylamide/MAPTAC were synthesized. The dielectric constant of the swelling medium, the degree of dissociation of the ionic groups of the alcogel, and its capacity for hydrogen bond formation are important influences on alcogel absorbency. Swelling capacity was found to increase with increasing dielectric constant and cationic monomer content. The maximum absorbency of any of the alcogels tested was 73.3 in ethanol and 105.5 g/g in methanol. These results indicate that cationic alcogels possess enhanced alcohol absorbency compared with anionic alcogels, as has also been reported in previous articles. The alcohol absorbencies of the anionic alcogels were usually less than 100 g/g. It was observed that counterion binding increased as the dielectric constant of the swelling medium decreased or the ionic content of the alcogel increased. Also, the counterions form clusters that can act as crosslinking points, leading to increased gel strength. Therefore, PMAPTAC—which had the highest charge density of all the samples—showed the highest gel strength and storage modulus in ethanol (which has a lower dielectric constant than methanol).

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