

# Design of weakly cationic alco-cryogels consisting of poly (alkylmethacrylates)-based sulfonated terpolymer network with tunable multiresponsive assembly

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## ARTICLE INFO

### Keywords:

Compression  
Multiresponsive networks  
Alkylmethacrylates  
Cationic alcogels

## ABSTRACT

Cryogels with ion-, and solvent-responsiveness have been designed by cryogelation of 2-(diethylamino)ethyl methacrylate (DEAEMA) as weakly cationic monomer, hydroxyethyl methacrylate as neutral comonomer and 2-acrylamido-2-methyl-1-propanesulfonic acid as anionic termonomer in ethanol-water mixture (50:50 v/v), which had been proved to offer a good miscibility of monomers. Influence of composition of terpolymer and polymerization temperature on the properties of terpolymer cryogels (Cgels) and hydrogels (Hgels) were evaluated by swelling kinetics, and response against rapid ionic strength change. Degree of swelling was extremely sensitive to salt concentration, cation/counterion type as well as the solvent type; acetone and monohydric alcohols with various hydrophobic alkyl groups; methanol, ethanol, and 2-propanol. Swelling of terpolymer networks in the form of Cgel and Hgel decreased with increase in the size of ions present in swelling medium and followed the order of swelling behavior  $\text{Cl}^- > \text{Br}^- > \text{I}^-$ . Terpolymer alcogels exhibited salting-out behavior in the presence of  $\text{Cl}^-$  and  $\text{Br}^-$  ions, while "salting-in" behavior was observed in KI solutions of high concentrations. Sensitivity sequence of terpolymer alcogels to mono- and di-valent cations with a common anion ( $\text{SO}_4^{2-}$ ) on swelling was  $\text{Na}^+ > \text{K}^+ > \text{Mg}^{2+} > \text{Zn}^{2+}$ . Variation of elastic moduli with swelling in salt solutions was investigated and for terpolymer hydrogels, possible contribution of ionic crosslinks to effective crosslinking density  $\nu_e$  was discussed. Increasing  $\text{Na}_2\text{SO}_4$  concentration up to 0.1 M induced a 2-fold increase in the elastic modulus of terpolymer alcogels. With attention to the polarity of solvent, terpolymer gels exhibited an irregular swelling profile with a change in composition of solvent, showing the so called cosolvency phenomena. After two successive cycles of swelling and shrinking promoted by the change of ionic strength of KCl solution, the terpolymer gels were stable and dynamic swelling process was reversible. Swelling data agree well with second-order kinetic model and with increasing amount of DEAEMA in terpolymer feed, diffusion mechanism changed from non-Fickian type to Fickian diffusion. In ionic environments, the salt-sensitivity and excellent water absorption/retention capability give this intelligentized terpolymer gels wide potential applications.

## 1. Introduction

Multiresponsive gels as structured biocompatible materials are endowed with tunable assembly, and with distinct responses to more than one environmental stimulus for tissue engineering, controlled drug delivery or regenerative applications [1–4]. Smart weakly cationic porous gels with tunable multiresponsive assembly have been recognized to improve the processes in drug delivery [5,6]. Although the macroporous gels offer interesting applications in which a fast response of the system is crucial, the use of cryogels produced from weakly

cationic polymers is not practically explored. The unique structure of cryogels formed as a result of cryogenic treatment, freezing, in combination with their mechanical stability, makes them attractive porous materials for their fast-response to external stimuli such as solvent and ionic strength. Due to the presence of large interconnected pores in their sponge-like structure, the stimulus-responsive cryogels respond much faster to the external stimuli than conventional hydrogels. Basically, in cryogelation process, the reaction mixture containing polymer precursors is concentrated in liquid micro-phase that is, cryoconcentration takes place as the solvent crystallization (which acts as a pore-forming

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<https://doi.org/10.1016/j.polymeresting.2020.107044>

Received 2 July 2020; Received in revised form 9 December 2020; Accepted 24 December 2020

Available online 29 December 2020

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agent) starts at a temperature below the freezing of solvent. The cryoconcentration of polymer precursors dramatically accelerates the rate of gelation and promotes the gel-formation by reducing the critical concentration required for gelation. After thawing, ice-crystals create voids corresponding the macropores. The size/shape of macropores and interconnectivity depend on the polymerization solvent, the content and composition of the reaction mixture, efficiency and type/rate of cross-linking, efficient cryoconcentration of the mixture, rate of initial cooling, the temperature and duration of cryogelation [7–9].

Cationic gels containing polycations such as poly(dimethylaminoethyl methacrylate) (PDMAEMA) and poly(diethylaminoethyl methacrylate) (PDEAEMA) are sensitive to external pH variations due to the presence of tertiary amine functional groups which are protonated below their dissociation constant in acidic solutions. By accepting positively charged mobile ions from the solvent, cationic gels tend to swell extensively [10–12]. Considering pH-induced assembly of PDEAEMA, Rodriguez and coworkers designed an amphiphilic block copolymer from poly(ethylene glycol)-*b*-poly(diethylaminoethyl methacrylate) via reversible addition-fragmentation chain transfer polymerization by varying length of PDEAEMA segment to encapsulate gold nanorods and doxorubicin (DOX) with good efficiencies. PDEAEMA content in the block copolymers was changed from 31% to 44% to test their potential use as nanometric photothermal agents and drug delivery systems. When pH was lowered from 7.4 to 5.8, the release rate of DOX was accelerated [13]. By changing the size of PDEAEMA block, Cortez-Lemus and coworkers prepared gold nanoparticles using PDEAEMA-based copolymers as nanoreactors in aqueous and alcoholic medium. Depending on the length of PDEAEMA segment and pH of the solution, the block copolymers were dispersed in water to form aggregates with sizes around 100 nm [14]. Pardini and coworkers evaluated the behavior of polyurethane/DEAEMA hybrids as pH-responsive systems for drug delivery development, using Rhodamine as a model drug. In accordance with  $pK_a$  value of functional groups, pH-responsive behavior and morphological changes were observed when pH solution varied from 9.0 to 4.0 [15].

Although pH-responsive swelling behavior of cationic gels has attracted substantial attention in the past decade, the issue of their monotonic or nonmonotonic swelling in salt solutions and in solvent mixtures has not been adequately evaluated experimentally, however, many theoretical studies have been done. Understanding physical origins for the monotonic/nonmonotonic swelling and co(non)solvency phenomena and modeling the swelling profile in binary solvents may be important for the interpretation of effects of components on polymer conformational structure and interaction combinations through the network. A co(non)solvency effect indicates a swelling-collapse-swelling transition upon changing the concentration of the cosolvents. In contrast, for the cosolvency effect, the maximum swelling occurs at a certain concentration of good solvent for the polymer [16,17]. A thermodynamic approach to explain co(non)solvency effect has been proposed by Xiao and coworkers. Using extended Flory-Huggins lattice model, the free swelling behaviors of gels in binary solvents has been described by defining the free energy density of polymer-cosolvent systems [18]. Zuo and coworkers investigated water/cosolvent attraction induced phase separation and proposed a molecular picture of co(non)solvency. By using combined molecular dynamic simulations, and neutron total scattering, it was demonstrated that the strong water/cosolvent attraction leads to the co(non)solvency and both water/cosolvent complexation and competitive hydrogen bonding are its results [19]. Drozdov developed a constitutive model to explain the elastic response of pH-sensitive cationic gels under unconstrained and constrained swelling. Diffusion of solvent and solute (mobile ions) through the polyelectrolyte network as a three-phase medium is modeled to establish correlations between the structure of gels and their ability to swell [20]. Based on Donnan equilibrium and large-deformation theory, a finite-element method of salt concentration-sensitive hydrogels proposed by Zhen and Liu to predict

the deformation behavior by linking the concentration of the salt solution with deformation [21].

According to what have been discussed above, weakly cationic alcogels consisting of poly(alkylmethacrylates)-based sulfonated terpolymer, P(AMPS-DEAEMA-HEMA), has been designed using ionic 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) segments as hydrophilic part, non-ionic hydroxyethyl methacrylate (HEMA) as biocompatible part and weakly cationic 2-(diethylamino)ethyl methacrylate (DEAEMA) as the thermo- and pH-responsive segments. The key feature of this weakly cationic terpolymer is that its multiresponsive property can be modulated by introduction of DEAEMA. Terpolymer P(AMPS-DEAEMA-HEMA) cryogels crosslinked by diethyleneglycol dimethacrylate were synthesized by free radical crosslinking (cryo) polymerization of monomer mixtures in cryoconditions, while for comparison conventional radical copolymerization was employed for the synthesis of terpolymer hydrogels by a simple one-step method in alcoholic medium; 50:50 ethanol/water mixture at room temperature. Since there is a lack on the characterization of weakly cationic gels consisting of poly(alkylmethacrylates)-based polymers in salt solutions and in solvent mixtures, the aim of this study was to examine the solvency properties of terpolymer alcogels and to open area for different applications of the present terpolymer systems. The ion-stimulus-responsive swelling of terpolymer alcogels was evaluated in various aqueous salt solutions to understand the effect of different halide ions ( $Cl^-$ ,  $Br^-$ ,  $I^-$ ) with a common cation ( $K^+$ ) and that of different mono- and di-valent cations ( $Na^+$ ,  $K^+$ ,  $Mg^{2+}$ ,  $Zn^{2+}$ ) with a common anion ( $SO_4^{2-}$ ) on the swelling. The response of elastic properties and swelling behaviors of terpolymer alcogels to mono/divalent salts in aqueous solutions has been evaluated. The immediate implications of obtained multi-responsive results are related to design of smart weakly cationic alcocryogels and hydrogels with controllable charge distribution and composition. To evaluate the effect of the chemical structure and polarity of the alcohol, the extent of swelling was studied in aqueous solutions of acetone and monohydric alcohols with various hydrophobic alkyl groups; methanol, ethanol and 2-propanol. The swelling profile of terpolymer alcogels was extremely sensitive to the ionic strength, cation, counterion species and solvent type.

## 2. Materials

Weakly cationic monomer 2-(diethylamino)ethyl methacrylate (DEAEMA, Merck), neutral monomer hydroxyethyl methacrylate (HEMA, Merck), and anionic monomer 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS, Merck) were used as received. Diethyleneglycol dimethacrylate (DEGDMA, Fluka) was selected as a tetrafunctional cross-linking agent. The redox-initiator system consisting of *N,N,N',N'*-tetramethylethylenediamine (TEMED, Merck) and ammonium persulfate (APS, Merck) was used as received. Acetone, ethanol, methanol and 2-propanol were used for solvent-dependent swelling studies. Potassium chloride (KCl, Merck), potassium bromide (KBr, Merck), potassium iodide (KI, Carlo Erba), sodium sulfate ( $Na_2SO_4$ , Merck), potassium sulfate ( $K_2SO_4$ , J.T.Baker), magnesium sulfate ( $MgSO_4$ , Sigma-Aldrich) and zinc sulfate ( $ZnSO_4$ , Sigma Aldrich) were used for the salt-sensitive swelling experiments. Distilled water was used for the preparation as well as for ion- and solvent-sensitive swelling measurements of the prepared terpolymer alcogels.

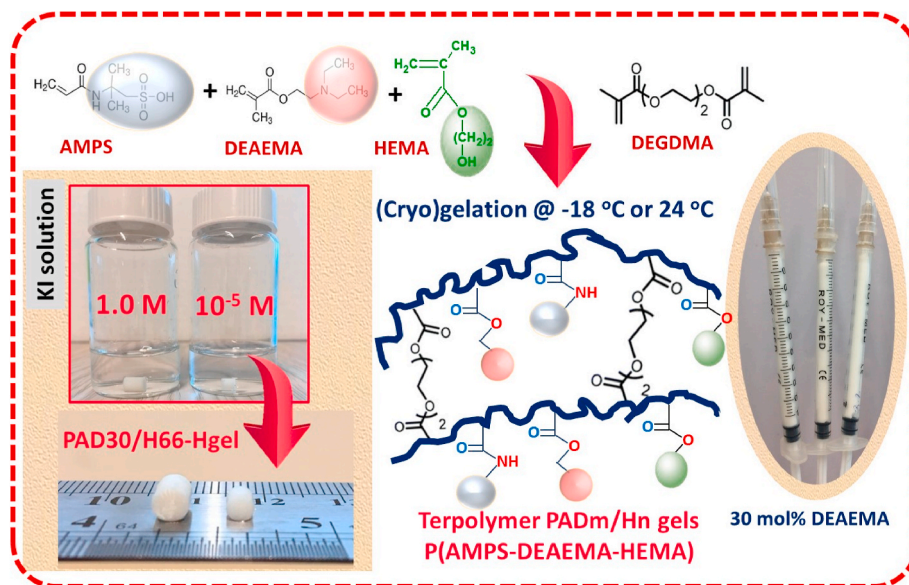
### 2.1. Preparation of terpolymer PADm/Hn alcogels

The terpolymer alcogels, including cryogels and hydrogels, were prepared in alcoholic medium; ethanol/water mixture (50:50 v/v) using different monomer feed compositions in the presence of 3.51 mM APS initiator and 0.375 v/v% TEMED accelerator. Poly(2-acrylamido-2-methyl-propanesulfonic acid-co-diethylaminoethyl methacrylate-co-hydroxyethyl methacrylate) cryogels and hydrogels were named as PADm/Hn-Cgel and Hgel related to the preparation temperature, "Cgel"

**Table 1**

Terpolymer composition and parameters used in the synthesis of PADm/Hn alcogels.  $\nu_{2,theo}^0$  = theoretical values of the volume fraction of crosslinked terpolymer network after preparation.  $\bar{V}_r$  = average molar volume of the P(AMPS-DEAEMA-HEMA) repeat units (in mL/mol).

Sample code PADm/Hn	Terpolymer AMPS/DEAEMA/HEMA mol%	AMPS (g)	DEAEMA (mL)	HEMA (mL)	$\nu_{2,exp}^0$	$\nu_{2,theo}^0$	$\bar{V}_r$
PAD0/H96	4-0-96	0.1160	0.0	1.719	0.2288	0.1405	93.9
PAD10/H86	4-10-86	0.1160	0.284	1.540	0.1763	0.1454	97.8
PAD20/H76	4-20-76	0.1160	0.568	1.361	0.1723	0.1504	101.7
PAD30/H66	4-30-66	0.1160	0.852	1.181	0.2385	0.1554	105.6
PAD40/H56	4-40-56	0.1160	1.136	1.002	0.2343	0.1604	109.5
PAD50/H46	4-50-46	0.1160	1.420	0.823	0.1988	0.1653	113.3
PAD60/H36	4-60-36	0.1160	1.704	0.644	0.2074	0.1703	117.2



**Scheme 1.** Synthesis mechanism of terpolymer PADm/Hn alcogels via free radical crosslinking (cryo)polymerization in alcoholic medium.

corresponds to “cryogel matrix” prepared at  $-18\text{ }^{\circ}\text{C}$  and “Hgel” corresponds to “hydrogel matrix” prepared at  $24\text{ }^{\circ}\text{C}$ , A is short for AMPS, D is for DEAEMA and H is for HEMA monomer. m and n correspond to the mole percent of DEAEMA and HEMA in terpolymer structure, respectively. All the polymerization reactions were carried out in plastic syringes of  $4 \times 12\text{ mm}$  in internal diameter and length. Terpolymer cryogels were prepared by free-radical cross-linking cryopolymerization of AMPS, DEAEMA and HEMA monomers with a small amount of DEGDMa cross-linker at  $-18\text{ }^{\circ}\text{C}$  for 48 h. The monomer feed compositions were adjusted as: the mole ratio of anionic monomer AMPS was fixed at 4 mol%, DEAEMA content in the terpolymer structure was varied between 0 and 60 mol% and correspondingly HEMA mol ratio was changed from 96 to 36 mol% in the pre-gel solution. The crosslinker ratio, that is the mole ratio of the crosslinker DEGDMa to the monomers AMPS + DEAEMA + HEMA was fixed at 1/81 and the initial total concentration of the monomers was fixed at 22.1 w/v%.

To illustrate the synthetic procedure, the details for the preparation of terpolymer alcogel with 10 mol % DEAEMA and 86 mol % HEMA in the feed composition, designated as PAD10/H86-gel: 0.116 g AMPS, 0.284 mL DEAEMA, 1.540 mL HEMA and 1.0 mL of TEMED stock solution was mixed in 5 mL of 50:50 water/ethanol mixture under continuous stirring. After bubbling nitrogen, 1.0 mL of APS stock solution was added to the mixture and the total volume was completed to 10 mL with ethanol/water mixture (1:1 by volume). Upon immediate mixing, the solution was poured into several plastic syringes which were sealed by parafilm from both ends. The cryogelation reaction were carried out in a freezer for 48 h at  $-18\text{ }^{\circ}\text{C}$  by reducing the gelation temperature down to  $-18\text{ }^{\circ}\text{C}$  with a slow cooling rate of  $5\text{ }^{\circ}\text{C}/\text{min}$ . For comparison purpose, the gelation for preparation of terpolymer

hydrogels was conducted at  $24\text{ }^{\circ}\text{C}$ . **Table 1** presents the composition and structural parameters used in the synthesis of terpolymer alcogels. The synthesis mechanism via free radical crosslinking (cryo)polymerization in 50:50 water/ethanol was illustrated in **Scheme 1**. It should be noted that terpolymer cryogels containing 0 mol% DEAEMA, referred to PAD0/H96, was too weak and since the samples cannot keep their cylindrical shape, they could not be used for the swelling and elasticity test. When the (cryo)gelation completed, the terpolymer gel rods were removed from the syringe and waited to rise to room temperature. After cutting into small disks of a thickness of 3 mm, the samples were stored in deionized water for several days to leach out of the unreacted monomers and crosslinking agents and then dried in air for two months to constant weight.

## 2.2. Dynamic swelling/shrinking kinetics of terpolymer alcogels

Swelling properties of terpolymer PADm/Hn alcogels were studied using conventional gravimetric and volumetric procedures. To evaluate the swelling kinetics, the dried gels were immersed in  $10^{-5}\text{ M}$  aqueous KCl solution at  $25\text{ }^{\circ}\text{C}$ . At regular period of time, the time-dependent swelling of circular terpolymer gel slides was followed by weighing the samples after wiping the excess surface solution by filter paper. The time-dependent water uptake  $\phi(t)$  at corresponding swelling time  $t$  was defined by:

$$\phi(t) = \frac{m_t - m_{dry}}{m_{dry}} \quad (1)$$

where  $m_t$  and  $m_{dry}$  are the mass of the swollen sample at time  $t$  and after

drying process. Each gel samples were kept in the aqueous salt solutions until they reached the equilibrium swelling and the corresponding equilibrium weight swelling ratio  $\phi_w$  was evaluated as the fractional increase in the mass of the sample by:

$$\phi_w = \frac{m_{sw} - m_{dry}}{m_{dry}} \quad (2)$$

where  $w_{sw}$  is the mass of equilibrium swollen sample. The kinetics of shrinking of terpolymer alcogels was also followed gravimetrically by transferring the samples previously swollen in  $10^{-5}$  M aqueous KCl solution into 1.0 M ones.

### 2.3. Equilibrium swelling ratio of terpolymer alcogels

The swelling studies of terpolymer PADm/Hn alcogels were conducted in different solvent/water mixtures of acetone, ethanol, methanol and 2-propanol. Salt tolerance of terpolymer alcogels was studied in aqueous salt solutions of KCl, KBr, KI as well as in  $\text{Na}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{MgSO}_4$ , and  $\text{ZnSO}_4$  solutions as the swelling medium at room temperature. In order to evaluate the equilibrium volume swelling ratio of terpolymer alcogels, their volume change was followed by a calibrated digital compass (Mitutoyo Digimatic Caliper, Series 500, resolution: 0.01 mm). After measuring the initial diameter of cylindrical gel samples, they were submerged into aqueous salt solutions or solvent/water mixtures. All the samples were kept in excess solution, at room temperature, until they attain their thermodynamic equilibrium swelling state which requires 15 days replacing the solutions several times. At equilibrium, the diameter of the swollen samples remained constant and the equilibrium volume swelling ratio  $\phi_v$  was determined by Refs. [22, 23]:

$$\phi_v = \frac{1}{\nu_2} = \frac{(D_{eq}/D_0)^3}{\nu_2^0} \quad (3)$$

where  $D_{eq}$  and  $D_0$  are the diameters of the terpolymer alcogel samples after equilibrium swelling state, and after preparation, respectively.  $\nu_2$  and  $\nu_2^0$  are the crosslinked terpolymer volume fraction in the swollen state and in the relaxed state (just after polymerization), respectively. Using the density of terpolymer P(AMPS-DEAEMA-HEMA) gel,  $\rho = 1.418 \pm 0.035$  g/mL, the masses of sample after preparation and after drying procedure, the experimental values of  $\nu_2^0$  were calculated based on the following expression:

$$\nu_{2,\text{exp}}^0 = \left[ 1 + \frac{((m_0/m_{dry}) - 1)\rho}{d_1} \right]^{-1} \quad (4)$$

where  $d_1$  is the density of polymerization solvent, 0.913 g/mL. Each measurement was followed with four gel samples for each synthesis and averaged, the standard deviations were <3%. Using the initial molar concentration of the monomer mixture  $C_0$  and the average molar volume of P(AMPS-DEAEMA-HEMA) repeat units,  $\bar{V}_r$  (in mL/mol), the theoretical values of  $\nu_2^0$  were determined using,  $\nu_2^0 = 10^{-3}C_0\bar{V}_r$ , and the results were compared in Table 1 against the amount of HEMA in the terpolymer network. It was observed that experimental  $\nu_2^0$  values were greater than the theoretical ones over the terpolymer composition.

### 2.4. Stress-strain measurements of terpolymer alcogels

The cylindrical terpolymer alcogels, as-equilibrated in aqueous salt solutions, were subjected to uniaxial compression experiments. Based on their swelling capacities in the aqueous salt solutions with different ionic strength, the size of the specimens were different. After measuring initial mass, diameter and length, the specimen was put on the fixed lower plate and then compressed using a vertically fitted circular probe with a diameter of 40 mm. The loading were performed using a circular probe speed of 10 mm/min. Each gel specimen is compressed once for the

compressive modul calculations and four samples of each kind of alvogel were used. Therefore, after adjusting the experimental parameters, the single compression measurements were performed in air medium taking into account the short duration of these tests. Each measurement was carried out in  $\leq 3$  min to minimize the loss of water by the compression. The change in the length of terpolymer alcogels,  $\Delta L$ , was followed using a digital comparator (IDC type Digimatic Indicator 543-262, Mitutoyo) which is sensitive to the displacements of  $10^{-3}$  mm. After each compressive force is applied, the initial  $L_{in}$  and compressed sample  $L$  lengths along the vertical axis, the change after each loading was followed as;  $\Delta L = L_{in} - L$  and the change in the length of compressed alcogel was recorded after 20 s of relaxation of chains. The corresponding change in the mass of specimen  $m$  was calculated from the balance reading, as  $f = mg$ , using gravitational acceleration,  $g = 9.803$  m/s<sup>2</sup>. To characterize the stiffness of terpolymer alcogels under tests, the elastic modulus,  $G$ , was determined from the mean slope values of the compression curves by Refs. [24,25]:

$$\sigma = f/A = G(\alpha - \alpha^{-2}) \quad (5)$$

where  $\sigma$  is the applied stress in  $\text{N m}^{-2}$ ,  $f$  is the applied compressive force by each loading,  $A$  is the cross-section of the undeformed specimen calculated by  $A = \pi(D_0/2)^2$  and  $\alpha$  is the relative deformation of the specimen determined as the ratio of measured displacement  $\Delta L$  to the initial specimen length  $L_0$  along the vertical axis.

### 2.5. Structural characterization of terpolymer alcogels

ATR-FTIR spectra of the dried powder samples were obtained with a Perkin Elmer Spectrum 100 FTIR spectrometer equipped with a universal attenuated total reflection (ATR) accessory in the range from 4000 to 650  $\text{cm}^{-1}$ , the resolution being 4  $\text{cm}^{-1}$ . XRD analyses of powder samples were performed with a Bruker D8 Advance X-ray diffractometer wide-angle XRD with Cu  $K\alpha$  radiation, running at 40 kV and 40 mA, scanning from 4 to 50° with a scan step time of 1°/min. Dehydrated samples were ground into powder for XRD. The thermo-gravimetric analysis (TGA) of terpolymer alcogels was performed with a SEIKO EXSTAR 6200 Model TG/DTA instrument under nitrogen atmosphere with the flow rate of 150 mL/min. The powder samples of about 10 mg were heated from ambient temperature to 700 °C at a heating rate of 10 °C  $\text{min}^{-1}$ . DSC measurements were performed with a Perkin Elmer DSC4000 calorimeter with an accuracy of  $\pm 0.001$ . 9–10 mg of samples were placed in a closed pan and the temperature scans were run on samples for successive heating and cooling cycles. The samples were heated twice and subsequently cooled under a nitrogen flow rate of 20 mL/min and then reheated to check the reversibility. The samples were heated from –20 to 200 °C at the heating rate of 10 °C/min and held at this temperature for 10 min, then cooled to –20 °C at the same rate, held for 10 min, followed by again heating to 200 °C at the heating rate of 5 °C/min. Again, the samples were cooled to the starting temperature at the same rate cooling rate. To evaluate the thermal behavior of samples, the second cycle which was slow enough to detect a  $T_g$  was used.

## 3. Results and discussion

To extend the application range of weakly cationic alco-cryogels, poly(alkylmethacrylates)-based sulfonated terpolymer cryogels with tunable multiresponsive assembly were synthesized in this work and the synthesis of alco-cryogels in ethanol/water mixture being conducted at cryoconditions. The chemical structure of terpolymer alcogels was confirmed by FTIR, XRD and TGA thermal analysis. The swelling behavior depends on the terpolymer network structure involving composition, type of charge, ionic content, crosslinking agent and the environmental conditions including the swelling temperature, various salt and solvent concentrations.

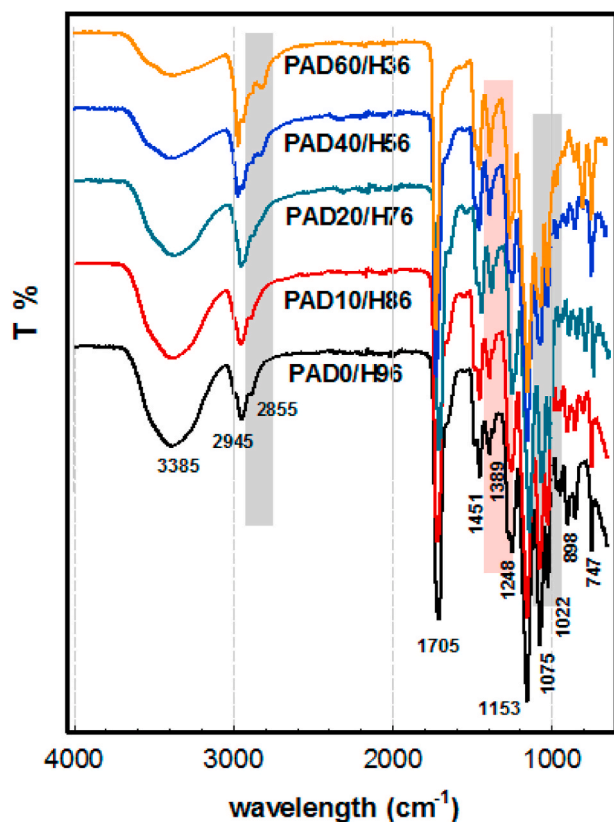


Fig. 1. ATR-FTIR spectra of terpolymer PADm/Hn alcogels prepared with different DEAEMA/HEMA ratio in the feed: 0/96, 10/86, 20/66, 40/56, and 60/36. Note that PAD0/H96 refers to the copolymer P(AMPS-co-HEMA) gel.

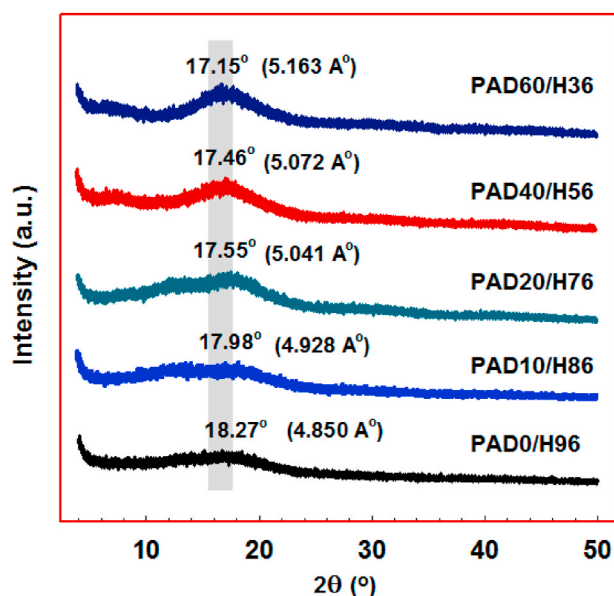


Fig. 2. XRD patterns of terpolymer PADm/Hn alcogels prepared with varying DEAEMA/HEMA ratios: 0/96, 10/86, 20/66, 40/56, and 60/36.

### 3.1. Infrared spectroscopic analysis of terpolymer alcogels

ATR-FTIR spectra of terpolymer PADm/Hn alcogels given in Fig. 1 indicated the presence of the functional groups; amino groups of DEAEMA, -OH groups of HEMA and sulfonic acid groups of AMPS: O-H stretching at 3400-3550  $\text{cm}^{-1}$ , and the strong band from carbonyl group

associated with carboxyl group were detected at 1705  $\text{cm}^{-1}$ .

The characteristic alkyl (R-CH<sub>2</sub>) stretching modes were observed between 2850 and 3000  $\text{cm}^{-1}$ . At around 1248  $\text{cm}^{-1}$  and 1153  $\text{cm}^{-1}$ , the stretching vibrations of C-O, and C-O-O bond of ester groups were observed, while the strong band from carbonyl group associated with carboxyl group was detected at 1705  $\text{cm}^{-1}$ . The methylene distortion vibration bands were observed at around 1022  $\text{cm}^{-1}$ , while the absorption peaks due to =C-H stretching were detected at around 747 and 898  $\text{cm}^{-1}$ . The strong bands at 1451  $\text{cm}^{-1}$  were attributed to -CH bending, 1389  $\text{cm}^{-1}$  referred to C-H rocking, while the peaks at around 2945 and 2855  $\text{cm}^{-1}$  were corresponded to symmetric and asymmetric CH<sub>2</sub> stretching. Amide group contribution of anionic comonomer AMPS was detected with absorption ranging from 1540 to 1650  $\text{cm}^{-1}$  due to CONH stretching of AMPS, while the asymmetric and symmetric stretching vibration of two S=O bonds in sulfonic group was appeared at 1247 and 1073  $\text{cm}^{-1}$ . As a result of amine-containing aliphatics, a broad structuring ranged between 2750 and 3090  $\text{cm}^{-1}$  was observed with increasing DEAEMA content. For terpolymer alcogels; the peaks assigned to C-N bond on the side chains were observed at 1150 and 750  $\text{cm}^{-1}$ , the vibrations of methylene groups on the main chain detected at 1400-1500  $\text{cm}^{-1}$  and the carbonyl stretching from ester groups detected between 1600 and 1800  $\text{cm}^{-1}$ . The terpolymer alcogels with a greater DEAEMA mol content showed stronger stretching vibration modes assigned to the diethylamino groups at around 2842  $\text{cm}^{-1}$  and from the methyl groups at around 2965  $\text{cm}^{-1}$ . The intensity of the bands detected around 1150  $\text{cm}^{-1}$  due to -CN of DEAEMA moieties and the contribution of the ester group of DEAEMA were increased with increasing DEAEMA content in terpolymer feed.

To determine the structure of terpolymer alcogels, XRD studies were performed at room temperature using a Bruker D8 Advance X-ray Diffractometer in the  $2\theta$  range of 4° - 50°. As seen in Fig. 2, a broad hump ranged between 17° - 18° observed for all the terpolymer samples. This result indicated that all the prepared terpolymer samples are amorphous in nature. It was also found that the hump shifts slightly towards left and also intensity of the scattering increases with increase in DEAEMA content in terpolymer feed. The inter-planar spacing of terpolymer PADm/Hn samples was calculated using Bragg's law;  $n\lambda = 2d \sin \theta$ , by setting  $n = 1$ ,  $\lambda =$  wavelength of X-ray (1.5405 Å), and  $\theta =$  angle of the diffraction. It was found that the corresponding  $d$  values increased and calculated as 4.850, 4.928, 5.041, 5.072 and 5.163 Å for 0, 10, 20, 40 and 60 mol% of DEAEMA, respectively. Using the equation;  $R = (7/2\pi)(\lambda/2 \sin \theta)$ , the inter-chain separation  $R$  of terpolymers was also calculated and the results showed that the inter chain separation increased gradually as 5.405, 5.492, 5.618, 5.653, and 5.755 Å with increasing DEAEMA content from 0 to 60 mol% in the feed, respectively. With the increase of DEAEMA content in the feed of terpolymers, the inter chain separation and inter planar spacing increased gradually. The observed increase may be assigned to the increase in regularity of the network chains arising from the possible chemical interactions between functional groups of AMPS, DEAEMA, HEMA and the crosslinker DEGMA monomer during the formation of network. The observed change indicated the inter- and intra-molecular hydrogen bond formation between the terpolymer chains which is responsible for the amorphous structure of the prepared alcogels.

### 3.2. Thermal analysis of terpolymer alcogels

To evaluate the effect of composition on the thermal stability of terpolymer PADm/Hn alcogels with different DEAEM/HEMA content, TG curves in the range from 20 °C to 600 °C were collected in Fig. 3. The data for % weight loss of terpolymer samples prepared with varying DEAEMA/HEMA ratio and the maximum temperature of rate decomposition were also presented in Table 2. PAD0/H96 sample, corresponding copolymer P(AMPS-HEMA), degraded in two steps: the first degradation step observed in a narrow temperature range from 282 to 324 °C is due to the degradation sulfonic groups and the ester bonds

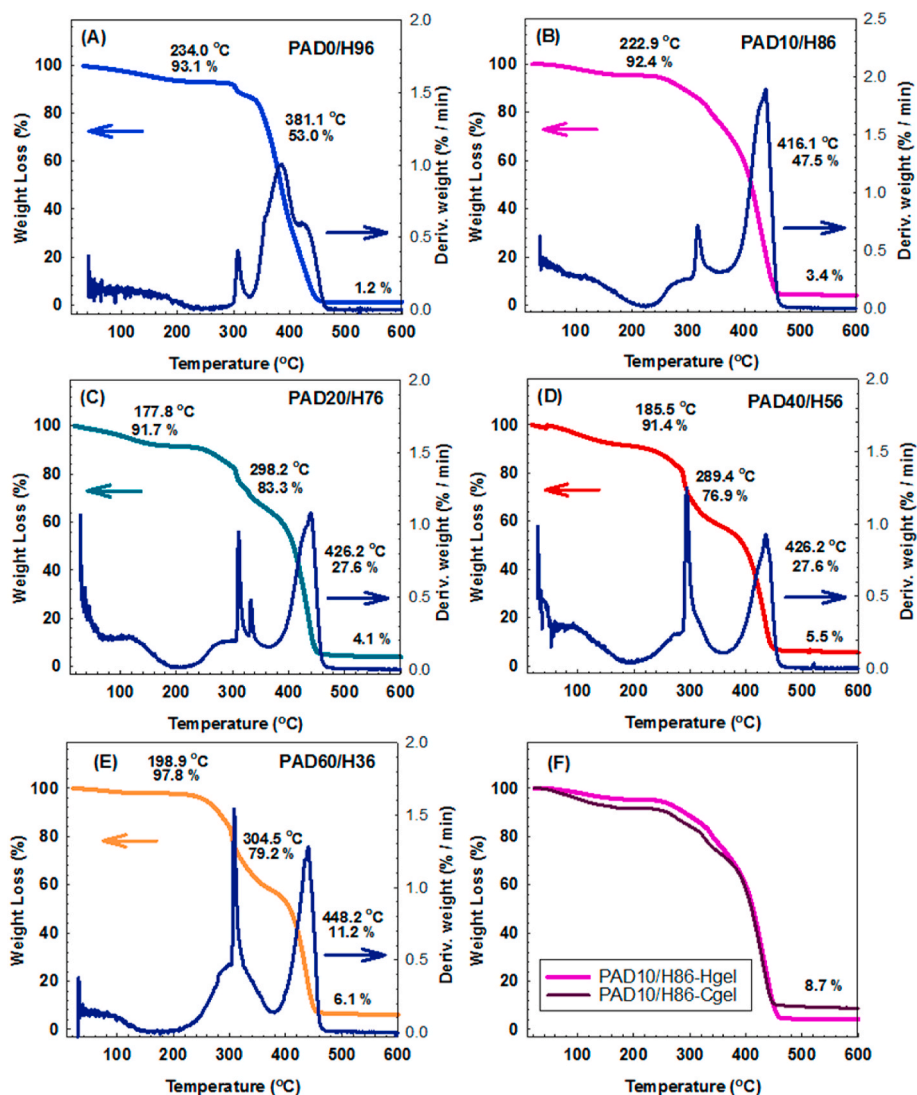


Fig. 3. TG and DTG curves of terpolymer PAD<sub>m</sub>/H<sub>n</sub> alcogels prepared with varying DEAEMA/HEMA ratios: (A) 0/96, (B) 10/86, (C) 20/66, (D) 40/56, (E) 60/36 and (F) comparison of TG curves of PAD10/H86-Hgel and Cgel samples.

Table 2

Data for % weight loss of terpolymer alcogels prepared with varying DEAEMA/HEMA ratios: 0/96, 10/86, 20/66, 40/56, 60/36 and the maximum temperatures of rate decomposition ( $T_{max}$ ).

Sample code	$T_{onset}$ (°C)	Weight loss % at $T_{onset}$	$T_{max_1}$ (°C)	Weight loss % at $T_{max_1}$	$T_{max_2}$ (°C)	Weight loss % at $T_{max_2}$	Residual mass at 600 °C (%)
PAD0/H96	220.4	92.9	296.1	92.4	381.1	53	1.2
PAD10/H86	191.7	92.8	312.3	83.4	416.1	47.5	3.4
PAD20/H76	149.9	92.5	298.2	83.3	426.2	27.6	4.1
PAD40/H56	146.6	92.8	289.4	76.9	432.3	24.5	5.5
PAD60/H36	142.9	97.9	304.5	79.2	448.1	11.1	6.1

breakdown on the copolymer network. The second up to 460 °C involves the rupture of secondary amide groups of AMPS and the total degradation of copolymer backbone [26,27]. The thermal stability of the terpolymer alcogels and the influence of the change in DEAEMA/HEMA ratio in the feed have been evaluated in Fig. 3. Two weight loss steps can be appreciated for each terpolymer alcogels. The degradation profile of terpolymer PAD40/H56 follows: the initial step, centered between 20 and 210 °C, assigned to loss of water adsorbed in the terpolymer network, and the first step centered between 210 and 345 °C with a maximum temperature at 289.4 °C (76.9 w%) can be attributed to the thermal decomposition of the lateral chains containing the amide-, carboxyl-groups and side groups near tertiary nitrogen belongs to

DEAEMA and hydroxyl ethyl groups from HEMA. The second region up to 464.3 °C with a maximum temperature at 432.3 °C (24.5 w%) corresponded mainly to the main chain of terpolymer breakdown and the sample remained about 6.1% at 600 °C. Very recently, Stawski and Nowak analysed the thermal decomposition of PDMAEM at thermo-oxidative conditions and measured the changes in its structure using FTIR spectroscopy. Thermal degradation of PDMAEMA occurred in two main steps. The first stage occurred in the 290–400 °C range and the decomposition of side groups was initiated in this stage. The destruction of the carbon-nitrogen bond is faster than that of the carbonyl group. In the second stage, which is located between 400 and 515 °C, two processes overlap; the destruction of side groups and the disappearance of

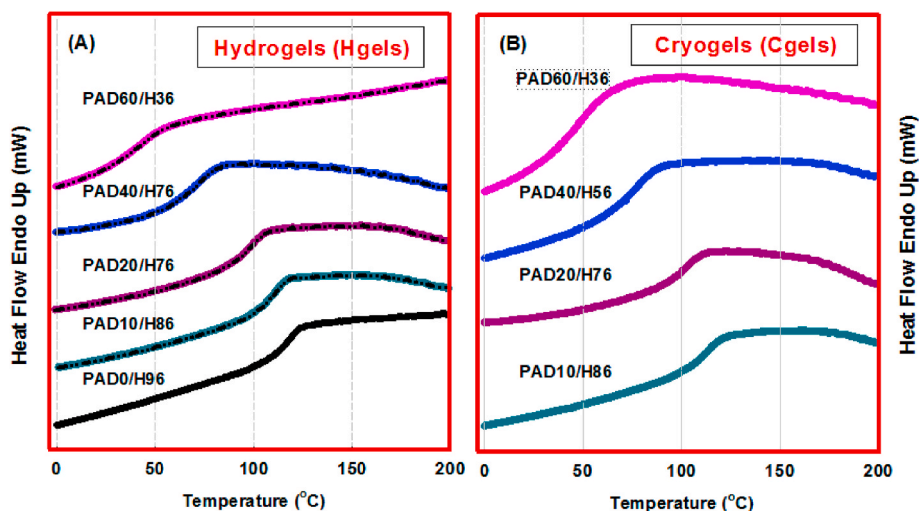


Fig. 4. DSC curves of terpolymer PADm/Hn-Hgel (A) and PADm/Hn-Cgel (B) prepared with varying DEAEMA/HEMA ratio: 0/96, 10/86, 20/66, 40/56, 60/36. The weight loss and corresponding temperature data were already indicated in figures.

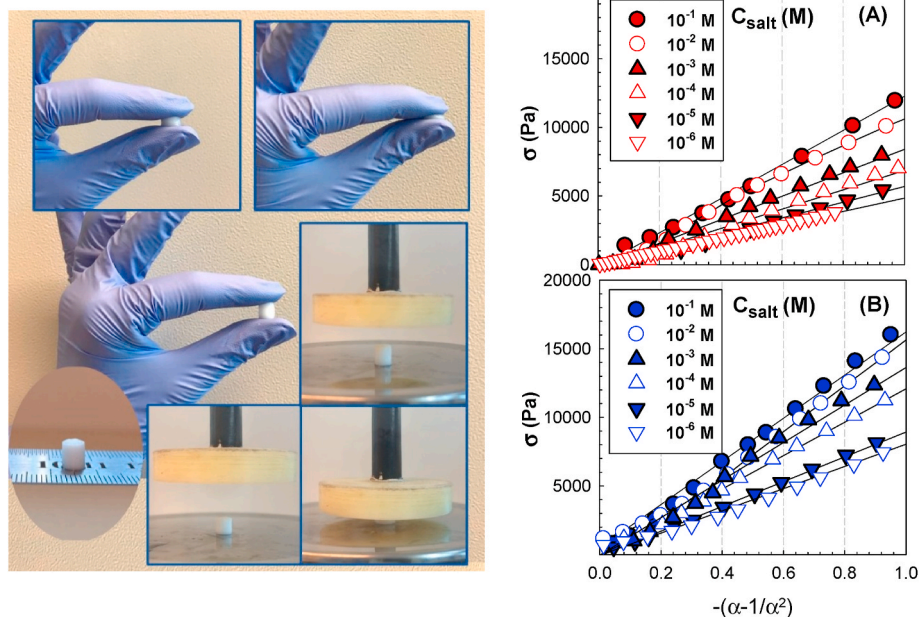


Fig. 5. Stress-strain curves obtained during the compression test of PAD10/H86-Hgel (A) and PAD10/H86-Cgel (B) samples with DEAEMA/HEMA ratio of 10/86 in the feed after equilibrium swelling in various concentration of aqueous  $\text{Na}_2\text{SO}_4$  solutions. The ionic strength of the solutions are indicated in the figure. Snapshots were taken for swollen terpolymer PAD10/H86-Cgel sample during the compression test.

the last groups of the main chain [28].

The results showed that the thermal properties of the terpolymer alcogels can be improved by modifying the DEAEMA/HEMA ratio and by reducing the polymerization temperature. A greater weight loss was observed for the first peak for DEAEMA-rich terpolymer gels. The greater decomposition rate can be assigned to the longer lateral chains of diethylamino ethyl groups from DEAEMA units in comparison with hydroxyl ethyl groups from HEMA units. In Fig. 3(C), for the sample PAD20/H76, the first decomposition was split in two parts. The first one was attributed to the amino group of DEAEMA, while the second to the lateral chains of both DEAEMA and HEMA units. The second thermal degradation temperature of terpolymer networks increased with increasing DEAEMA content as the decomposition of carbon chains requires high temperature.

In their work Yang and coworkers showed that the decomposition of

PDMAEMA and its copolymers began with the DMAEMA group due to its weak ester bonds ( $-\text{O}-\text{C}=\text{O}$ ) and their results indicated that the thermal stability of DMAEMA-based polymers is greatly affected by the presence of this ester bond [29]. Fig. 3(F) presents the comparison of TG curves of PAD10/H86-Cgel and Hgel samples. In general, cryogelation at  $-18^\circ\text{C}$  slightly changed the initial degradation behavior, while the second stage weight loss was almost same. The residue of terpolymer Cgel and Hgel were 8.7% and 3.4% indicated a high amount of ashes and reticulation in the terpolymer cryogel matrix as a result of porous and dense network structure. This finding indicates that the thermal stability of terpolymer alcogels can be tuned by modifying the polymerization temperature and conducting the polymerization under cryo-conditions.

Heat flow curves of terpolymer alcogels from DSC measurements were compared in Fig. 4. The glass transition temperature  $T_g$  determined by the midpoint of the transition region varied as a function of the

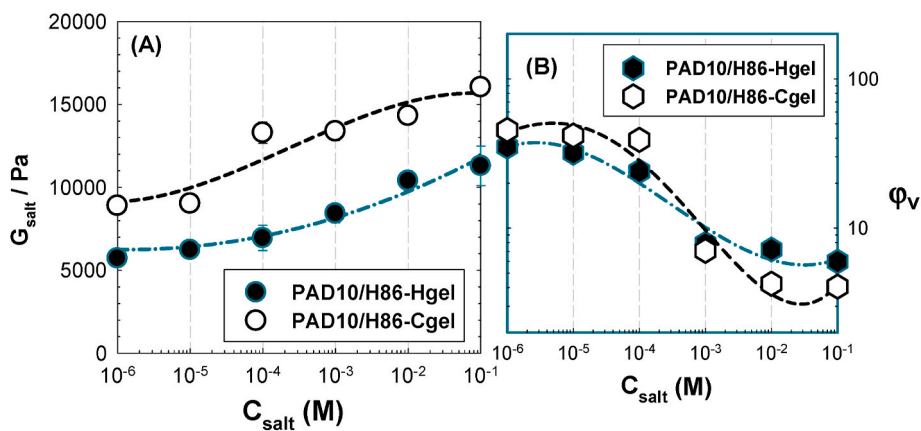


Fig. 6. Comparison of (A) the compressive elastic moduli of swollen PAD10/H86-Hgel and Cgel samples with DEAEMA/HEMA ratio of 10/86 in the feed in various concentration of  $\text{Na}_2\text{SO}_4$  solution. (B) Equilibrium volume swelling ratio  $\phi_v$  of PAD10/H86-Hgel and Cgel samples as a function of the ionic strength of aqueous  $\text{Na}_2\text{SO}_4$  solution. Where not shown, error bars were smaller than the data symbols.

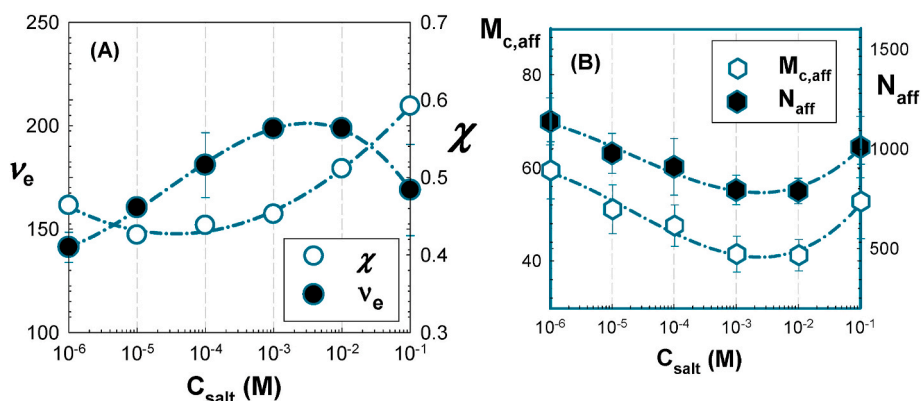


Fig. 7. (A) Variation of effective cross-linking density  $\nu_e$  and Flory-Huggins interaction parameter  $\chi$ , and (B) Average network chain length  $N$  and average molecular weight of network chains  $M_c$  assuming affine network model as a function of the ionic strength of aqueous  $\text{Na}_2\text{SO}_4$  solution.

Table 3

Data for PAD10/H86-Hgel with DEAEMA/HEMA ratio of 10/86 in the feed.  $\nu_e$  = effective cross-linking density,  $\chi$  = Flory-Huggins interaction parameter,  $N$  = average network chain length and  $M_c$  = average molecular weight of network chains assuming affine network model.

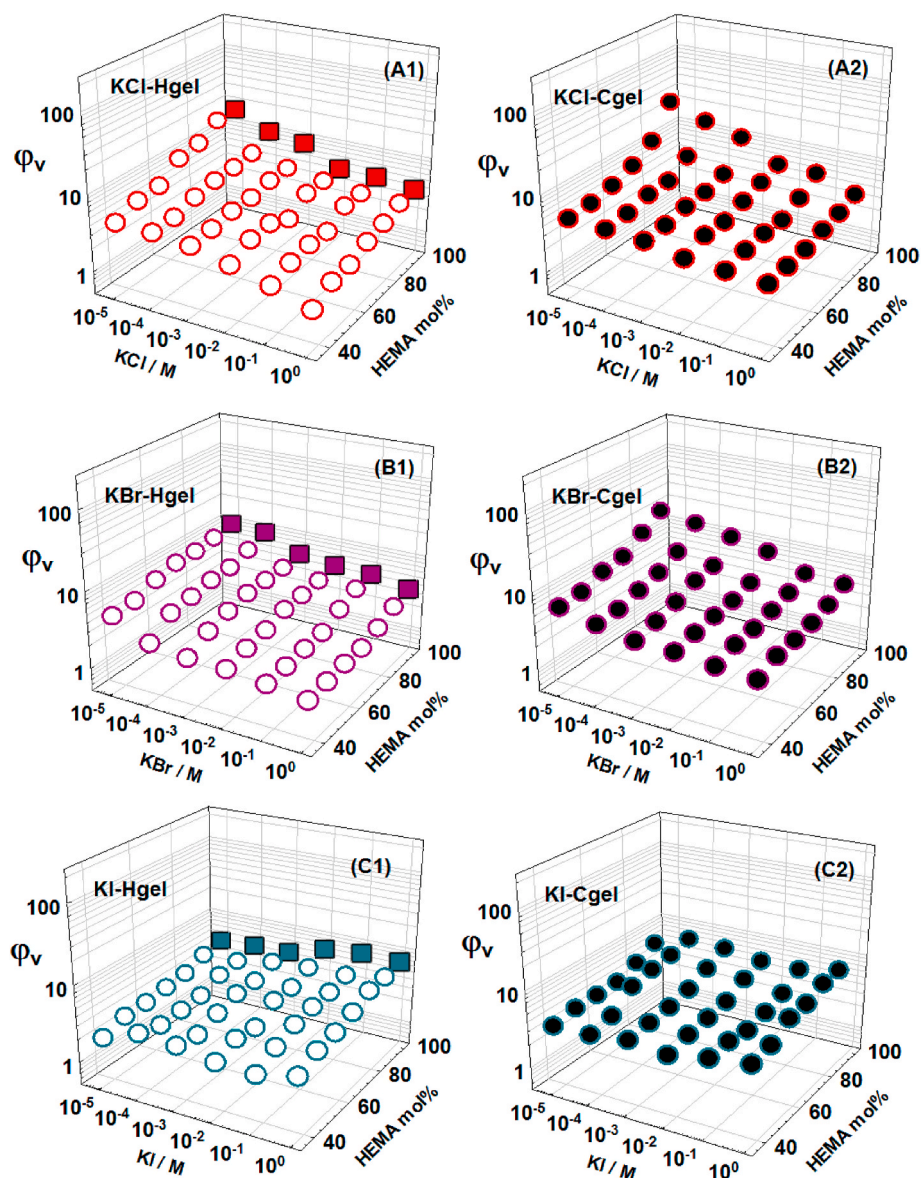
$C_{\text{salt}}$ (M)	$\nu_e$	$N_{\text{aff}}$	$M_{c,\text{aff}}$	$\chi$
$10^{-1}$	168.8 (8.7)	1009.2 (153)	52.7 (8.0)	0.5919
$10^{-2}$	198.6 (2.8)	788.5 (64)	41.2 (3.3)	0.5112
$10^{-3}$	198.5 (4.4)	793.2 (73)	41.7 (3.8)	0.4525
$10^{-4}$	180.9 (5.6)	910.0 (42)	47.6 (7.4)	0.4383
$10^{-5}$	160.8 (2.2)	977.5 (100)	51.9 (5.2)	0.4257
$10^{-6}$	141.1 (7.2)	1137.4 (76)	59.4 (6.1)	0.4639

terpolymer composition. A single glass transition temperature observed for all terpolymer Cgel and Hgel samples confirmed successful formation of terpolymer structure and the presence of strong specific interactions that occurred between AMPS, HEMA and DEAEMA. The unique transition observed for terpolymer gels corresponded to the glass transition of soft DEAEMA segments and appeared at lower temperatures and this result was attributed to the extent of the miscibility of all types of segments in the terpolymer during the polymerization. The observation of a single  $T_g$  for all terpolymers supported the uniform distribution of AMPS, HEMA and DMAEMA among the terpolymer chain. Upon decreasing DEAEMA/HEMA ratio between 60/36 and 0/96, the glass transition temperatures of terpolymer PADm/Hn-Hgels were ranged between 55.5 and 120.1 °C and that of PADm/Hn-Cgels was observed

between 62.3 and 118.9 °C. This indicates that HEMA-rich terpolymer sample is a rigid polymer due to strong intermolecular hydrogen bonds, whereas DEAEMA-rich terpolymer sample is a soft polymer [30]. The  $T_g$  values shifted to lower temperatures by increasing DEAEMA/HEMA mole ratio that can be associated with a slightly lower free volume. This result can be explained by the interactions between pendant functional groups of DEAEMA segments and terpolymer network chains containing HEMA and AMPS moieties. Interactions of these moieties limited the movement of the terpolymer chains, leading to a decrease in  $T_g$  of terpolymers. The results showed that  $T_g$  values of terpolymer PADm/Hn alcogels can be tailored by DEAEMA/HEMA mole ratio.

### 3.3. Physico-mechanical considerations in salt solutions

To reveal the rigidity of terpolymer alcogels after equilibrium swelling in aqueous salt solutions, the uniaxial compression measurements were performed on PAD10/H86-Hgel and Cgel samples after their equilibrium swelling in various concentrations of aqueous  $\text{Na}_2\text{SO}_4$  solutions. The stress-strain graphs of the swollen terpolymer samples with DEAEMA/HEMA ratio of 10/86 in the feed were collected in Fig. 5 as a function of the ionic strength of  $\text{Na}_2\text{SO}_4$  solutions. There was a linear relationship between the stress and strain data for PAD10/H86-Hgel and Cgel samples, and the correlation coefficients changed between 0.9917 and 0.9996. Although DEAEMA/HEMA ratio, 10/86, in the feed of terpolymer samples was the same, the slope of the stress-strain curves changed depending on the ionic strength of  $\text{Na}_2\text{SO}_4$  solutions. The compressive elastic modulus ( $G_{\text{salt}}$ ) was calculated from the slopes of the



**Fig. 8.** The equilibrium volume swelling ratio  $\phi_v$  of PADm/Hn-Hgel (left) and Cgel (right) samples as a function of the ionic strength of aqueous salt solutions of KCl (A), KBr (B) and KI (C). The data shown by solid square symbols in the left-side plots belong to PAD0/H96-Hgel samples, corresponds to copolymer P(AMPS-HEMA) hydrogel.

straight lines presented in the stress - strain plots and the results were collected in Fig. 6(A) as a function of the ionic strength of  $\text{Na}_2\text{SO}_4$  solution. Terpolymer PAD10/H86 Cgel sample prepared via cryogelation at  $-18^\circ\text{C}$  exhibited greater compressive moduli than that of PAD10/H86-Hgel sample prepared at room temperature via conventional radical polymerization. The elastic modulus of both terpolymer Cgel and Hgel samples markedly increased with the ionic strength of the salt solution. Upon increasing the ionic strength of  $\text{Na}_2\text{SO}_4$  solution from  $10^{-6}$  M–0.1 M, the compressive moduli of terpolymer PAD10/H86-Cgel sample increased from 8.8 kPa to 16.0 kPa. In the same range of the ionic strength, the elastic moduli of terpolymer PAD10/H86-Hgel increased from 5.7 kPa to 11.3 kPa. Increasing the concentration of  $\text{Na}_2\text{SO}_4$  solution up to 0.1 M induced a 2-fold increase in the elastic modulus of terpolymer Cgel and Hgel samples. The observed increase in the elastic modulus was connected with the salt-sensitive swelling of terpolymer alcogels; the compressive modulus terpolymer alcogels increased upon the shrinkage of the terpolymer networks. As seen in Fig. 6(B), the terpolymer Cgel and Hgel samples tend to shrink as  $\text{Na}_2\text{SO}_4$  concentration increases. Therefore, the equilibrium swelling of

terpolymer alcogels decreased with the increasing ionic strength of the solution as the concentration difference of counterions  $\text{SO}_4^{2-}$  inside and outside the terpolymer network decreased. The dilution of  $\text{Na}_2\text{SO}_4$  solution up to  $10^{-6}$  M induced a 6-fold increase in the swelling degree of terpolymer Hgels, while a 11-fold increase was observed for terpolymer Cgels. Ikehata and Ushiki studied the effect of salt on the elastic modulus of poly(N-isopropylacrylamide) (PNIPA) gels. They reported that the tensile modulus of PNIPA gel in the solution of salt depends on the volume of gel [31]. The elasticity of PNIPA gel in the deswollen state depended on the kind and concentration of the salt as the viscoelasticity emerged due to the shrinkage of polymer network.

The key topological parameters including the effective cross-linking density  $\nu_e$ , the average network chain length  $N$  and the average molecular weight of network chains  $M_c$  were estimated on the basis of rubber elasticity theory and this estimation was limited to terpolymer hydrogels assuming the network chains are Gaussian chains with homogeneous distribution. Among the methods for estimating the network chain density (also called effective cross-linking density,  $\nu_e$ ) from the elastic modulus of the gel sample  $G$ , the simplest one is using the following

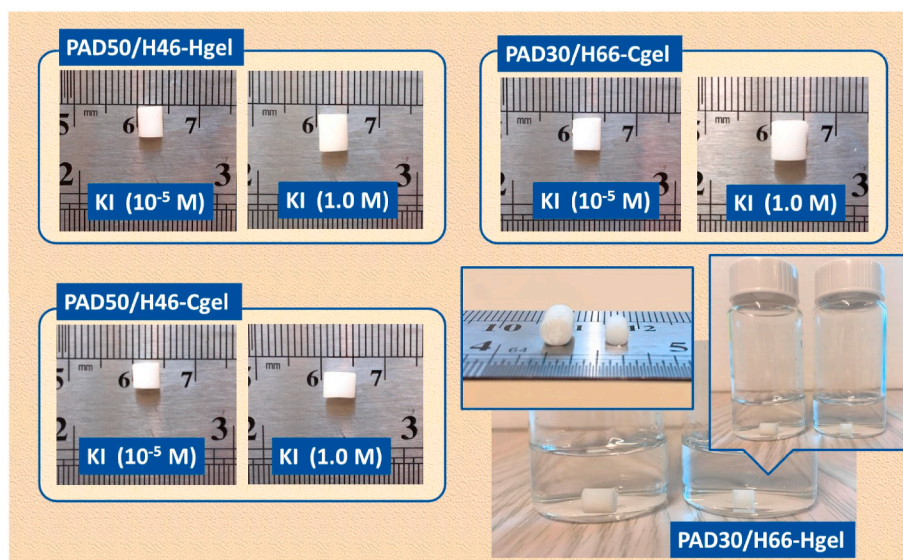


Fig. 9. Photographs of PADm/Hn-Hgel and Cgel samples with DEAEMA/HEMA mol ratio 30/66 and 50/46 after their swelling in  $10^{-5}$  M and 1.0 M KI solutions.

relation which is valid for homogeneous network of Gaussian chains by Refs. [22,23]:

$$G_{\text{salt}} = \beta \frac{RT}{N\bar{V}_1} \nu_2^{1/3} (\nu_2^0)^{2/3} = \beta RT \nu_e \nu_2^{1/3} (\nu_2^0)^{2/3} \quad (6)$$

with the front factor  $\beta = 1$  for affine networks, and  $1-2/\phi$  for phantom networks (better valid for highly swollen networks), in which  $\phi$  is the crosslinker functionality and for DEGDMA equals 4.  $\bar{V}_1$  is the molar volume of solvent,  $R$  is the universal gas constant and  $T$  is the absolute temperature in K.

Using the compressive modulus values,  $G_{\text{salt}}$  and the experimentally determined values of structural parameters;  $\nu_2$  and  $\nu_2^0$  evaluated by assuming affine network model in Eq. (6),  $\nu_e$  values of terpolymer hydrogels were determined and the results were shown in Fig. 7(A) as a function of the ionic strength of aqueous salt solution. The calculated  $\nu_e$  values through the elastic properties indicate the density of junction points joined to the elastically effective chains and thus contribute to the elastic free energy of a network of Gaussian chains [32]. In their work, Tanaka and Ishida proposed a criterion for a network subchain to be elastically effective and only a subchain connected to junctions at both ends is regarded as elastically effective [33]. The effective cross-linking density,  $\nu_e$  which can directly be obtained from the measurement of the compressive modulus through the relation (6), would be meaningful to obtain information on the key topological parameters; including the number of repeating units and the average molecular weight between two successive crosslinks, through the relation  $\nu_e = (1/N\bar{V}_1) = \rho/M_c$ . The calculated results were compared in Fig. 7(B). Using the elastic modulus data in  $10^{-6}$  M of salt solution, the effective cross-linking density  $\nu_e$  of terpolymer PAD10/H86-Hgel was calculated as  $141.1 \text{ mol/m}^3$ , and  $\nu_e$  values first increased with increasing the ionic strength of the  $\text{Na}_2\text{SO}_4$  solution and reached a maximum at  $10^{-3}$  M and then slightly decreased. This may be attributed to the collapsing of terpolymer Hgels with increased ionic strength of salt solution which tends to form more compact terpolymer clusters and increases the compressive elastic moduli. It is clear that the volume of terpolymer Hgels was reduced with increase of salt concentration (Fig. 6(B)). But at the same time, the ions tend to interact with the functional groups of terpolymer chains and exhibit ion-bonding property and this creates additional crosslinking points that contribute positively for the elastic modulus [34]. Li and coworkers studied the effect of ionic strength on the swelling behavior of the amphiphilic gels based on hydrophobically modified DMAEMA [35]. It was reported that the formation of

ion-clusters between the quaternary ammonium pendant groups and anions with low hydration energies acts as physical crosslinking sites and disfavor the swelling of gels.

Using  $\nu_e$  values of terpolymer Hgels in the present work, Flory-Huggins interaction parameter  $\chi$  for terpolymer network-water system was determined from the following expression of Flory-Rehner equation [23]:

$$\chi = - \frac{\ln(1 - \nu_2) + \nu_2 + 0.5\nu_e \left( (\nu_2)^{1/3} (\nu_2^0)^{2/3} - \nu_2/2 \right)}{(\nu_2)^2} \quad (7)$$

which describes the overall interactions between the terpolymer network-water depending on the swelling extent in various concentration of salt solutions in the range of interest. It is expected that the specific interactions between cations and side groups of terpolymer network affect the mixing term of the free energy. As seen in Table 3,  $\chi$  parameters increased from 0.4639 to 0.5919 with increasing salt concentration. In diluted range of the salt solutions, the low values of  $\chi$  parameters indicated a weak interaction between hydrophobic side groups of the terpolymer chains and a strong interaction between the terpolymer network-water.

#### 3.4. Ion-induced swelling of terpolymer alcogels

The effect of type and concentration of salt on the swelling for a series of terpolymer alcogels was discussed. To understand the salt-induced swelling characteristics of terpolymers in presence of different cations and anions, the halide anions of potassium (KCl, KBr and KI) solutions and the sulfonate salts of  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Zn}^{2+}$  were employed as swelling media. From the reversible swelling/shrinking testing, swelling kinetics, the type of mechanism and diffusion parameters were also determined as a function of the terpolymer composition.

#### 3.5. Effect of different halide ions with a common cation ( $\text{K}^+$ ) on swelling

Fig. 8 shows the swelling ratio of terpolymer PADm/Hn-Hgel and Cgel as a function of concentration in aqueous KCl, KBr and KI solutions. Note that the swelling of a gel in water may be increased (salting-in effect) or decreased (salting-out effect) by the presence of a salt, depending on the cation and anion of the salt used, and the ionic strength of the salt solution. At low ionic strength, the degree of swelling increases by the addition of salt, in what is termed the salting-in region.

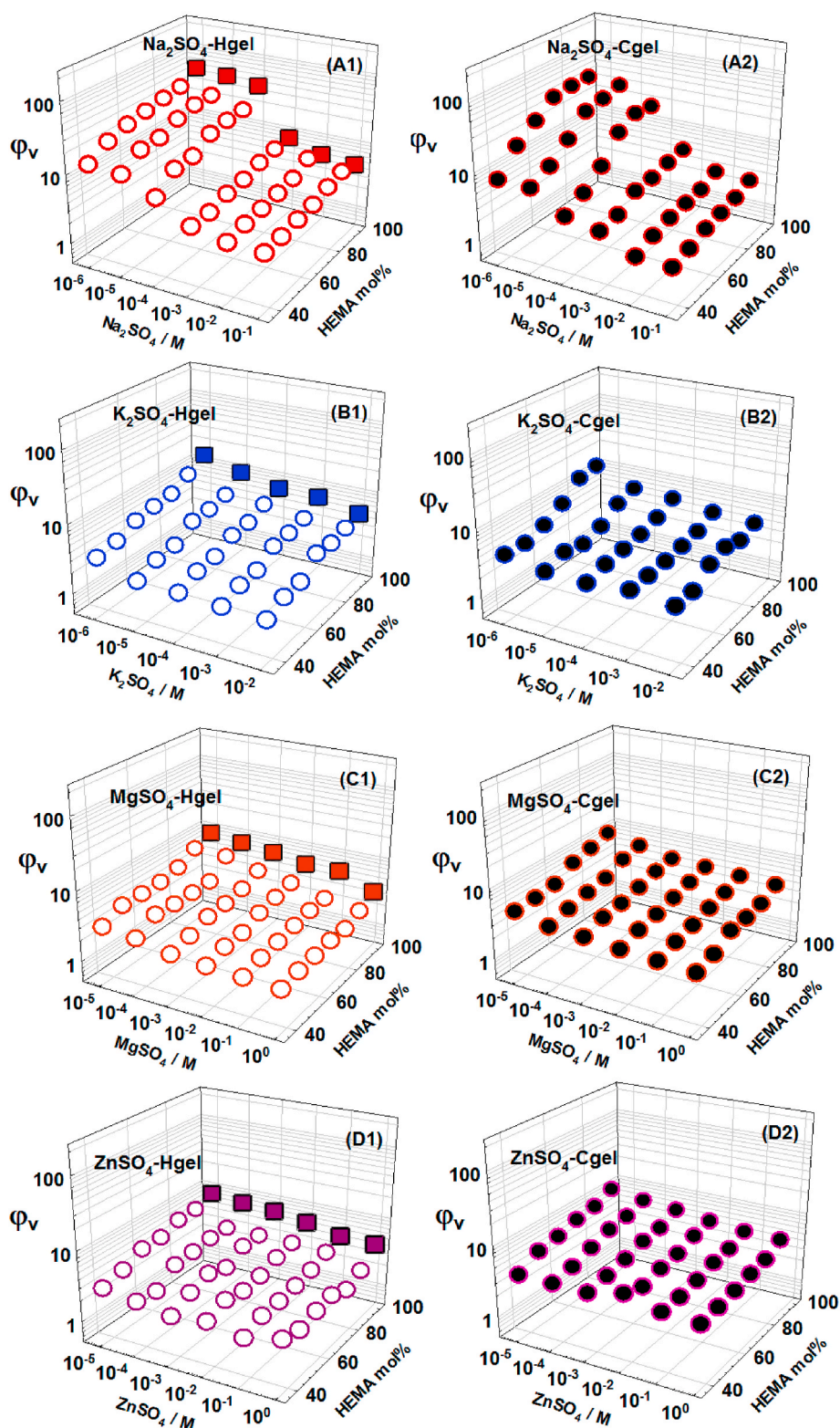


Fig. 10. The equilibrium volume swelling ratio  $\phi_v$  of PADm/Hn-Hgel (left) and Cgel (right) samples as a function of the ionic strength of aqueous salt solutions of Na<sub>2</sub>SO<sub>4</sub> (A), K<sub>2</sub>SO<sub>4</sub> (B), MgSO<sub>4</sub> (C) and ZnSO<sub>4</sub> (D). The data shown by solid square symbols in the left-side plots belongs to PAD0/H96-Hgel samples, corresponds to copolymer P(AMPS-HEMA) hydrogel.

It was reported that the salting-in effect results from a direct binding of the cations to the ether oxygens of the polymers [36]. The salting-out behavior results from the formation of anion-water hydration complexes, which in turn, decreases the degree of swelling as a function of the ionic strength. Salt-induced swelling results in potassium salts

clearly demonstrated the salting-out behavior and the swelling ratio of terpolymer alcogels decreased upon increasing the ionic strength of the solutions and with an increase in the size of anions present in the swelling medium. This nature is due to the decreasing extent of the osmotic pressure difference between the terpolymer networks and the

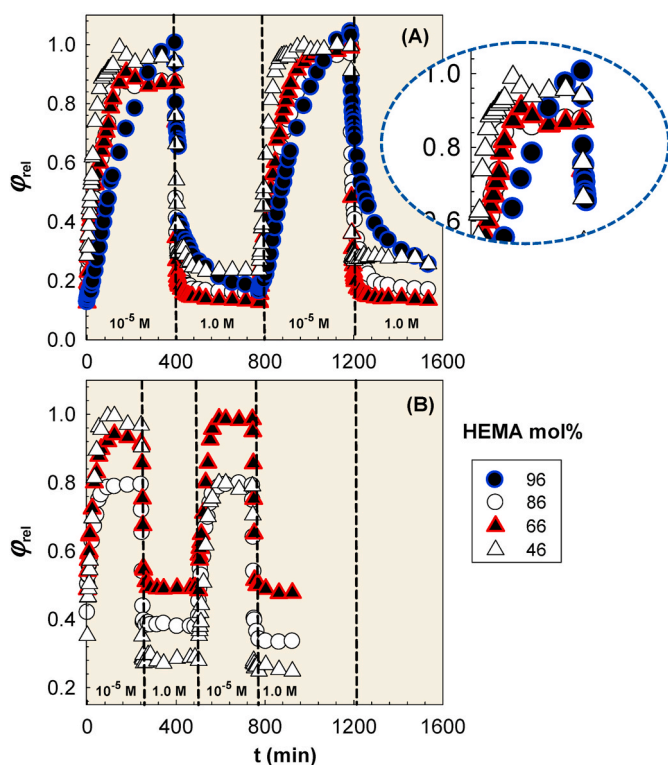


Fig. 11. Relative weight swelling ratio  $\phi_{rel}$  of terpolymer PADm/Hn-Hgel (A) and Cgel (B) with different HEMA content as a function of the swelling time in  $10^{-5}$  M of KCl solution and shrinking time in 1.0 M.

external solution upon increasing the ionic strength of salt solution. Although the swelling capacity of terpolymer alcogels was not very high, they showed distinct and systematic swelling behavior in the salt solutions. As can be seen in Fig. 9, terpolymer PADm/Hn-Cgels showed high swelling capacity as a result of their porous morphology induced by the cryogelation when compared with terpolymer PADm/Hn-Hgels. The swelling ratio of terpolymer PADm/Hn alcogels increased with an increase of HEMA content in the feed. The equilibrium swelling ratio of PAD0/H96-Hgel samples corresponding to copolymer P(AMPS-HEMA) hydrogels (presented by solid square symbols in Fig. 8) was larger than those of terpolymer hydrogels as a result of the intramolecular hydrogen bonding between hydroxyl and carbonyl groups and intermolecular hydrogen bonding between hydroxyl groups as well as due to the presence of AMPS units increasing the anionic character of the copolymer network. Because of the tendency of HEMA to interact with water molecules, the swelling degree was possibly controlled by HEMA part of terpolymers. In the presence of different halide ions with a common cation ( $K^+$ ), the swelling degree of terpolymer Cgels and Hgels decreased with larger ratio of charge/radius due to difficulty in the penetration of  $Cl^-$ ,  $Br^-$ , and  $I^-$  anions into terpolymer network. According to their hydration abilities, the swelling degree followed the order of  $Cl^- > Br^- > I^-$  (anions) in consistent with a typical Hofmeister order in KCl, KBr and KI, respectively.

A strong ability for hydration resulted in the salting-out effect that forces the terpolymer alcogels to shrink in aqueous salt solutions, while at moderate concentrations of KI, the terpolymer alcogels displayed a so-called anti-polyelectrolyte behavior, that is, the terpolymer chains expand with increase of the ionic strength in the external solution, resulting in an increase in the water content and higher swelling capacity. For both terpolymer Cgels and Hgels, the swelling increased especially at 1.0 M as a result of salting-in behavior. In Fig. 9, photographs of PADm/Hn-Hgel and Cgel samples with DEAEMA/HEMA mol ratio 30/66 and 50/46 after swelling in  $10^{-5}$  M and 1.0 M KI solutions clearly showed the observed swelling behavior.

### 3.6. Effect of different mono- and di-valent cations with a common anion ( $SO_4^{2-}$ ) on swelling

Fig. 10 shows the swelling of terpolymer PADm/Hn-Hgel and Cgel as a function of the concentration of  $Na_2SO_4$ ,  $K_2SO_4$ ,  $MgSO_4$  and  $ZnSO_4$  solutions, respectively. In salt solutions with a common anion ( $SO_4^{2-}$ ), terpolymer alcogels exhibited an increase in the swelling degree in the order of  $Zn^{2+} < Mg^{2+} < K^+ < Na^+$  in accordance with their cationic radius. The less the radius of the same valent monatomic cation, the more the swelling capacity in the salt solutions in the order of  $Na^+ > K^+$  and  $Mg^{2+} > Zn^{2+}$ . This was corresponded to their cationic radius or their hydration forces. These results are similar to hydroxyethyl methacrylate/*N,N*-dimethyl-(acrylamido propyl) ammonium propane sulfonate (HEMA/DMAAPS) copolymeric gels reported by Lee and Chen [37]. They investigated the salt-sensitive swelling of HEMA/DMAAPS gels in LiCl, NaCl, KCl,  $MgCl_2$ ,  $CaCl_2$ , and  $SrCl_2$  solutions and reported the effect of mono- and divalent cations with a common anion  $Cl^-$  on the equilibrium swelling degree. Their results showed that the swelling ratios increased rapidly with smaller ratio of charge/radius and the hydration grows by the small cations surrounded with a large amount of water. In the presence of high charge of cations, the swelling degree of terpolymer alcogels decreased as divalent  $<$  monovalent arising from the coordination of the divalent cations with functional groups of terpolymer chains.

In  $MgSO_4$  and  $ZnSO_4$  solutions, the swelling decreased even more with increasing the concentration of  $MgSO_4$  and  $ZnSO_4$  in the outer solution as a result of the lower amount of di-valent cations than monovalent cations required to maintain the charge balance. The divalent  $Mg^{2+}$  and  $Zn^{2+}$  ions can possibly serve as cross-link points between charged segments along terpolymer chains and result in an increase in the apparent crosslinking density because of "ionic crosslinking". Comparing Figs. 8 and 10, the swelling of terpolymer alcogels is profoundly influenced by the type and concentration of salts. Considering that  $SO_4^{2-}$  with larger size and higher valence, the anionic effect is larger than the cationic effect.

### 3.7. Ion-triggered swelling kinetics of terpolymer alcogels

Analyzing the obtained results, salt-triggered swelling/shrinking of PADm/Hn-Hgel and Cgel were investigated as successive cycles at different ionic strengths; swelling in aqueous KCl solution of  $10^{-5}$  M followed by shrinking in 1.0 M solution. The alternative immersion was repeated two times to ensure an abrupt swelling/shrinking. The variation of the relative weight swelling ratio  $\phi_{rel}$  with swelling/shrinking time against rapid ionic strength change was depicted in Fig. 11. During the swelling process in  $10^{-5}$  M KCl solution, it was observed that the dynamic swelling profiles of DEAEMA-rich terpolymer PADm/Hn-Hgels and Cgels exhibit an overshooting behavior in which the relative weight swelling ratio  $\phi_{rel}$  curve attains a maximum point called the overshooting value. This behavior could be attributed to the molecular chain relaxation as well as the dynamic conformational changes of the side chains of DEAEMA units during the swelling process. The overshooting phenomenon of terpolymer alcogels disappeared at a lower DEAEMA content, hence at a higher HEMA content, in the terpolymer network. This result is similar to that reported by Lee and Lin for the swelling behavior of the 2-hydroxyethyl methacrylate-co-acrylic acid-co-sodium acrylate copolymeric hydrogels [38]. It was found that the overshooting phenomenon is displayed at a higher HEMA content and lower temperature. This behavior was connected to network chain relaxation. The water molecules tend to diffuse into network before the relaxation of network chains. By the relaxation of network chains, water molecules are forced out of the network, and the swelling ratio decreases until its equilibrium value. In another work, Li and coworkers studied the dynamic swelling of the PDMAEMA gels in NaCl solutions with different concentrations [39]. Their results showed that the overshooting behavior mainly observed in lower concentration NaCl solutions. This

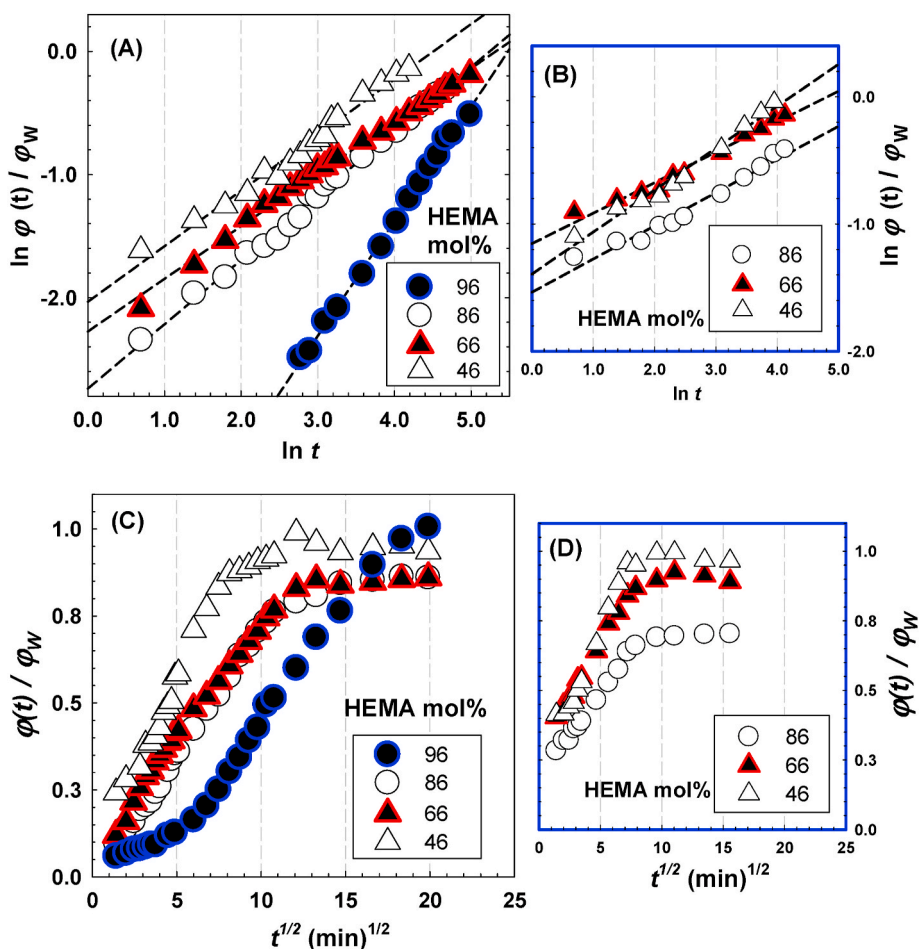


Fig. 12. Plots of  $\ln \phi(t)/\phi_w$  versus  $\ln t$  (A, B) and water fraction  $\phi(t)/\phi_w$  against  $t^{1/2}$  (C, D) for PADm/Hn-Hgel (A,C) and Cgel (B, D) with different HEMA content from the swelling in  $10^{-5}$  M of KCl solution.

Table 4

Kinetic parameters of PADm/Hn-Hgel and Cgel determined from the swelling data in aqueous KCl solutions of  $10^{-5}$  M: Kinetic exponent  $n$ , characteristic diffusion constant  $k$ , early-time diffusion coefficient of water  $D_e$ , late-time diffusion coefficient of water  $D_l$ , and swelling rate constant  $k_s$ .

	Sample code	$n$	$k$	$D_e \times 10^7$ ( $\text{cm}^2/\text{s}$ )	$D_l \times 10^7$ ( $\text{cm}^2/\text{s}$ )	$k_s \times 10^2$
PADm/Hn						
Hydrogels Hgel	PAD0/H96	0.9303	0.0061	2.2813	2.3781	0.0183
	PAD10/H86	0.5222	0.0647	2.3659	2.6359	0.2417
	PAD30/H66	0.4519	0.0992	3.1828	4.4345	0.2991
	PAD50/H46	0.4253	0.1414	4.8305	5.7608	0.8417
Cryogels Cgel						
Cryogels Cgel	PAD10/H86	0.2608	0.2151	2.5093	2.7870	7.2428
	PAD30/H66	0.2884	0.2681	3.6167	5.0731	5.2825
	PAD50/H46	0.3789	0.2123	5.7824	6.7033	1.3899

behavior of PDMAEMA gels was due to the dynamic conformational changes of DMAEMA side chains during the swelling process; the stretched conformation and the cyclic conformation which is a thermodynamically stable status. When the gel is immersed in solution, the side chains of the DMAEMA units tend to adopt the stretched

conformation, the hydrogen-bond interaction between the water molecules and the tertiary amino groups overwhelm the conjugation interaction between the carboxyl and amino groups and therefore favors the swelling of the gel. Li and coworkers also showed that the overshooting effect was indiscernible since the stretching of the network chains consisting DMAEMA units were weakened in concentrated salt solutions. Another point shown from the dynamic swelling profile of terpolymer alcogels was that the terpolymer PADm/Hn-Cgel samples exhibited very fast swelling profile in  $10^{-5}$  M of KCl solution. PAD50/H46-Cgel sample containing 46 mol% HEMA reached the maximum swelling within 82 min, while the hydrogel sample PAD50/H46-Hgel sample containing same amount of HEMA required 146 min to reach the maximum swelling.

To evaluate the swelling profile and diffusion characteristics, the following time-dependent power law equation was used [40–42]:

$$\frac{\phi(t)}{\phi_w} = kt^n \quad (8)$$

with  $\phi(t)$  and  $\phi_w$  representing dynamic swelling at time  $t$ , and the equilibrium weight swelling ratio, respectively.  $k$  is a characteristic kinetic constant of terpolymer gel depending on the geometry of the sample and  $n$  is a characteristic exponent describing water diffusion toward the inside of the terpolymer gel matrices. For cylindrical-shaped gels, a value of  $n$  equals to 0.43–0.45 indicates the water uptake to follow the Fickian behavior and the rate of water diffusion is slower than the terpolymer chain relaxation rate. Any value between 0.45 and 0.89 indicates that the water uptake is controlled by the terpolymer chain

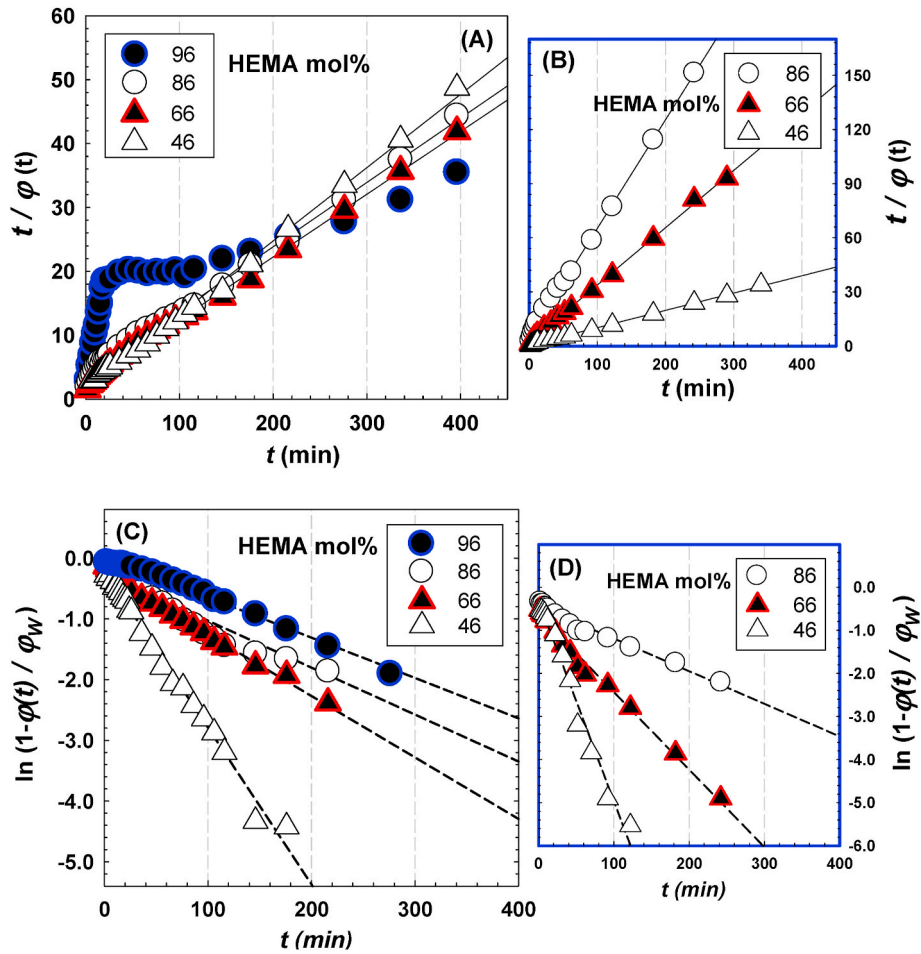


Fig. 13. Plots of Schott model for evaluation of the swelling rate constant  $k_s$  (A, B) and  $\ln(1-\phi(t)/\phi_w)$  against  $t$  curves for evaluation of the diffusion coefficient  $D_l$  of water for longer diffusion times (C, D) of PADm/Hn-Hgel (left plots) and PADm/Hn-Cgel (right plots) with different HEMA content from the swelling in  $10^{-5}$  M KCl solution.

relaxation and diffusion while the water uptake in terpolymer samples follows non-Fickian or anomalous diffusion. From the slope and intercept of  $\ln \phi(t)/\phi_w$  vs  $\ln t$  curves presented in Fig. 12 (A,B), the power-law coefficients  $n$  and  $k$  with Eq. (8) were determined and collected in Table 4.

According to Fick Model (first order), for the study of swelling of terpolymer hydrogels in  $10^{-5}$  M KCl solution,  $n$  values decreased from 0.9303 to 0.4253 with increasing the amount of DEAEEMA content in the terpolymer feed, and the diffusion mechanism changed from non-Fickian type to Fickian diffusion in which the rate of diffusion is low relative to the chain relaxation rate, and process controlled by diffusion. As terpolymer network becomes more hydrophilic, for HEMA-rich terpolymer hydrogels, the diffusion of water into terpolymer network was taken as a non-Fickian as a consequence of comparable rates of the diffusion and chain relaxation. In the case of terpolymer PADm/Hn-Cgels, as a result of fast swelling process due to porous structure of cryogel matrices,  $n$  parameters yielded Less Fickian diffusion  $n < 0.3789$  for all samples. The dynamic swelling process was reversible and terpolymer gels were stable after two-repeating cycles of swelling/shrinking promoted by the change of ionic strength of KCl solutions. Considering “short time approximation method” for the first 60% of swelling data given in Fig. 11, the early stage diffusion coefficients  $D_e$  of terpolymer alcogels were determined using the following square root time-dependent relation [43]:

$$\frac{\phi(t)}{\phi_w} = 4 \left[ \frac{D_e t}{\pi L^2} \right]^{1/2} \quad (9)$$

where  $L$  is the thickness of sample. Since the water fraction  $\phi(t)/\phi_w$  is proportional to  $t^{1/2}$ ,  $D_e$  values of terpolymer alcogels calculated from the slope of the initial linear part of curves given in Fig. 12 (C,D). As seen in Table 4, for PADm/Hn-Hgels,  $D_e$  values changed between  $2.2813-4.8305 \times 10^{-7}$  cm<sup>2</sup>/s and that of PADm/Hn-Cgels changed between  $2.5093-5.7824 \times 10^{-7}$  cm<sup>2</sup>/s. As a result of rapid swelling rate of resulting terpolymer cyogels, their diffusion coefficients were greater than those for terpolymer hydrogels. Fig. 13 (A, B) presents the results based on Schott model for longer periods of swelling time.

The swelling mechanism described by a second-order kinetics was fitted with the following equation [44]:

$$\frac{t}{\phi(t)} = \frac{1}{\phi_w^2 k_s} + \frac{t}{\phi_w} \quad (10)$$

where  $k_s$  is the swelling rate constant.  $t/\phi(t)$  against time  $t$  plots in Fig. 13 showed excellent straight lines with good linear correlation coefficients for all terpolymer hydrogels and cryogels (except for copolymer hydrogel referred as PAD0/H96). Therefore, the present terpolymer alcogels followed second order kinetic for longer times, which is to conclude, relaxation of the terpolymer chains occurs.

Considering “late-time approximation method”, the diffusion coefficients  $D_l$  for longer diffusion times were determined by the following equation [44]:

$$\frac{\phi(t)}{\phi_w} = 1 - \frac{8}{\pi^2} \exp\left(\frac{-\pi^2 D_l t}{L^2}\right) \quad (11)$$

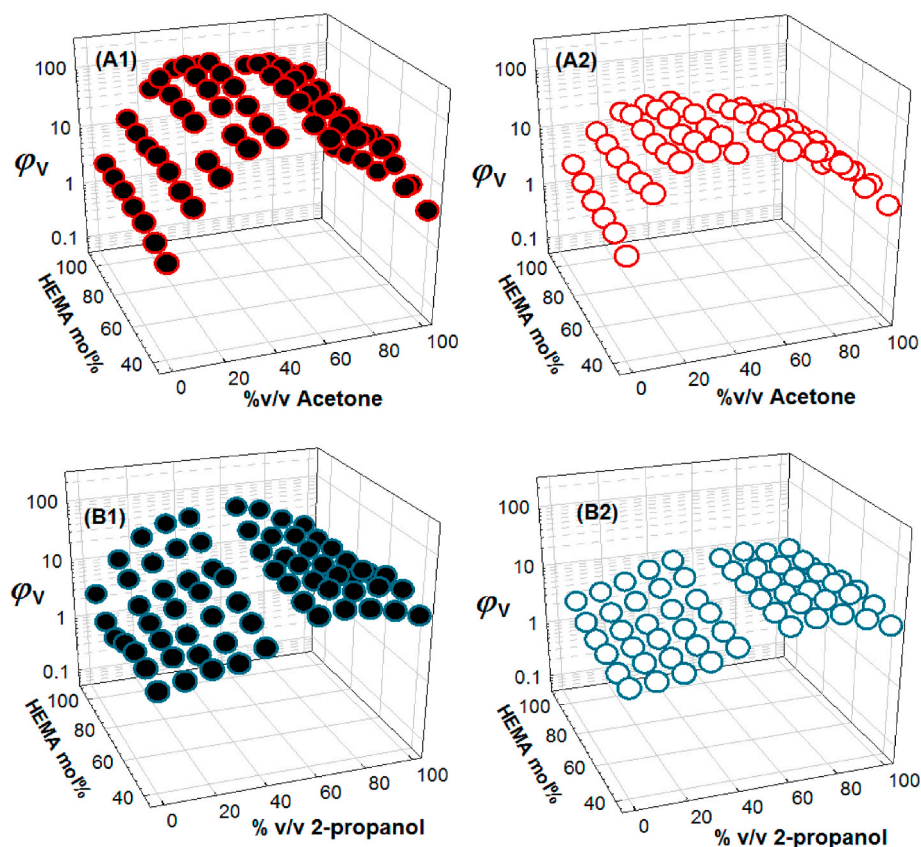


Fig. 14. The equilibrium volume swelling ratio  $\phi_v$  of PADm/Hn-Hgel (left) and Cgel (right) shown in different water/solvent mixtures: Acetone (A1, A2) and 2-propanol (B1, B2).

From the slope of  $\ln(1 - \phi(t)/\phi_w)$  versus  $t$  plots presented in Fig. 13 (C D),  $D_l$  values of PADm/Hn-Hgels increased with increasing DEAEMA content and ranged between  $2.3781\text{--}5.7608 \times 10^{-7} \text{ cm}^2/\text{s}$  and that of PADm/Hn-Cgel ranged between  $2.7870\text{--}6.7033 \times 10^{-7} \text{ cm}^2/\text{s}$ .

The calculated results are in good agreement with the results reported by Tomic and coworkers for the diffusion coefficients of water in HEMA-based ionic copolymeric hydrogels [45]. It was observed that the values of  $D_e$  and  $D_l$  of the present terpolymer alcogels given in Table 4 were of the same magnitude but smaller than the copolymeric poly(2-hydroxyethyl methacrylate-itaconic acid) P(HEMA-ITA) hydrogels. In their copolymeric systems, the values of coefficients of water diffusion for early- and late-time approximations for P(HEMA-ITA) hydrogels were found to be in the range of  $1.10\text{--}1.61 \times 10^{-7}$  and  $11.6\text{--}28.2 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ . The swelling governed by Fickian transport mechanism as the diffusional exponents,  $n$ , were near 0.5 and the effective diffusivity increased with increasing ITA content in the copolymer. The values of late-time diffusion coefficients were also higher than the early time values in accordance with the higher water contents. This observation indicated that the terpolymer network structure in the present system have a more compact structure, which hinders the penetration of water during the initial swelling stage. Probably the intra- and inter-molecular bonding between the hydroxyl groups of HEMA and the amide groups of AMPS in the present terpolymers are responsible for this decrease. The obtained results indicated that the equilibrium water content of terpolymer alcogels was found to vary systematically with the network composition.

### 3.8. Solvent-triggered swelling properties of terpolymer alcogels

In order to evaluate the solvency properties and conformational changes in water-nonsolvent mixtures, the equilibrium swelling of terpolymer alcogels was tested in aqueous solutions of acetone and

monohydric alcohols with various hydrophobic alkyl groups; methanol, ethanol and 2-propanol as presented in Figs. 14–15. As shown, the swelling behavior of terpolymer alcogels strongly depended on the acetone and alcohol species. The solvent composition was changed by progressive substitution of water. The extent of swelling did not monotonically change with the amount of solvent present in the outer solution. A pronounced swelling/shrinking behavior and cosolvency effect was observed due to the specific interactions of water and solvent molecules with the functional side groups in the terpolymer chains. The hydroxyl groups of an alcohols tend to interact with water and produces hydrogen bonding between these molecules. At low concentration of nonsolvent in the outer water-nonsolvent solutions, the equilibrium swelling of HEMA-rich terpolymer alcogels increased up to 40% v/v. In this range, DEAEMA-rich terpolymer alcogels exhibited relatively lower swelling ratio and with further increasing the nonsolvent concentration in the outer solution up to 100% v/v, DEAEMA-rich terpolymer alcogels swelled. However, the swelling degree of HEMA-rich alcogels was decreased with further increasing the nonsolvent concentration. Comparison of the equilibrium volume swelling ratio  $\phi_v$  of terpolymer alcogels containing 96 mol% and 86 mol% of HEMA in different water/solvent mixtures was given in Fig. 16.

The swelling degree in solvent mixtures depends on the extent of solvation of functional groups in the terpolymer chains which overcomes the polymer-polymer interactions. In the presence of solvent, dissolution of the terpolymer network chains between the crosslinking points leads to the expansion of terpolymer gels until the elastic force of the crosslinked terpolymer network is balanced. The main interactions between solvent molecules and terpolymer chains involve the hydrogen bonding with the hydroxyl and amide groups. It is possible to build an acceptor hydrogen bond with  $-\text{OH}$  and  $-\text{NH}$  groups a donor hydrogen bond with  $-\text{C}=\text{O}$  of AMPS, DEAEMA and HEMA segments. Therefore, for dominating the swelling of polymer network in the solvent, the

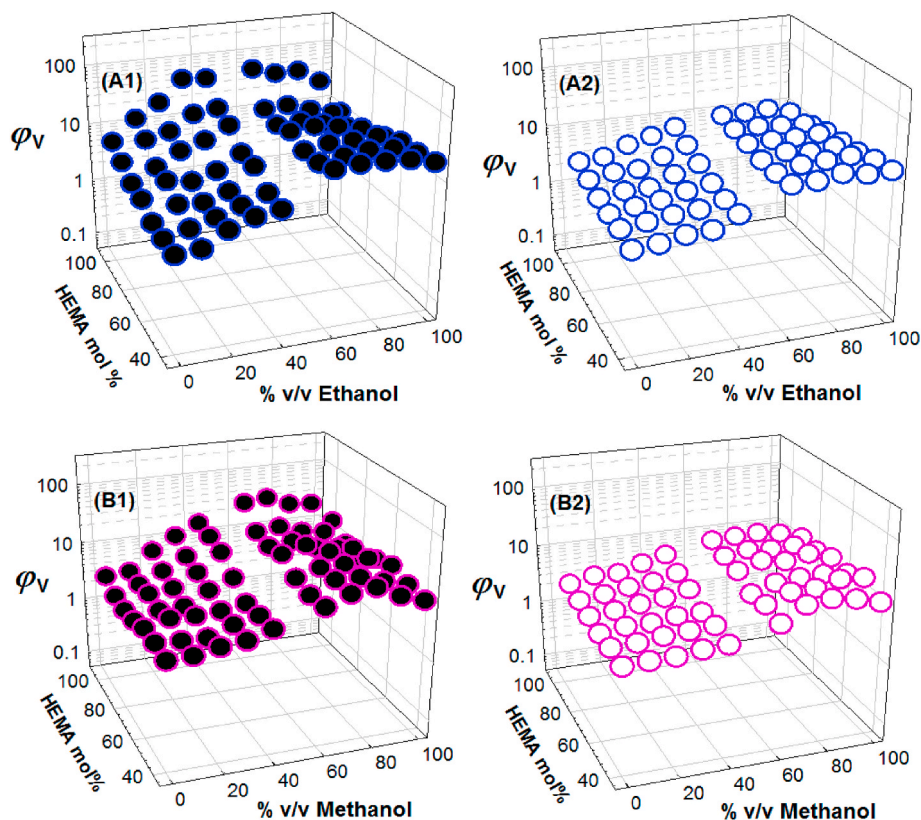


Fig. 15. The equilibrium volume swelling ratio  $\phi_v$  of PADm/Hn-Hgel (left) and Cgel (right) shown in different water/solvent mixtures: Ethanol (A1, B1) and methanol (A2, B2).

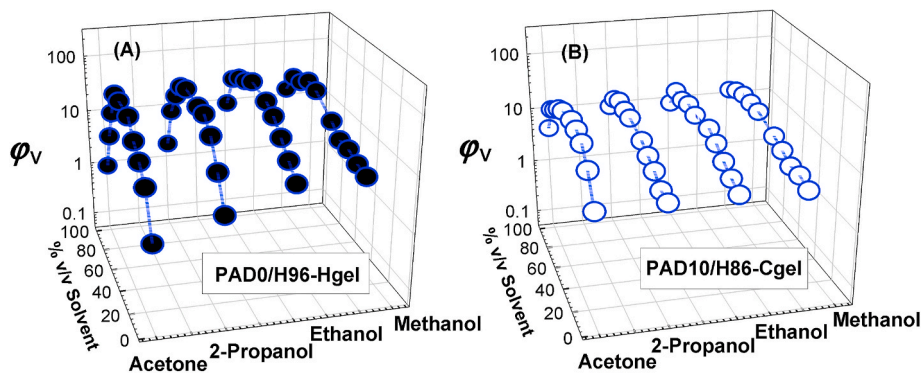


Fig. 16. Comparison of the equilibrium volume swelling ratio  $\phi_v$  of PAD0/H96-Hgel (A) and PAD10/H86-Cgel (B) in different water/solvent mixtures as a function of the solvent volume fraction.

interactions between polymer chains and solvent molecules play an important role. Hansen solubility parameter for hydrogen bonding ( $\delta_h$ ) predicts a reasonable correlation indicating the importance of hydrogen bond interaction, while the other factors; dispersion forces, polar effects could also play some role [46]. PDEAEMA has a defined hydrophobic nature due to the vinylic backbone and the presence of the diethyl groups on tertiary amine. As seen in Fig. 16(A), the swelling of both PADm/Hn-Hgel and Cgel increased rapidly up to 40% v/v of acetone due to strong attractive interactions between the acetone and terpolymer network, then remained nearly constant in the range of 50–60% v/v, and deswelled in the medium with a much higher acetone composition as a result of weak attractive interactions.

Since acetone forming moderate hydrogen bonds in the mixtures with water compared to water/monohydric alcohol mixtures, so that hydrophobic interactions dominate the swelling behavior of terpolymer

alcogels. In the water/solvent mixtures, the terpolymer alcogels passed to a more collapsed state as hydrogen bonding interactions  $\delta_h$  decreased. For the solvents used in the swelling tests, the hydrogen bonding components of the solubility parameter values  $\delta_h$  vary as 22.3 (methanol), 19.4 (ethanol), 16.4 (2-propanol) and 7.0 (acetone)  $\text{Mpa}^{1/2}$  [46,47]. The extent of the observed swelling degree tends to decrease in the order; methanol > ethanol > 2-propanol > acetone which is driven by the competition between PADm/Hn terpolymer network-water interactions and PADm/Hn terpolymer network-solvent interactions. In the case of a higher concentration of solvent in the outer solution, the attractive water-solvent interactions together with the intramolecular hydrophobic forces within the terpolymer network seem to dominate over the solvent-PADm/Hn network or water-PADm/Hn network interactions. Therefore, addition of water to solvent or solvent to water results in a decrease in the solvent content of the terpolymer network, so that

PADm/Hn-Hgel and Cgel tend to collapse and attain a minimum volume. Alcogels based on poly(ethylene glycol methylether methacrylate) macromer and acrylic acid were synthesized by Najafi and coworkers via solution polymerization using trimethyl propane triacrylate as cross-linker. The swelling behavior of alcogels was investigated in water, ethanol and methanol and it was found that the alcogels absorb methanol and ethanol up to 17.4 and 14.8 g/g, respectively. With increasing anionic comonomer content, increased alcohol absorbency was assigned to the formation of H-bonding and dissociation of COOH groups producing mobile ions [48].

#### 4. Conclusions

Fabrication of weakly cationic alco-cryogels by cross-linking cryopolymerization of 2-(diethylamino)ethyl methacrylate (DEAEMA) in the presence of hydroxyethyl methacrylate and ionic monomer 2-acrylamido-2-methyl-propanosulfonic acid was performed. XRD analysis of terpolymer alcogels revealed that the samples are amorphous in nature and with increase in DEAEMA content in the feed, inter-planar spacing and the inter chain length were increased. The thermal stability of the terpolymer alcogels can be tuned by modifying DEAEMA/HEMA ratio and by reducing the polymerization temperature. DEAEMA-rich terpolymer alcogels exhibited the highest rate of decomposition. For all terpolymer samples, a single glass transition temperature was detected, further confirming the successful formation of a terpolymer. Effect of ionic strength, and various cations/anions on the elasticity and degree of water absorbency were evaluated. By increasing the concentration of Na<sub>2</sub>SO<sub>4</sub> solution up to 0.1 M, a 2-fold increase in the compressive modulus of terpolymer alcogels was observed. The calculation of the interaction parameter  $\chi$  between terpolymer and water indicated that the specific interactions between ions and functional groups of terpolymer network affect the mixing term of the free energy. The swelling capacity of terpolymer networks in the form of Cgel and Hgel decreased with an increase in the size of the counterion species present in the swelling medium and followed the order of swelling behavior Cl<sup>-</sup> > Br<sup>-</sup> > I<sup>-</sup> (anions). The terpolymer alcogels exhibited salting-out behavior in the presence of Cl<sup>-</sup> and Br<sup>-</sup> ions, but exhibited salting-in behavior in KI solutions. The sensitivity sequence of the terpolymer alcogels to cations was Na<sup>+</sup> > K<sup>+</sup> > Mg<sup>2+</sup> > Zn<sup>2+</sup>. The swelling behavior of terpolymer alcogels in various water/solvent mixtures including acetone and monohydric alcohols with various hydrophobic alkyl groups; methanol, ethanol, and 2-propanol was studied with attention to the polarity of the nonsolvent component. After two successive cycles of swelling/shrinking in KCl solution, the terpolymer alcogels showed better recovery properties and responsiveness at different ionic strengths. The swelling data agreed well with the second-order kinetic model. For HEMA-rich terpolymer hydrogels, as PADm/Hn-Hgel becomes more hydrophilic, the diffusion of water into terpolymer network was a non-Fickian type due to comparable rates of the diffusion and chain relaxation. Upon increasing the amount of DEAEMA content in the terpolymer feed, the diffusion mechanism changed from non-Fickian type to Fickian diffusion in which the rate of diffusion is low relative to the chain relaxation rate. Due to their porous structure, terpolymer alco-cryogels exhibited very rapid swelling kinetics and  $n$  parameters yielded Fickian diffusion for all cryogel samples. In ionic environments, the salt-sensitivity of terpolymer alcogels will lead to their unique applications.

#### CRediT authorship contribution statement

**Nur Sena Ökten Besli:** Investigation, Experimental Methodology, Data curation, Editing, **Nermin Orakdogen:** Supervision, Data curation, Writing - review & editing.

#### Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

#### CRediT authorship contribution statement

**Nur Sena Okten Besli:** Investigation, Experimental Methodology, Data curation, Writing - review & editing. **Nermin Orakdogen:** Supervision, Data curation, Writing - review & editing.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Acknowledgements

Financial support of this work from the Istanbul Technical University Research Fund (BAP, 40763) was gratefully acknowledged. The authors also thank the Istanbul Kultur University, Department of Civil Engineering for ATR-FTIR and TGA-DTA measurements.

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.polymertesting.2020.107044>.

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