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ORIGINAL PAPER

Ion-stimuli responsive dimethylaminoethyl methacrylate/hydroxyethyl methacrylate copolymeric hydrogels: mutual influence of reaction parameters on the swelling and mechanical strength

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Abstract Novel ion-stimulus-responsive copolymeric hydrogels were synthesized by free radical crosslinking copolymerization from the monomers *N,N*-dimethylaminoethyl methacrylate (DMAEMA) and 2-Hydroxyethyl methacrylate (HEMA) in the presence of a crosslinker, diethyleneglycol dimethacrylate (DEGDMA). The influences of the reaction parameters, the comonomer composition and the ionic strength of salt solutions on the swelling behavior of P(DMAEMA-co-HEMA) hydrogels were examined. The ion-stimulus-responsive swelling behavior of the prepared copolymers was studied in water as well as in aqueous solutions of NaCl, KCl, KBr, KI, $CaCl_2$, $BaCl_2$ and $MgCl_2$. It was found that, starting from some characteristic concentration of a salt, a further increase of the salt concentration results in the shrinking of copolymeric P(DMAEMA-co-HEMA) hydrogels. The Flory-Rehner theory correctly predicts the swelling behavior of the hydrogels in salt solutions if the variation of the comonomer HEMA content is taken into account. The calculation of the interaction parameter χ between P(DMAEMA-co-HEMA) network and water showed that the specific interactions between cations and side groups of polymeric network affect the mixing term of the free energy. The extent and kinetics of water absorption were studied to determine their relationship with the reaction parameters. The kinetics of the hydrogel collapse is strongly dependent on the kind of salt used. The swelling results will be useful in designing and developing novel controlled delivery systems.

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Introduction

Since the research and development of smart polymers have been very active in recent years, significant advances in the field of stimuli-responsive polymers have been achieved to meet the industrial and scientific applications [1–9]. Based on the crosslinked polymeric network structure containing stimuli-responsive groups which cause the rapid swelling/deswelling, the stimuli-responsive hydrogels could be dramatically changed their volume by an alternative change of hydrophobicity/ydrophilicity in the molecular structure of the chains according to the external stimuli. Owing to their biocompatibility and special surface properties, stimuli-responsive hydrogels have been extensively studied as applications for molecular recognition in the material sciences toward intelligent materials [10–18].

Studies on the stimuli-responsive hydrogels containing weakly acidic or basic groups in polymeric backbone have been performed by several research groups [19–22]. Stimuli-responsive hydrogels based on poly(*N,N*-dimethylaminoethyl methacrylate) (PDMAEMA) have been widely used in the development of therapeutic drug delivery formulations. PDMAEMA has dual temperature and pH-stimuli responsive properties and contains tertiary amino groups which can be protonated in acidic solutions, thus affording the polymer pH-tunability. Due to its multi-responsive characteristic, PDMAEMA hydrogels have been synthesized with other co-monomers for applications in biotechnology, medicine or pharmacy [23–26]. Xu et al. prepared PDMAEMA cylindrical brushes and demonstrated the response of brushes on pH and monovalent salt [27]. The responsiveness of the brushes could

be potentially applied in nano-scale sensor systems and nano-actuator systems. Recently, Chen et al. synthesized polyhedral oligomeric silsesquioxane hybrid hydrogels with organic–inorganic co-crosslinked networks by free-radical polymerization of *N*-isopropylacrylamide and *N,N*-dimethylaminoethyl methacrylate (DMAEMA) in the presence of both organic crosslinker N,N'-methylenebis(acrylamide) (BAAm) and inorganic crosslinker octavinyl polyhedral oligomeric silsesquioxane (OPOSS). The resulting hydrogels displayed obvious temperature and pH double responsiveness, and OPOSS particles dispersed in polymer made a dominant effect on the properties of resulting gels [28]. Studies have certified that hydrogels can hydrate, and therefore contain a great amount of bound water when polymer backbone contains a large number of hydrophilic groups. Thus, the hydrophilicity of the polymer chains can significantly affect the swelling and transporting properties of hydrogels. Li et al. successfully prepared PDMAEMA hydrogels containing cholic acid (CA) by radiation crosslinking. The introduction of 10 and 20 mol% CA into PDMAEMA network decreased the maximum swelling ratio from 40 to 6 and 5, respectively. The incorporation of CA led to a decrease in the lower critical swelling temperature, but did not exert big influence on the ion-stimulus-responsive properties of PDMAEMA hydrogels [29]. Stimulus-responsive behavior according to the ionic balance in the composition was studied by Sutani and coworkers [30]. DMAEMA as a cationic monomer was copolymerized by UV with anionic monomer acrylic acid and pH- and electro-responsive drug release functions of polyampholyte hydrogels were investigated. Their results showed that the copolymer of cation rich composition swelled at acidic condition, and shrank at alkaline condition.

Moreover, the presence of ionic units in the polymer matrix could arouse specific interactions between the ions/water molecules and the charged groups when immersing the gels in different swelling media. These interactions will lead to different stimuli-responsive swelling behavior of hydrogels which provide the possibility on the designation of novel smart materials. Highly charged copolymeric gels of 2-acrylamido-2-methylpropanesulfonic acid (AMPS) and *N,N*-dimethylacrylamide (DMAA) with the content of AMPS up to 60 mol % were succesfully prepared by Liu and coworkers [31]. The effect of charge density, the salt concentration and the valence of the counterion was investigated and the dependence of swelling capacity of strong polyelectrolyte gels on the chemical nature of counterions even at low and moderate salt concentrations was reported [31]. To understand the general swelling in the presence of salts, Jeon et al. studied the kinetics of the shrinking of weakly crosslinked polyelectrolyte gels based on sodium methacrylate and diallyldimethylammonium chloride in the presence of different types of salts; NaCl, arginine hydrochloride, cetylpyridinium chloride, sodium dodecyl sulfate and sodium dodecylbenzenesulfonate. The kinetic of the gel collapse in many cases is independent of the kind of salt used, but depends on the salt concentration in the external solution. The increase of salt concentration results in an acceleration of the gel collapse [32]. The water-absorbing copolymeric poly(potassium acrylate-co-acrylamide) gel beads were synthesized by an inverse suspension copolymerization using BAAm as a crosslinker in an effort to investigate the effect of salt concentration on the swelling capacity of the copolymers. The water absorption ability decreased with increasing crosslinker and salt concentration due to the osmotic pressure differential between the inside and outside of the swollen gel [33]. Recently, Tomic et al. prepared poly(2-hydroxyethyl methacrylate-co-itaconic acid) P(HEMA-co-IA) hydrogels by free-radical copolymerization in order to evaluate as controlled release drug delivery system. The swelling behavior is highly influenced by the composition and the low swelling of PHEMA gel was increased by copolymerization with IA, due to high hydrophilicity and electrostatic repulsion of ionized carboxylate groups in the polymer matrix [34].

While most of the earlier studies have focused on pH- and temperature- dependent swelling of PDMAEMA-based hydrogels, the effect of the comonomer type and composition on the swelling of PDMAEMA hydrogels in salt solutions has not been investigated to date. It is important to understand the osmotic and structural change of hydrogels induced by addition of salts with respect to the physical and chemical processes in biological systems. Two main issues that can be considered for the application of PDMAEMA-based hydrogels are their swelling capacity and elasticity with predetermined crosslinking structure including the degree of crosslinking. Since the polymer chains in the copolymer network occupy the same macroscopic volume and yet they are connected by chemical bonds, it is possible to obtain a unique set of material properties that is not attainable in the case of a single polymer network. PDMAEMA is pH, temperature and ion-responsive polymer, but the mechanical properties of PDMAEMA hydrogels are not good enough to be used in drug release formulations. It assumes that the introduction of HEMA via copolymerization to PDMAEMA network significantly increases the resulting mechanical properties. In this work, the focus was on the synthesis of salt-responsive copolymeric hydrogels based on the change in the swelling and mechanical properties induced by the salt as stimuli. P(DMAEMA-co-HEMA) copolymeric hydrogels were synthesized by simple and efficient aqueous copolymerization method. This study mainly covers the effect of comonomer composition on the salt-sensitive swelling and the mechanical behavior of P(DMAEMA-co-HEMA) hydrogels. The equilibrium and dynamic swelling/deswelling properties of the prepared hydrogels were investigated as a function of the comonomer composition, the salt concentration, the valence of the counterion and co-ion. Since the swelling is a simple and low-cost

technique to characterize polymeric gels, the network parameters of the copolymeric hydrogels were determined using their equilibrium swelling values. To analyze the mechanical properties of the resulting hydrogels, the uniaxial compression testing was performed on the equilibrium swollen samples. The experimental results thus obtained were compared with an earlier theory describing the swelling of hydrogels and the important network parameters characterizing crosslinked hydrogels were calculated using the well-known Flory-Rehner equation.

Experimental section

Materials

N,N-dimethylaminoethyl methacrylate (DMAEMA) as main monomer, 2-Hydroxyethyl methacrylate (HEMA, Merck) as a comonomer, diethylene glycol dimethacrylate (DEGDMA, Fluka) as crosslinking agent were used as received. Ammonium persulfate (APS, Merck) and *N,N,N',N'*-tetramethylethylenediamine (TEMED, Merck) were used as redox-initiator system. Sodium chloride (NaCl, Merck), Potassium chloride (KCl, Merck), Potassium bromide (KBr, Merck), Potassium iodide (KI, Carlo Erba) as monovalent salts, Calcium chloride ($CaCl_2$, J.T. Baker), Magnessium chloride ($MgCl_2$, J.T. Baker) and Barium chloride ($BaCl_2$, Merck) as divalent salts were used for the salt-sensitive swelling experiments. All of the reagents and the solvents were of the highest available purity and were used as received. Distilled water was used for the preparation of hydrogels.

Synthesis of P(DMAEMA-co-HEMA) hydrogels

The copolymeric hydrogels were synthesized based on two types of acrylate monomers DMAEMA and HEMA by free-radical crosslinking copolymerization. DMAEMA and HEMA with various proportions were poured into a flask and then, double-distilled deionized water, the redox initiator system consisting of 2.63 mM APS and 24.9 mM TEMED and the difunctional crosslinker DEGDMA were added into the monomer mixture in turn. APS and TEMED stock solutions were freshly prepared by dissolving 0.080 g APS and 0.375 mL TEMED separately in 10 mL of water. The total concentration C_0 of all monomers, including DEGDMA in the pregel solution was fixed at 33 *w*/*v*%, while the crosslinker ratio X (the mole ratio of the crosslinker DEGDMA to the monomers DMAEMA and HEMA) was fixed at 1/80. The pre-gel solution was bubbled with nitrogen for 20 min to remove the dissolved oxygen that could inhibit the reaction. After shaking the flask, the solution was poured into several syringes and the polymerization reaction was conducted at 21 °C for 24 h. The crosslinked rods were cut into disks of a thickness of 4 mm. Subsequently, the disks were flushed with deionized water for one week to remove the residue of unreacted monomers and crosslinking agents. The sol part of the copolymer hydrogel samples was extracted by deionized water and then dried in vacuum oven at 40 °C to constant weight. The composition and characteristic data of P(DMAEMA-co-HEMA) copolymer hydrogels were given in Table 1.

Polymer network concentration at the state of preparation

The swelling capacity and the mechanical properties of hydrogels sensitively depend on the degree of dilution at which they are formed. The presence of water during the hydrogel formation process is known to produce supercoiled polymer chains in the dry state so that the increase of their dimensions during swelling does not require much loss of their conformational entropy. The degree of dilution of the networks after their preparation denoted by ν_2^0 is known as the volume fraction of crosslinked polymer after the hydrogel preparation and was experimentally determined according to the following expression:

$$\nu_{2,\mathrm{exp}}^0 = \left[1 + \frac{(q_F - 1)\rho}{d_1}\right]^{-1} \quad (1)$$

where q_F is the dilution degree after the hydrogel preparation (mass of hydrogel after preparation / mass of dried hydrogel), ρ and d_1 are the densities of the polymer and water, respectively. The values ρ and d_1 used in this study were 1.2 g / mL for P(DMAEMA-co-HEMA) hydrogels, and 1.0 g / mL for water, respectively. The experimental values of ν_2^0 of copolymeric hydrogels were given in Table 1. By assuming that the monomer conversion is complete after the crosslinking, the theoretical values of ν_2^0 were calculated from the initial molar concentration of the monomers C_0 using the equation, $\nu_2^0 = 10^{-3} C_0 \overline{V}_r$, where $\overline{V}_r$ is the average molar volume of the P(DMAEMA-co-HEMA) repeat units (in mL / mol). In Fig. 1, the experimental and theoretical values ν_2^0 of P(DMAEMA-co-HEMA) copolymer hydrogels were plotted against the amount of HEMA in the network chains. It was observed that ν_2^0 values decrease slightly with increasing comonomer composition.

Measurement of the swelling capacity of hydrogels

In order to examine the swelling ability of P(DMAEMA-co-HEMA) hydrogels in harsh environments of the stomachs and the intestines, the swelling ratio of the hydrogels was measured in deionized water as well as in aqueous solutions of NaCl, KCl, KBr, KI, $CaCl_2$, $BaCl_2$ and $MgCl_2$. After swelling reached equilibrium, P(DMAEMA-co-HEMA) hydrogel sample was taken out and the excess surface water was gently

Table 1 The composition and characteristic data of P(DMAEMA-co-HEMA) copolymer hydrogels. $\overline{V}_r$ = the average molar volume of the P(DMAEMA-co-HEMA) repeat units (in mL / mol), $\nu^0_{2,theo}$ = the theoretical values of the polymer network concentration after the gel preparation, V_{eq} = the volume of the equilibrium swollen hydrogels in water, ν_2 = the volume fraction of crosslinked polymer after equilibrium swelling calculated using Eq.(2)

DMAEMA mol%	HEMA mol%	$\overline{V}_r$	$\nu^0_{2,\text{theo}}$	V_{eq}	$\nu_2 \times 10^{-1}$
100	0	108.4	0.2801	244 (22)	0.011
90	10	110.7	0.2765	143 (0.56)	0.027
80	20	112.9	0.2730	18.9 (0.45)	0.147
70	30	115.2	0.2695	9.61 (0.20)	0.281
60	40	117.4	0.2660	2.62 (0.24)	1.015
50	50	119.7	0.2624	2.32 (0.12)	1.132
40	60	121.9	0.2589	1.68 (0.04)	1.533
60	70	124.2	0.2554	1.49 (0.11)	1.709
20	80	126.5	0.2519	1.36 (0.15)	1.846
10	90	128.7	0.2484	1.21 (0.10)	2.046
0	100	131.0	0.2449	1.03 (0.02)	2.384

removed by filter paper; then by using the volumetric and gravimetric techniques, the equilibrium swelling of P(DMAEMA-co-HEMA) hydrogels was tested both by measuring the diameters and by weighing the gel samples. The equilibrium weight swelling ratio of P(DMAEMA-co-HEMA) hydrogels, SR_{eq}, was calculated as:

$$SR_{eq} = \frac{w_s - w_d}{w_d} \tag{2}$$

where w_s is the weight of the swollen hydrogel at equilibrium and w_d is the weight of the dried hydrogel. The diameter of P(DMAEMA-co-HEMA) hydrogel samples both after equilibrium swelling and after preparation was measured by a calibrated digital compass (Mitutoyo Digimatic Caliper, Series 500, resolution: 0.01 mm). Four measurements were carried out on each hydrogel sample to achieve good precision and the volume of the equilibrium swollen hydrogels, V_{eq}, that is the ratio of the volume of equilibrium swollen hydrogel to volume of the hydrogel just after preparation was calculated as:

$$V_{eq} = \left(\frac{D}{D_o}\right)^3 \tag{3}$$

where D and D_o are the diameters of P(DMAEMA-co-HEMA) hydrogel samples after equilibrium swelling and after preparation, respectively. The volume fraction of the crosslinked polymer in the equilibrium swollen hydrogel $\nu_{2,eq.}$ were calculated from the polymer network concentration after the hydrogel preparation ν^0_2 as:

$$\nu_2 = \nu^0_2 / V_{eq} \tag{4}$$

The swelling behavior of P(DMAEMA-co-HEMA) hydrogels were performed in aqueous solutions at room temperature. The diameter of P(DMAEMA-co-HEMA) hydrogel samples was first measured and then transferred to the vials containing the least concentrated aqueous salt solution. The concentration of the salt solutions ranged from 10^{-5} to 1.0 M. The hydrogel samples were allowed to swell in the solution at least 10–14 days, during which the salt solution was refreshed once to keep the concentration as feeded. When the swelling equilibrium was established, the diameter of the hydrogel samples was measured again and then transferred into the next higher salt solution. The sample diameters were monitored until the changes were within 1 % of the previous measurement. Each swelling data reported in this study is an average of at least four separate measurements.

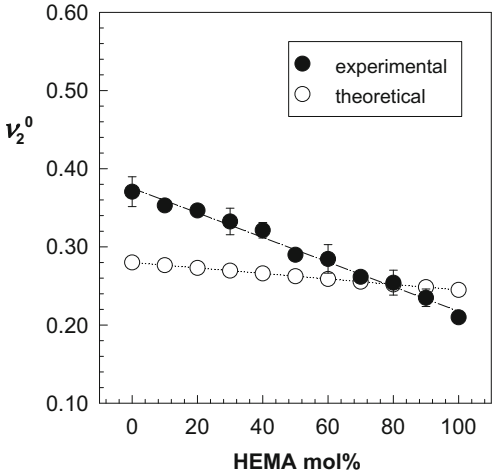

Fig. 1 Experimental and theoretical values ν^0_2 of P(DMAEMA-co-HEMA) copolymeric hydrogels shown as a function of the HEMA mol%

Swelling and deswelling rates

The dried hydrogel samples were immersed in 10^{-5} M salt solution at room temperature, and the swelling was measured by weighting the hydrogel sample with time and the water uptake, WU(t), was calculated by:

$$WU(t) = \frac{w_t - w_d}{w_d} \quad (5)$$

where w_t is the weight of the wet copolymer hydrogel sample at time t and w_d is the weight of dry hydrogel. The deswelling of hydrogel samples was measured by placing it into 1.0 M salt solution at room temperature. At predetermined time intervals, the hydrogel sample was taken out from the salt solution and weighed after blotting excess water on the surface by filter paper. The water retention, WR(t), was defined as follows:

$$WR(t) = \frac{w_t - w_d}{w_s - w_d} \quad (6)$$

Mechanical strength of P(DMAEMA-co-HEMA) hydrogels

The elastic modulus of P(DMAEMA-co-HEMA) copolymer hydrogels was evaluated by the uniaxial compression measurements performed on the sample at equilibrium swollen state. All the mechanical measurements were conducted in a thermostated room at 21 °C after determining that, for the characteristic testing times, temperature and testing medium did not affect the results. The cylindrical P(DMAEMA-co-HEMA) hydrogel sample was placed on a digital electronic balance. The sample size was approximately 4 mm in diameter and 7 mm in height. Then, a load was transmitted vertically to the hydrogel through a rod fitted with a PTFE (Teflon) endplate. Each sample was subjected to a compressive force and measurements were made immediately following the application of the force, approximately ten records were taken during the elasticity tests, which required 180 s. The force acting on the hydrogel F was calculated from the reading of the balance m as $F = mg$, where g is gravitational acceleration. The resulting deformation $\Delta l = l - l_o$ where l_o and l are the initial un-deformed and deformed lengths, respectively, was measured using a digital comparator (IDC type Digimatic Indicator 543–262, Mitutoyo). The deformation ratio α (deformed length / initial length) was calculated using the equation, $\alpha = 1 - \Delta l/l_o$. The force and the resulting deformation were recorded after 20 sec of relaxation and all the measurements were conducted up to a maximum of 20 % of its original length over a 180 s time interval [35–38]. This ensured results within the linear range of behavior for the material. The strain rates for compressive testing were chosen in order to adhere to previously developed laboratory protocols. The time elapsed between the application of the force and the measurement was in the order of seconds. The deformation ratio of the hydrogel samples under the applied force remained constant after about 10 s, indicating that the 20 s of relaxation time for the network chains was sufficient for the present hydrogels. This time was sufficiently long for the equilibrium state measurements. The stress f was calculated as $f = F/A$, where A, is the cross-sectional area of the specimen, i.e., $A = \pi(D_0/2)^2$. For uniaxial deformation, the statistical theories of rubber elasticity yield for Gaussian chains an equation of the form [39, 40]:

$$f = G\left(\alpha - \alpha^{-2}\right) \quad (7)$$

where the elastic modulus of the hydrogel sample G is given by the following equation [41, 42]:

$$G = A\frac{RT}{NV_1}\nu_2^{1/3}\left(\nu_2^0\right)^{2/3} \quad (8)$$

where V_1 is the molar volume of solvent, N is the average network chain length, i.e., the number of segments between two successive crosslinks, the front factor A equals to 1 for an affine network and 1–2 / ϕ for a phantom network, in which ϕ is the functionality of the crosslinks, R and T are in their usual meanings. The compressive moduli of hydrogels were calculated from the average slope of the initial linear portion (5 % strain) of the stress vs. strain curve using Eq.(7). At least four independent samples were tested for each set of hydrogels and the standard deviations in the modulus value were less than 3 %.

Results and discussion

A series of poly(*N,N*-dimethylaminoethyl methacrylate-co-2-Hydroxyethyl methacrylate) P(DMAEMA-co-HEMA) copolymeric hydrogels was prepared with various compositions as a new alternative ion-stimulus-responsive matrix. The swelling equilibria of the copolymeric hydrogels was carried out in water and in aqueous solutions of NaCl, KCl, KBr, KI, $CaCl_2$, $BaCl_2$ and $MgCl_2$ with concentrations ranging from 10^{-5} to 1.0 M.

Influence of salts on the equilibrium swelling

Since the swelling ability of hydrogels depends on the structure of the polymer network, the nature of the swelling medium, the charged groups attached to the network and the degree of ionization, the influence of salts on the swelling behavior of P(DMAEMA-co-HEMA) hydrogels in aqueous solutions is of obvious practical interest. In the presence of salts, the crosslinked polymers with pendent cationic groups imbibe a solvent to an extent which depends on pH and the ionic

composition of the solution. The extent of ionization in the structure of hydrogels containing cationic groups varies with pH and this variation of ionization results in pH-responsive swelling equilibria. Since the aliphatic tertiary amino groups on DMAEMA are weakly basic and the protonation of these groups becomes easier in acidic medium, the hydrogel becomes positively charged in the solutions of low pH. Incorporation of positively charged amino groups into the polymer network results in the swelling of the hydrogel in the low pH region, due to the ionic repulsion between these groups. The hydrogel collapses in the high pH region due to unprotonated amino groups [43, 44]. Li and coworkers reported the overshooting effect observed during the swelling procedure of PDMAEMA hydrogels which was attributed to the dynamic conformational changes of the side chains of DMAEMA units during the swelling process of PDMAEMA hydrogels; the cyclic conformation and the stretched conformation. It was observed that, in acidic solution, the protonation of amino groups in the DMAEMA units makes the side chains of the DMAEMA units change from the cyclic conformation to the stretched one which results in the increase of the swelling degree of hydrogels [29, 45].

For P(DMAEMA-co-HEMA) hydrogels prepared at various comonomer HEMA concentrations, the equilibrium swollen volume of hydrogels V_{eq} (volume of equilibrium swollen hydrogel / volume of hydrogel after preparation) was calculated using Eq.(2). The results for the swelling of P(DMAEMA-co-HEMA) hydrogels in pure water at 25 °C and the volume fraction of crosslinked polymer in the equilibrium swollen hydrogels ν_2 were presented in Table 1 as a function of the mole fraction of HEMA in the comonomer feed. It was observed that the swelling capacity of P(DMAEMA-co-HEMA) hydrogels decreases with increasing HEMA content in the feed. The water swelling of P(DMAEMA-co-HEMA) hydrogel containing 20 mol% HEMA was ca. 18 fold to that of corresponding homopolymeric PHEMA. This may be attributed to the formation of hydrophobic domains including pendant moieties belonging to different network subchains which lowers the entrance of water molecules inside the network, leading to a decrease in the swelling degree of the hydrogels. A lesser H-bond formation with hydroxyl group of HEMA reduces the swelling. This finding is consistent with the results reported by Li et al. [29, 45] who observed that the side chains of DMAEMA units of the hydrogels preferentially adopted a cyclic conformation, which was thermodynamically stable. It was reported that the formation of the cyclic conformation is considered a kind of aggregation, which decreased the swelling capacity and, therefore, led to water expulsion. Brahim et al. synthesized an amphiphilic hydrogel containing crosslinked HEMA, DMAEMA, and a third methacrylate-based monomer 3-(trimethoxy-silyl) propyl methacrylate and characterized the pH-dependent swelling properties. As the amount of DMAEMA incorporated into the hydrogel was increased up to 15 mol % there was a 30–40 % increase in hydration as the pH was lowered from 8.0 to 2.0. It was proposed that by creating hydrophilic as well as hydrophobic microdomains throughout the hydrogel network, there may be more controlled regulation of hydrogel swelling [46]. A similar phenomenon was observed by You and Auguste for the swelling studies of DMAEMA/HEMA nanoparticles performed in buffered solutions of pH 5.5, 6.5, and 7.4. pH-sensitivity of DMAEMA/HEMA nanoparticles crosslinked with 3 mol% tetraethyleneglycol dimethacrylate was characterized and high swelling ratios were achieved at low pH, high DMAEMA content, and low crosslinking density [47]. Zhang et al. prepared novel pH/temperature sensitive hydrogels of DMAEMA and diallyldimethyl ammonium chloride (DADMAC). The equilibrium degree of swelling of hydrogels was rather high in acidic buffer (pH 1.5-3) and deswelled dramatically with the increase of pH, the curve leveled off when pH is higher than 3.3. Compared with PDMAEMA hydrogel, P(DMAEMA-co-DADMAC) showed enhanced equilibrium degree of swelling [48]. In another work, the effects of pH and polymer concentration on the swelling pressure and elastic modulus of pH-responsive hydrogels of hydroxypropyl methacrylate and DMAEMA were studied by Horkay and coworkers. The pH effect is more pronounced than the volume effect, thus the hydrogel stiffens as it swells in response to pH change [49].

In order to determine the effect of salt on the water absorbency of P(DMAEMA-co-HEMA) copolymeric hydrogels, two series of salt solutions were used: chlorides with variable cations and potassium salts with different anions. Figure 2 shows the equilibrium volume swelling ratio V_{eq} of P(DMAEMA-co-HEMA) hydrogels in monovalent salt solutions of KI (A), KBr (B), KCl (C) and NaCl (D) with concentrations from 10^{-5} to 1.0 M, respectively. The water absorbency of P(DMAEMA-co-HEMA) hydrogels in divalent salt solutions of $MgCl_2$(A), $CaCl_2$(B) and $BaCl_2$ (C) was given in Fig. 3. The swelling measurements in all types of salt solutions showed that P(DMAEMA-co-HEMA) hydrogels exhibit strong salt-sensitive swelling behavior over the entire range of the comonomer HEMA concentrations. The swelling of P(DMAEMA-co-HEMA) hydrogels in saline solutions was distinctly decreased when compared to the values measured in deionized water given in Table 1. It can be seen from the figures that, in the medium range of salt concentration, the swelling ratio of P(DMAEMA-co-HEMA) hydrogels increases with decreased comonomer HEMA concentration in the feed. The change of salt cations in the case of the chlorides as well as the change of anions for the potassium salts does not lead to a significant effect on the swelling behavior of homopolymeric PHEMA hydrogels. In all cases the increase of salt concentration leads to a hydrogel shrinking. Figure 4 shows the photographs of P(DMAEMA-co-HEMA) copolymeric

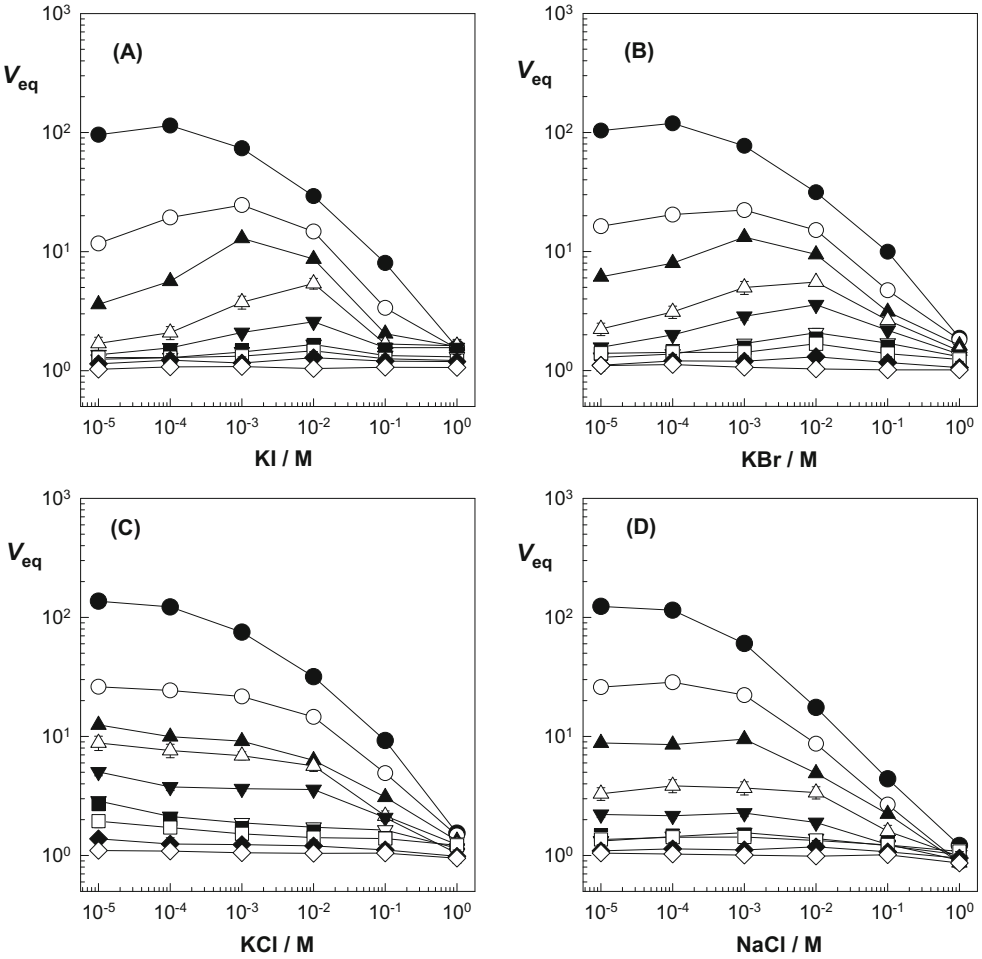

Fig. 2 The equilibrium swelling ratio of P(DMAEMA-co-HEMA) hydrogels as a function of the concentration of aqueous salt solutions of KI (**a**), KBr (**b**), KCl (**c**) and NaCl (**d**). The *solid curves* only show the trend of the data. HEMA mol%: 10 (●), 20 (○), 30 (▲), 40 (△), 50 (▼), 60 (▽), 70 (■), 80 (□), 90 (◆), 100 (◇)

hydrogel sample containing 20 mol% HEMA in the feed after equilibrium swelling in aqueous KCl solutions ranging from 10^{-5} to 1.0 M from right to left.

As shown in the Figs. 2 and 3, the swelling ratio of P(DMAEMA-co-HEMA) hydrogels decreases with increasing salt concentration in the external solution from 10^{-5} to 1.0 M. However, three distinct regions can be described in the salt concentration dependence of the swelling of P(DMAEMA-co-HEMA) hydrogels: (1) when the salt solution is diluted up to about 10^{-4}–10^{-5} M, the swelling curve of hydrogel samples holds horizontally and the copolymeric hydrogels are in fully swollen state; (2) while the decrease in V_{eq} is rapid up to 10^{-2} M salt concentration; (3) as the salt concentration further increases, the decrease in V_{eq} slows down between 10^{-1} and 1.0 M and the swelling curves converge together in the concentrated salt solution (1.0 M). The charged groups attached to the polymer network play an important role in the phenomenon, which could be interpreted by Donnan equilibrium theory [50]. This phenomena can be attributed to the electrostatic repulsion between charged groups on the network chains and to the concentration difference of mobile ions inside the hydrogel and the external solution governed by the Donnan potential. During the swelling of P(DMAEMA-co-HEMA) hydrogels in salt solutions, the mobile counterion concentration in the external solution is higher than that of in the hydrogel phase, which results in an osmotic pressure that water molecules flow from the hydrogel to the solution phase so that P(DMAEMA-co-HEMA) hydrogels deswell as observed. In Figs. 2a–b and 3a–c, for the polymer network with low comonomer HEMA content, the swelling ratio could be divided into two stages: an increase of swelling ratio for some extent, followed by a continuous shrinkage with increased salt concentration. The initial increase in the swelling ratio could be explained by the ion-cluster formation in the network. It is known that the anions with low hydration energies can strongly interact with the quaternary ammonium pendant groups in backbone chains through ion pair interactions. Similar results were reported by Li et al. for the swelling behavior of amphiphilic gels based on hydrophobically modified dimethylaminoethyl methacrylate. The special swelling behavior was attributed to the aggregation gel structure caused by the hydrophobic interaction among alkyl groups and the formation of ion-clusters between tetra-alkyl ammonium cation and Br^- [51]. Another result obtained from Fig. 3 is that

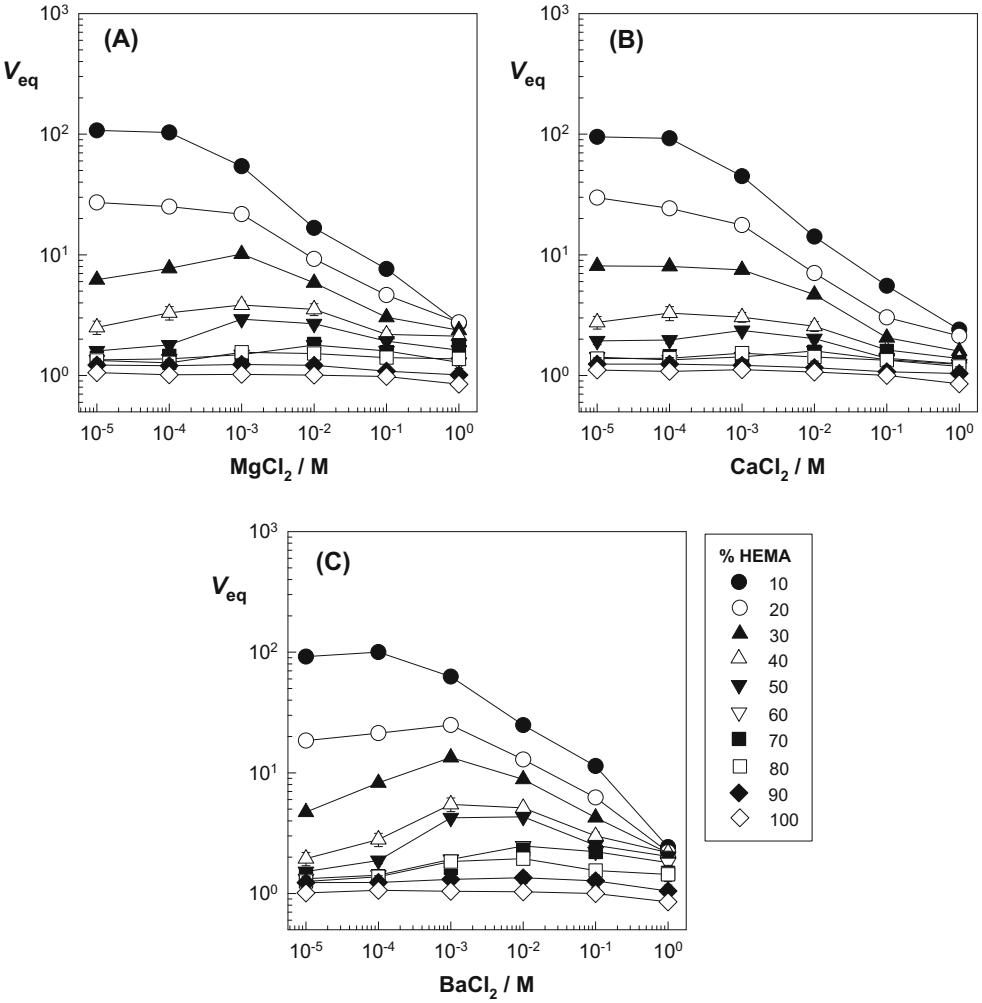

Fig. 3 The equilibrium swelling ratio of P(DMAEMA-co-HEMA) hydrogels as a function of the concentration of aqueous salt solution of $MgCl_2$ (**a**), $CaCl_2$ (**b**), and $BaCl_2$ (**c**). The HEMA content of the hydrogels (HEMA mol%) are already indicated in the figure

quite concentrated (>1.0 M) salt solutions would be required to make these gels behave like an uncharged one since DMAEMA is a weak electrolyte.

In order to make comparison, the equilibrium swollen volume V_{eq} data of P(DMAEMA-co-HEMA) hydrogels in two series of salts: potassium salts with different anions (A) and chlorides with variable cations (B) were presented in Fig. 5. The effect induced by the co-ion species of a series of potassium salts was monitored and the swelling curves of P(DMAEMA-co-HEMA) hydrogels containing 10 and 20 mol% HEMA in salt solutions having the same cation K^+ and different co-ions were presented in Fig. 5a. It was found that the salt-dependent swelling ratio of hydrogels decreases with increasing HEMA concentration and in the series of alkali halides, P(DMAEMA-co-HEMA) hydrogels shows an increase in their swelling ratio in KCl, KBr, and KI solutions when the concentration is belove 10^{-3} M. The swelling behavior of P(DMAEMA-co-HEMA) hydrogels can be explained by the small charge/radius ratio of the anion which is found to be easily bound to the ammonium group of DMAEMA. This is

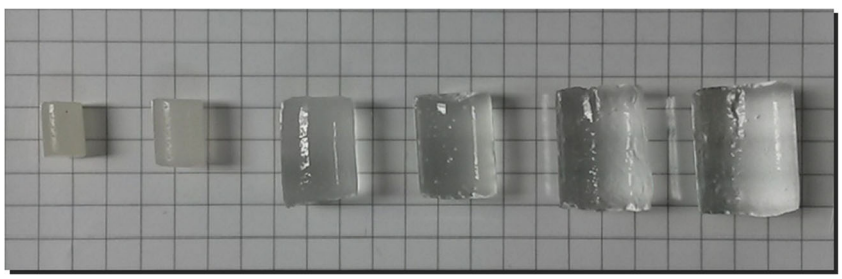

Fig. 4 Photographs of P(DMAEMA-co-HEMA) copolymeric hydrogel sample containing 20 mol% HEMA in the feed after equilibrium swelling in KCl solutions ranging from 10^{-5} to 1.0 M from right to left

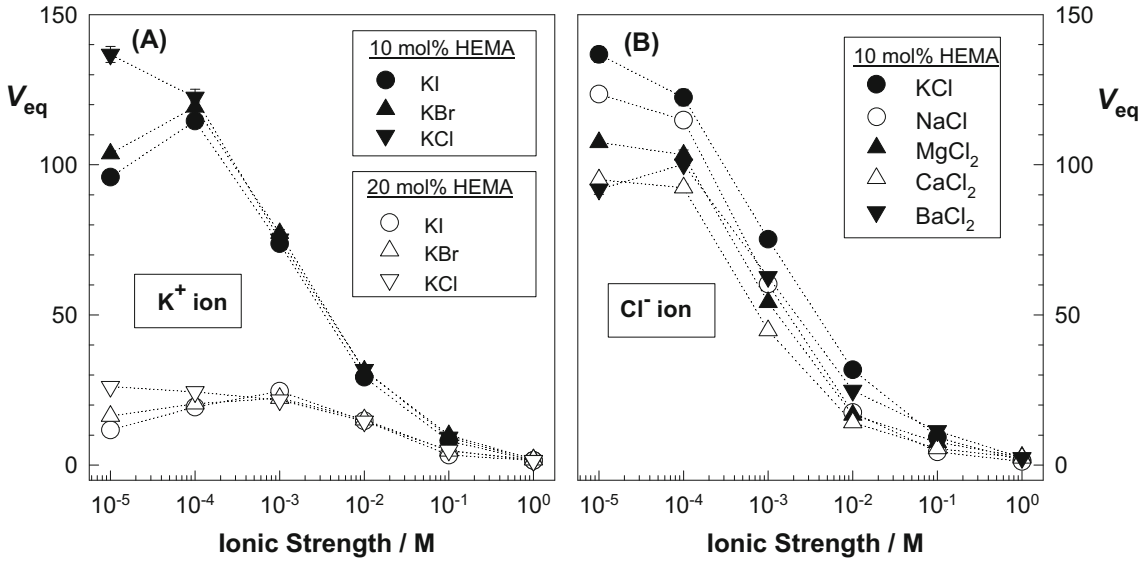

Fig. 5 (**a**) Swelling curves of P(DMAEMA-co-HEMA) hydrogels containing 10 mol% HEMA (solid symbols) and 20 mol% HEMA (open symbols) in salt solutions with the same cation K+ and different anions. (**b**) Swelling curves of P(DMAEMA-co-HEMA) hydrogels containing 10 mol% HEMA in chlorides with variable cations, showing the dependence on the counterion species K^+, Na^+, Mg^{2+}, Ba^{2+} and Ca^{2+}

because the smaller anion easily infiltrates into the crosslinked network and expands the polymer chain. This observation is in accordance to the experimental results observed by Xu and coworkers [27]. It was reported that bromide ions may have specific interactions with cationic polyelectrolyte chains. Hence, a solution of NaBr of sufficient concentration will lead to an adsorption of bromine ions onto the polyelectolyte. Lee and Chen reported the copolymeric gels prepared from the copolymerization of HEMA and a zwitterionic monomer, 3-dimethyl-(methacryloyloxyethyl) ammonium propane sulfonate (DMAPS) copolymeric gels to survey the swelling behavior in the presence of the KF, KCl, KBr, and KI solutions. It was observed that the iodine ions combine with HEMA, producing various degrees of a yellow color in the gel, depending on the solution concentration [52].

The swelling curves of P(DMAEMA-co-HEMA) hydrogels containing 10 mol% HEMA were presented in the salt solutions with different counterions K^+, Na^+, Mg^{2+}, Ba^{2+} and Ca^{2+} in Fig. 5b. The co-ions in the salts are identical in each hydrogel; i.e., $C1^-$. The results indicated that the swelling curves of P(DMAEMA-co-HEMA) hydrogels have a significant difference and the swelling data of the resulting hydrogels cannot be fit with a single curve especially at low and moderate salt concentrations due to the the dependence of the swelling degree on the chemical nature of counterions. Looking at the swelling curves corresponding to the copolymer hydrogel soaked a fixed ionic strenght, given in Fig. 5b, it can be seen that the swelling ratio decreases with the change in counterion species as the sequence of K^+, Na^+, Mg^{2+}, Ba^{2+} and Ca^{2+} for KCl, NaCl, $MgCl_2$, $BaCl_2$, and $CaCl_2$, respectively. The similar results were reported for the swelling behavior of DMAA-based sulfonate gels in water and in aqueous solutions of NaCl, KCl, $CaCl_2$, Na_2S0_4, K_2S0_4, and $CaS0_4$. It was found that the extent of equilibrated volume decreases with the counterion in the following sequence of K^+, Na^+, and Ca^{2+} at the same ionic strength. This dependence on counterion species appears to relate to the formation of the counterion condensation in which the binding of counterions on network chains of the polyion reduces the repulsion force between the charged groups, leading to the decrease in the swelling capacity of the resulting hydrogels [31]. In another work done by Lee and

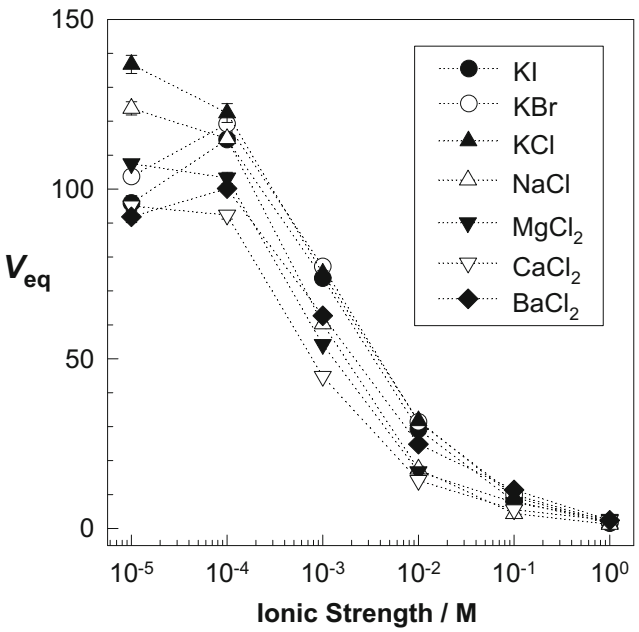

Fig. 6 Swelling curves of P(DMAEMA-co-HEMA) hydrogels containing 10 mol% HEMA in the feed plotted against the ionic strength in the seven salt solutions as indicated

Chen, the swelling ratio of HEMA/DMAPS copolymeric gels increases rapidly with increasing of concentration of the salt with a smaller ratio of the charge/radius [52]. The swelling curves of P(DMAEMA-co-HEMA) hydrogels containing 10 mol% HEMA against the ionic strength in the salt solutions were presented in Fig. 6. When comparing the swelling ratios for one hydrogel with different counterions, one can find its decrease with counterion change in the order of K^+, Na^+, Mg^{2+}, Ba^{2+} and Ca^{2+}, irrespective of the co-ions Cl^-, Br^- and I^-. At higher ionic strength, the swelling curves of hydrogels in salts having univalent cations Na^+ and K^+ merge into one. Decreasing trend in the swelling ratio of copolymeric hydrogels is due to their cationic radius or their hydration forces. The hydration radius grows as a result of the larger cation (K^+) surrounded with a large amount of water. Therefore, the swelling ratio of P(DMAEMA-co-HEMA) hydrogels was higher in the KCl solution than that in the NaCl solutions. In addition, it may be caused by the complexing ability arising from the coordination of the divalent Mg^{2+} cations with the cationic polyelectrolyte chains. This behavior was also observed in the swelling of HEMA/DMAPS copolymeric gels system [52]. The prediction of the effect of a particular ion on the swelling capacity of a hydrogel is not easy and is connected to several factors such as charge on the polymer network, solubility of the polymer segment and the secondary interactions in the hydrogel. The significant impacts of ionic size have been observed in many polyelectrolyte systems. Bodrova and Potemkin investigated the effect of the counterion size, the short-range interaction of counterion-counterion and counterion-monomeric units on the swelling of a weakly charged polyelectrolyte gel. It was proposed that an increase in the counterion size facilitates a decrease in the fraction of ion pairs and an increase in the gel swelling ratio in a good solvent [53]. Hua et al. developed a theory for polyelectrolyte gel and proposed that charge regularization which is related to the ionic size and caused by counterion condensation had great effects on the volume transition [54]. Recently, Qu and collaborators theoretically explored the effect of ionic size on the critical points and phase diagram of the volume phase transition of the polyelectrolyte gels. The theoretical results suggesedt that the swelling behavior of polyelectrolyte gel might be tuned with salt of different volumes [55].

Elasticity of P(DMAEMA-co-HEMA) hydrogels in salt solutions

To reveal the effect of salt on the elasticity of P(DMAEMA-co-HEMA) copolymeric hydrogels, the uniaxial compression measurements were performed on hydrogel samples in equilibrium with salt solutions. The deformation as a function of the applied force was measured and the elastic modulus, G_{salt}, was calculated from the nominal stress, f (force per unit undeformed cross-section), using the Eq.(7). In Fig. 7, the stress - strain data of P(DMAEMA-co-HEMA) hydrogel sample containing 20 mol% HEMA in the feed after equilibrium swelling in different salt solutions was presented. The ionic strength of the solutions are already indicated in the figure. Although the comonomer HEMA content of P(DMAEMA-co-HEMA) hydrogel samples is the same, the slope of the stress–strain isoterms varies depending on the type of the salt and also the ionic strength of the solutions. Figure 7 also shows the photographs of P(DMAEMA-co-HEMA) hydrogel sample containing 20 mol% HEMA during the compression tests after equilibrium swelling in 1.0 M NaCl solution. The strength of P(DMAEMA-co-HEMA) hydrogels was evaluated from the stress - strain plots and the results were presented in Figs. 8 and 9. The influence of different type of salts on the elasticity indicated that the elastic modulus of P(DMAEMA-co-HEMA) hydrogels increases as the comonomer HEMA content in the feed increased. The elastic moduli G_{salt} data of P(DMAEMA-co-HEMA) hydrogels after equilibrium swelling in seven salt solutions were presented in Table 2 as a function of the ionic strength of salt solutions. The elastic modulus of hydrogels increases with increasing the ionic strength of the salt solution. As seen in Figs. 2 and 3, the equilibrium swelling ratio of hydrogels decreased with the increase of salt concentration in the external solution. This effect was attributed to the addition of salt to the solution which screens the electrostatic interaction within the network and to the reduced water activity of salt solutions. The difference in the concentration of mobile ions between the interior of the hydrogel matrix and the exterior salt solution decreases as the ionic strength increases, thereby decreases the osmotic swelling pressure of these mobile ions inside the gel. Li and Yew investigated the influence of the ionic strength of surrounding solution and discussed on the responsive performance of soft pH-sensitive hydrogels to environmental change in solution pH [13]. Their results for the distributions of diffusive Na^+ and Cl^- ion concentrations showed that the mobile cations, Na^+ ions, have higher densities in the interior hydrogel than those in the exterior solution; while the mobile anions, Cl^- ion, show a contrary pattern and the requirement of electroneutrality condition is always met everywhere in the domains of solution. In the present system, the dilution of the salt solution up to 10^{-5} M induces a 3.0 fold decrease in the elastic modulus of P(DMAEMA-co-HEMA) hydrogels in NaCl, KBr, KI and KCl solutions whereas 2.5 fold decrease in $CaCl_2$, $BaCl_2$ and $MgCl_2$ solutions is obtained. When the salt solution is diluted, the ions may interact with the side groups of the chains and exhibit ion-bonding property. Therefore, the binding of ions to the P(DMAEMA-co-HEMA) network chains causes an external swelling of the hydrogels which results in decreasing of the elastic modulus. This result can be reflected by the effective crosslink density ν_e and the average network chain length, in terms of the

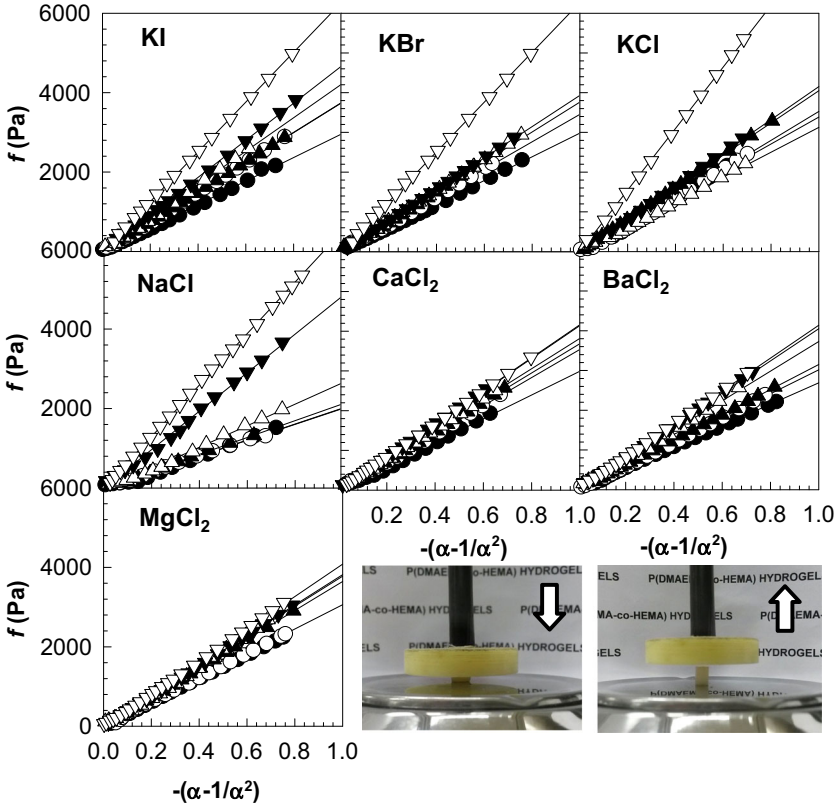

Fig. 7 Typical stress - strain data of P(DMAEMA-co-HEMA) hydrogels containing 20 mol% HEMA in the feed obtained from the compression tests after equilibrium swelling in salt solutions. Photographs show the copolymeric hydrogel sample containing 20 mol% HEMA in the feed during the compression tests after equilibrium swelling in 1.0 M NaCl solution. Ionic strength / M: 10^{-5} (●), 10^{-4} (○), 10^{-3} (▲), 10^{-2} (△), 10^{-1} (▼), 1.0

average molecular weight of the network chains between the crosslink points $\overline{M}_c$ which can be given by the relation as:

$$\nu_e = \frac{1}{N V_1} = \frac{\rho}{\overline{M}_c} \tag{8}$$

By using the G_{salt}, ν_2 and ν_2^0 values of hydrogels; the average molecular weight of the network chains $\overline{M}_c$ and the effective crosslink densities ν_e of P(DMAEMA-co-HEMA) hydrogels were calculated and the results for the phantom network model ($\phi = 4$) were presented in Fig. 10 as a function of the ionic strength of the salt solutions. From the comparison of Figs. 8, 9 and 10, it is seen that $\overline{M}_c$ values of P(DMAEMA-co-HEMA) hydrogels decrease first slightly up to 10^{-3} M, but then increase rapidly with increasing salt concentration. The effective crosslink density values ν_e of hydrogels first increase with increasing salt concentration up to 10^{-3} M and then decrease with further increasing salt concentration. Since the crosslinker DEGDMA with oxyethylene repeating units bears long chain spacer between two vinyl groups and the absorption of water causes the network to expand and its chains to stretch. As a result, the chains making up the network structure is assumed in a stretched conformation as the polymer network swells. Since the network chains in these swollen hydrogels are in the expanded configuration, the increase of the elastic modulus is connected with high stretching of the

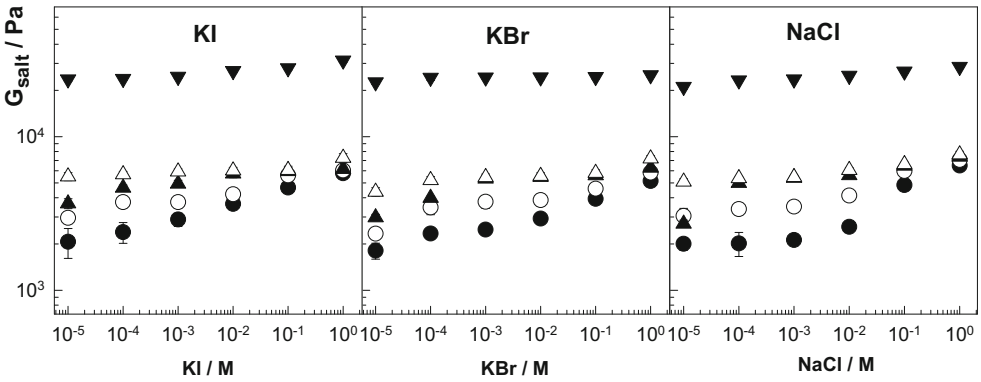

Fig. 8 Elastic modulus G_{salt} of P(DMAEMA-co-HEMA) hydrogels after equilibrium swelling in salt solutions of KI, KBr and NaCl shown as a function of the ionic strength. HEMA mol%: 20 (●), 40 (○), 60 (▲), 80 (△), 100 (▼)

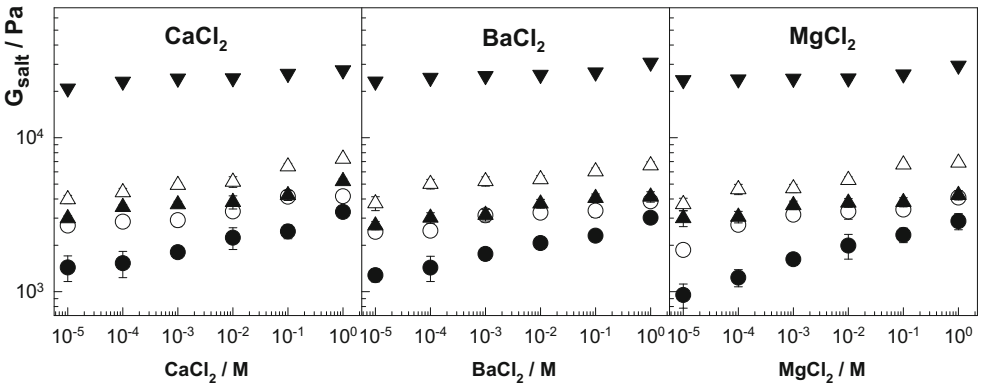

Fig. 9 Elastic modulus G_{salt} of P(DMAEMA-co-HEMA) hydrogels after equilibrium swelling in salt solutions of $CaCl_2$, $BaCl_2$ and $MgCl_2$ shown as a function of the ionic strength. HEMA mol%: 20 (●), 40 (○), 60 (▲), 80 (△), 100 (▼)

network chains. In this region, the higher crosslink density may cause stronger thermodynamic force which makes water to diffuse faster and results in a higher rate of swelling.

In polymeric networks, the thermodynamic interaction indicated by χ designates the change in the interaction energy when the polymer and solvent are mixed together. For the calculation of the interaction parameter χ between P(DMAEMA-co-HEMA) network and water, the following expression of Flory-Rehner equation for phantom chains was used [41]:

$$\chi = -\frac{\ln(1-\nu_2) + \nu_2 + 0.5\left(\rho/\overline{M}_c\right) V_1 (\nu_2)^{1/3} \left(\nu_2^0\right)^{2/3}}{(\nu_2)^2} \quad (9)$$

By using the experimentally determined equilibrium swelling ratio and $\overline{M}_c$ values, the interaction parameter χ of the P(DMAEMA-co-HEMA)-water system was calculated and the results were presented in Table 3 for all type of salt solutions. It was found that the χ parameter of P(DMAEMA-co-HEMA)-water system which describes the total interaction between the network and water is dependent on the salt concentration in the range of interest. It is expected that the specific interactions between cations and side groups of polymeric network affect the mixing term of the free energy. The low value of χ parameters between the P(DMAEMA-co-HEMA) network and water in diluted range of the salt solutions means a strong interaction between the polymer and water and a weak interaction between hydrophobic groups of the polymer chains.

Analysis of the diffusion process of P(DMAEMA-co-HEMA) hydrogels in salt solutions

To understand the swelling behavior of P(DMAEMA-co-HEMA) hydrogels in the presence of salts, the dynamic kinetics of swelling/shrinking process have been studied and the results were presented in Figs. 11 and 12. Different mathematical models have been developed to define the swelling and shrinking kinetics of ion-responsive hydrogels and by applying these models, it is possible to estimate the diffusion coefficient of water within the hydrogel matrix. The results for P(DMAEMA-co-HEMA) hydrogels were analyzed in terms of a simple, non-Fickian transport equation given by Ritger and Peppas [56–59]:

$$F = \frac{M_t}{M_\infty} = \frac{WU(t)}{SR_{eq}} = kt^n \quad (10)$$

Table 2 The elastic modulus G_{salt} of (DMAEMA-co-HEMA) hydrogel containing 20 mol% HEMA in the feed after equilibrium swelling in salt solutions

Conc.	NaCl	KBr	KI	KCl	$CaCl_2$	$BaCl_2$	$MgCl_2$
M	G / Pa	G / Pa	G / Pa	G / Pa	G / Pa	G / Pa	G / Pa
1.0	6481 (298)	5145 (181)	5776 (234)	5749 (126)	3290 (82)	3017 (243)	2868 (345)
10^{-1}	4844 (262)	3932 (261)	4666 (342)	4157 (162)	2460 (254)	2308 (156)	2335 (254)
10^{-2}	2587 (176)	2926 (225)	3647 (245)	2829 (143)	2239 (363)	2066 (145)	1990 (365)
10^{-3}	2122 (156)	2483 (193)	2887 (287)	2349 (135)	1802 (142)	1756 (359)	1622 (125)
10^{-4}	2018 (359)	2340 (195)	2388 (369)	2184 (259)	1529 (297)	1430 (268)	1232 (158)
10^{-5}	2004 (185)	1810 (216)	2066 (456)	1977 (147)	1433 (272)	1277 (324)	950 (169)

The standard deviations of the separate measurements are also given

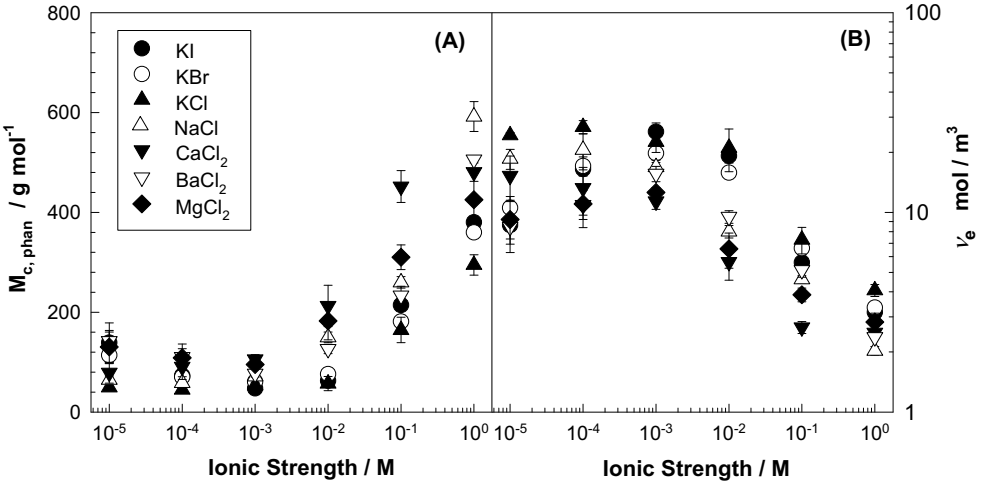

Fig. 10 The average molecular weight of the network chains $M_{c,phan}$ (**a**) and the effective crosslink density ν_e of P(DMAEMA-co-HEMA) hydrogels containing 20 mol% HEMA in the feed shown as a function of the ionic strength of the salt solutions

where F denotes the water fraction at time t, M_t represents the amount of water absorbed at time t, M_∞ is the water uptake at equilibrium, k is a constant related to the structure of the network, and the exponent n is an indicator of type of the diffusion. The Eq.(10) couples both Fickian and non-Fickian mechanisms and is strictly dependent on the geometry as well as the thickness of the hydrogel sample used in dynamic swelling/deswelling experiments. The value of $n = 0.5$ indicates Fickian kinetics in which the rate of diffusion of the solvent is rate-limiting; the diffusion rate of the solvent is much lower that polymer relaxation. Although the initial portion of the swelling curves is approximately linear, the swelling curve being concave to time axis at higher times has to be established for Fickian diffusion. The values between 0.5 and 1 indicate contributions from non-Fickian or anomalous transport when both diffusion and polymer relaxation control water penetration into the network, while $n = 1$ shows a Case II transport; polymer relaxation controls the water diffusion into the network [58]. Only the data fulfilling the condition $WU(t)/SR(eq) \leq 0.6$ were taken into account and Equation (11) was applied to calculate the diffusion coefficient of water moving through the P(DMAEMA-co-HEMA) hydrogels and the results were summarized in Table 4:

$$D = \pi\, l^2 \left(\frac{k}{4}\right)^{1/n} \tag{11}$$

where D is the diffusion coefficient (cm^2/s) and l is the initial dry diameter of the hydrogel. The kinetics of swelling of P(DMAEMA-co-HEMA) hydrogels are shown in Fig. 11a, giving the effects of NaCl, KBr, KI, KCl, $CaCl_2$, $BaCl_2$ and $MgCl_2$ solutions. It is interesting to note that three different regions are seen on the kinetic dependencies of the change of water content in P(DMAEMA-co-HEMA) hydrogels. For all studied systems an initial linear dependence of the fraction of water uptake of the gel, *WU(t),* as a function of t was observed. The rapid initial mass increase of the hydrogels is governed by the diffusion of water from the external solution to the hydrogel, induced by the difference of salt concentration inside the hydrogel and in the external solution. The second region is characterized by a smaller slope, i.e., the swelling speed is reduced. This second stage can be connected with the structural relaxation of the polymer chains of the network while complexes of the polymer network are formed. The process of formation of such complexes proceeds with a considerably smaller speed in comparison with water diffusion. Finally, a plateau region is observed when the equilibrium swelling is reached after second stage. The data from the kinetics of swelling in salt solutions for the copolymer hydrogels were analyzed by Eq. (10) and the values of the exponent n, characteristic of the transport mode, were determined from ln$F$ versus ln$t$ plot given in Fig. 11b. These values obtained by regression were already listed in Table 4. The observation of the values of n

Table 3 The values of the Flory-Huggins interaction parameter for P(DMAEMA-co-HEMA) hydrogels containing 20 mol% HEMA in salt solutions

Conc. M	χ (NaCl)	χ (KCl)	χ (KBr)	χ (KI)	χ($CaCl_2$)	χ ($BaCl_2$)	χ($MgCl_2$)
1.0	0.63	0.57	0.55	0.56	0.54	0.54	0.53
10^{-1}	0.53	0.50	0.51	0.52	0.53	0.50	0.51
10^{-2}	0.49	0.42	0.44	0.42	0.50	0.47	0.49
10^{-3}	0.40	0.39	0.38	0.33	0.45	0.39	0.43
10^{-4}	0.34	0.34	0.40	0.41	0.41	0.40	0.42
10^{-5}	0.37	0.35	0.45	0.48	0.37	0.46	0.43

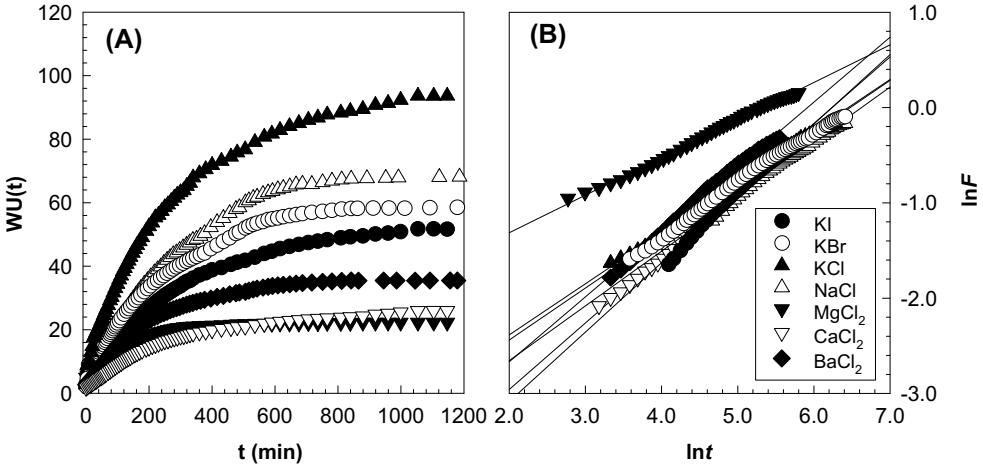

Fig. 11 Swelling dynamic curves of P(DMAEMA-co-HEMA) hydrogels containing 20 mol% HEMA in 10^{-5} M salt solutions as indicated (**a**) and ln-ln plots of *F* versus *t* (**b**)

between 0.68 and 0.70 for KI, $CaCl_2$ and $BaCl_2$ -neither 0.5, which would mean Fickian diffusion, nor 1, which would be case II-indicates non-Fickian behavior. The results indicated that the swelling transport mechanism for the swelling in KI, $CaCl_2$ and $BaCl_2$ solutions was a non-Fickian type. For KBr, KCl and NaCl, *n* values between 0.53 and 0.57 indicated that the diffusion was Fickian or anomalous, but not "case II" type. For $MgCl_2$, *n* was below 0.50 which shows that the water penetration rate is much below the polymer chain relaxation rate. This situation, which is still regarded as Fickian diffusion, is named as "Less Fickian" behavior. pH-sensitive hydrogels composed of N[−3(dimethylamino)propyl] methacrylamide (DMAPMA) and HEMA was prepared by Mishra et al. using BAAm as crosslinker and sodium persulfate/ammonium persulfate as joint initiator system. It was observed that the calculated value of *n* for the hydrogel at both physiological fluids is 0.79 and 0.87, respectively, which confirms the non-Fickian release mechanism [60]. Sideridou and Papanastasiou determined the diffusion coefficient of water at 50 °C in methacrylate-based biomaterials and found that the sorption of water in PHEMA and P(HEMA-co-TEGDMA) proceeds via a Fickian process. It was proposed that the polar interactions between polymer and water and not the geometrical characteristics of the polymer structure provide the rate-limiting step of water sorption. The obtained values of *D* for PHEMA and P(HEMA-co-TEGDMA) prepared by light curing at room temperature were equal to 2.35×10^{-7} and 2.83×10^{-7} cm^2 s^{-1}, respectively. The addition of TEGDMA units in P(HEMA-co-TEGDMA) removes some of the hydroxyl groups and introduces some less polar/hydrophilic groups which cause a decrease to equilibrium water uptake and increase of the diffusion coefficient [61]. pH sensitive hydrogel based on P(HEMA-co-DMAEMA) were prepared in the presence of chemically crosslinking agent ethylene glycol methacrylate (EGDMA). Physically crosslinked hydrogels were also prepared without the addition of EGDMA. The diffusion coefficient of water was found to depend on DMAEMA content and crosslinking agent concentration in polymer. Physically crosslinked hydrogels showed higher diffusion coefficient values than the corresponding chemically crosslinked hydrogels [62].

The dynamic shrinking of P(DMAEMA-co-HEMA) hydrogels from the swollen state (in 10^{-5} M salt solution) to the shrunken state (in 1.0 M salt solution) was measured and the curves were presented in Fig. 12. The shrinking of

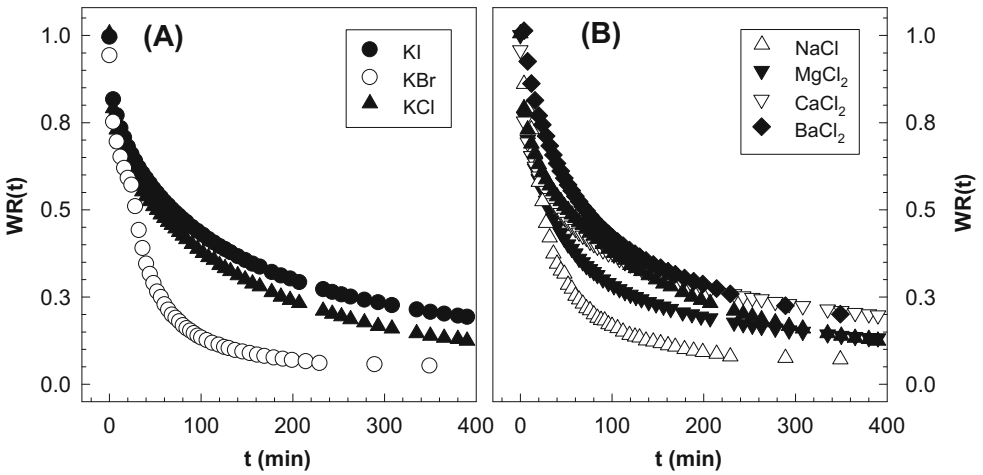

Fig. 12 Shrinking dynamic curves of P(DMAEMA-co-HEMA) hydrogels containing 20 mol% HEMA in 1.0 M salt solutions as indicated

Table 4 Parameters for the kinetic swelling for the salt solutions: Initial diffusion coefficient D (cm^2/s), kinetic exponent n and characteristic constant k from fitting experimental data to Ritger-Peppas model

Saline solution	n	k	r^2	$Dx10^{-6}$ (cm^2/s)
KI	0.7088	0.0116	0.9884	1.02
KBr	0.5449	0.0293	0.9954	3.07
KCl	0.5362	0.0314	0.9944	3.37
NaCl	0.5742	0.0222	0.9943	3.13
$MgCl_2$	0.3934	0.1226	0.9960	8.26
$CaCl_2$	0.6863	0.0134	0.9963	1.13
$BaCl_2$	0.6813	0.0177	0.9950	1.68

P(DMAEMA-co-HEMA) hydrogels in the presence of different salts depends on the specific interaction of the salt with the polymer chains of network. In 1.0 M salt solutions, the swelling ratio of P(DMAEMA-co-HEMA) hydrogels decreases rapidly due to the difference between the mobile ion concentration inside and outside of the hydrogel matrix. However, the data illustrate that the initial collapse rate of hydrogels is differ from each other due to the specific interactions between the salt and polymer chains. P(DMAEMA-co-HEMA) hydrogels in KBr and NaCl solutions shrank significantly faster than the other types of salt solutions. The equilibrium state of the hydrogel collapse is reached in 6 h, while for the hydrogel samples in KBr and NaCl solutions, the processes are completed after ca. 3 h. P(DMAEMA-co-HEMA) hydrogel sample had its water retention reduced from 100 % to close 8.5 % within 200 min in NaCl solution and to 7.4 % in KBr solution, whereas it was reduced to only about 21.9 % in $BaCl_2$ solution within the same time frame. The initial shrinking is mainly determined by the difference of the salt concentration and is unaffected by the specific interactions and the hydrophobic forces.

Conclusıons

Salt-sensitive copolymeric hydrogels have been fabricated by free radical copolymerization of DMAEMA and HEMA in the presence of DEGDMA. The dependency of swelling capacity of P(DMAEMA-co-HEMA) copolymeric hydrogels on the salt concentration, the comonomer composition as well as on the specific interaction of the salt with the polymer chains were investigated. In order to determine the effect of salt on the water absorbency of P(DMAEMA-co-HEMA) hydrogels, two series of salt solutions were used: chlorides with variable cations and potassium salts with different anions. The swelling studies performed by changing the salt concentration yielded interesting results. The extent of equilibrium hydrogel volume increases with the counterion in the following sequence of Ca^{2+}, Ba^{2+}, Mg^{2+}, Na^{+}, and K^{+} at the same ionic strength. Three distinct regions can be described in the salt concentration dependence of the swelling of P(DMAEMA-co-HEMA) hydrogels. When the salt solution is diluted up to about 10^{-4}–10^{-5} M, the swelling curve of hydrogel samples holds horizontally and the copolymeric hydrogels are in fully swollen state. Then, the decrease in V_{eq} is rapid up to 10^{-2} M salt concentration. As the salt concentration further increases, the decrease in V_{eq} slows down between 10^{-1}–1.0 M and the swelling curves converge together in the concentrated salt solution (1.0 M). This effect was due to the reduced water activity of salt solutions and to the shielding effect exerted by free electrolytes on the polymeric bulk charges. The influence of different type of salts on the elasticity indicated that the elastic modulus of P(DMAEMA-co-HEMA) hydrogels increases as the comonomer HEMA content in the feed as well as the ionic strength of the salt solution increased. The dilution of the salt solution up to 10^{-5} M induces a 3.0 fold decrease in the elastic modulus of hydrogels in NaCl, KBr, KI and KCl solutions whereas 2.5 fold decrease in $CaCl_2$, $BaCl_2$ and $MgCl_2$ solutions is obtained. The analysis of the swelling characteristics and water diffusion in the hydrogels showed that the structure of the hydrogels, the type of the salt used in the swelling is the main factor affecting the diffusion coefficient D and transport mechanism of water. The dynamic swelling studies indicated that the composition of the comonomers had significant influence on the swelling behavior. The swelling measurements in all types of salt solutions showed that P(DMAEMA-co-HEMA) hydrogels exhibit strong salt-sensitive swelling behavior over the entire range of the comonomer HEMA concentrations.

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