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ORIGINAL PAPER

Hydrogels from 2-(dimethylamino)ethylacrylate with 2-acrylamido-2-methyl-1-propanesulfonic acid: synthesis, characterization, and water-sorption properties

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Abstract A novel series of copolymer hydrogels of 2-(dimethylamino)ethylacrylate (DMAEA)/2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) were prepared by solution free radical polymerization at different feed monomer mol ratios. The monomer reactivity ratios were determined by Kelen–Tüdös method. According to that, the monomer reactivity ratios for poly(DMAEA-*co*-AMPS) were $r_1 = 0.125$ and $r_2 = 2.85$, ($r_1 \times r_2 = 0.356$). The effect of reaction parameters, including the concentration of cross-linking reagent *N*,*N*′-methylene-bis-acrylamide (MBA) and initiator ammonium persulfate (APS), the monomer concentration, pH, temperature, salt solutions, and solvent polarity on the water absorption have been also studied. The hydrogels achieved water-absorption values of 430 g of water/g of xerogel for the copolymer 1:2 richest in AMPS moiety. This copolymer is also very stable to the temperature effect. The optimum pH for the copolymers is 7. Aqueous solutions of the copolymers showed lower critical solution temperature behaviour (LCST). The phase transition temperatures of aqueous solutions of these copolymer increased with increasing of hydrophilic AMPS unit content in the copolymers. The glass transition temperature (Tg) of hydrogels showed a decrease by increasing of comonomer DMAEA content.

Keywords Hydrogels · Radical polymerization · Swelling ·
Stimuli-sensitive polymers

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Introduction

Hydrogels are cross-linked, three dimensional hydrophilic polymer networks that swell but do not dissolve when brought into contact with water. There are hydrogels that undergo a volume change in response to change in the surrounding conditions [1–17]. As a result of important research during the last two decades, hydrogels are now recognized as a well established class of polymers with widespread applications in agriculture, medicine, the food industry, biotechnology, and environmental sciences.

Hydrogel is a class of polymeric material with the ability to hold a substantial amount of water, presenting a soft, rubbery-like consistency, and low interfacial tension parameters [3, 14, 15]. The structural feature of these materials dominates its surface properties, permeselectivity, and permeability, giving to hydrogels their unique, interesting properties, and the similarity of their physical properties to those of living tissue [18, 19].

Polymer hydrogels derived from poly(acrylamide), cross-linked by a small amount of a bifunctional compound have found wide applications in the fields of agriculture and medicine [20–22]. Water-containing polymeric gels, hydrogels derived from poly(acrylamide) are among the most widely investigated.

Due to their high water content, low water contact angle, high permeability, and low friction coefficient, hydrogels are studied extensively as a replacement for soft tissue [4].

Hydrogel properties mainly depend on the degree of cross-linking, the chemical composition of the polymeric chains, and the interaction between the network and surrounding liquids. Hydrophilicity or high water retention in hydrogels is attributed to the presence of hydrophilic groups, such as carboxylic acids, amides, and alcohols [5, 14].

The use of acrylic acid based hydrogels to concentrate environmental samples by absorbing excessive amounts of water for pesticide residue analysis is a unique application in environmental monitoring [23].

In stimuli responsive hydrogels, the response of the functional group depends on the type, changing according to the scale of external stimuli, such as pH, temperature, and salt concentration. These environmental variables are always found in controlled drug delivery, immobilized enzyme reactors, and separation processes. The relationship between the gels' swelling behavior and the feed monomer ratios were studied at different temperatures and in different pH solutions. The transition temperature of the cross-linked gels changed according to the feed monomer ratio used in the copolymerization reaction. The pH value of the solution strongly affected the swelling ratio [14–22].

The network density of the polymeric gels is also an important factor that is responsible for controlled release of active molecules. For example, it has been reported diffusion of agrochemical drug release systems [22].

One of the most intensively studied polymers in this field is poly(*N*-isopropylacrylamide) (PNIPAAm) which exhibits a sharp phase transition in water. PNIPAAm has a lower phase transition temperature at around 32 °C. The reason for this sharp phase transition is a good balance between hydrophilic and hydrophobic interactions in the polymer [24]. It undergoes a temperature induced collapse from an extended coil into a globule structure, a transition revealed on the macroscopic scale by a sudden decrease of the degree of swelling of PNIPAAm gels [25–30]. Raising the temperature of an aqueous PNIPAAm solution above the LCST causes a coil-to-globule transition, followed by a phase separation. This phase transition is accompanied by a release of water bound to the polymer chain, which is an endothermic process. In the literature some methods for the detection of the LCST have been reported. For example, light scattering to detect the coil-to-globule transition [31], turbidimetric measurements to achieve phase transition [32], or differential scanning calorimetry (DSC) to measure the transition heat [33]. The proposed application of these polymers is their use in the preparation of thermosensitive polymers (microsystems). As these devices are employed in real world environments, the copolymers will encounter temperatures far in excess of their LCSTs (typically ca. 30 °C for PNIPAAm) in the course of their lifetime. Generally, in the case of temperature sensitive polymers, incorporation of a hydrophilic comonomer leads to an increase in LCST, whereas incorporation of a hydrophobic comonomer leads to a decrease.

We have previously published [34–36] the synthesis and swelling properties of hydrogels from functional vinyl monomers. These systems showed that the copolymers containing acrylic acid and acrylamide derivative moieties are very sensitive to stimuli as pH, temperature, ionic strength, and copolymer composition. Thus, the influence of water absorption at room temperature was strong at pH 5 and pH 7, with maximum between 1,200 and 1,600% when the poly(2-hydroxyethylmethacrylate-*co*-maleoylglycine) P(HEMA-*co*-MG), was richest in HEMA monomer unit.

The aim of this paper is to synthesize by solution free radical polymerization copolymers of 2-(dimethylamino)ethyl acrylate with 2-acrylamido–2-methyl-1-propanesulfonic acid at different feed monomer ratios with different degrees of cross-linking, and to study the swelling properties of these hydrogel systems in distilled water and ethanol at different pH, temperature, time, and salt concentration. The thermal properties of the copolymers, especially the glass transition temperatures (Tg), and the thermal decomposition were also investigated.

Experimental part

Materials

2-(dimethylamino)ethylacrylate (DMAEA, Aldrich) was purified by distillation. All the other reagents were used as received without further purification.

Synthesis of poly[2-(dimethylamino)ethylacrylate-co-2-acrylamido-2-methyl-1-propanesulfonic acid], P(DMAEA-co-AMPS)

Cross-linked poly(DMAEA-*co*-AMPS) hydrogels containing 25, 33, 50, 66, and 75 mol% of DMAEA were prepared by solution free radical polymerization. DMAEA was dissolved in water, AMPS, MBA, and APS were added to the above DMAEA solution, the reaction solution was heated and polymerized for 24 h at

70 °C in a Teflon tube of 40 mm diameter. The product was cut into small discs 5 mm × 20 mm and immersed in deionized water to remove the residual unreacted monomers and dried until constant weight. Finally, the dried product was characterized and the swelling properties were determined.

The feed mol ratios of DMAEA and AMPS are 1:1; 1:2; 1:3, 2:1, and 3:1. The total weight percentage of both monomers in the solution is 15%. The weight-percentage of the cross-linking reagent respect to the monomers is 2, 3, 4, and 5%. The amount of initiator respect to the monomer was always 1 mol%.

Characterization

The dried copolymers were ground to a suitably sized powder for FT-IR analysis. The FT-IR spectra (KBr) of the copolymers were obtained with a Magna Nicolet IR-550 spectrophotometer.

The thermogravimetric analysis of the copolymers was performed using TGA (Polymer Laboratories, STA-625 thermobalance). Measurements of 5 mg of dry samples were carried out with a heating rate of 10 °C/min from room temperature to 550 °C under nitrogen atmosphere.

Copolymer morphology was examined by scanning electron microscopy (SEM) (Jeol, GSM-6380LV) after sputtering with gold.

The thermal analysis of the copolymers was determined by recording DSC under nitrogen atmosphere (flow rate = 150 and 50 $cm^3\ min^{-1}$, respectively). A sample soft 3–4 ± 0.1 mg was used in each experiment. Thermal stability studies were performed using a Mettler Toledo Star System 822e (TG) (Spain) at a heating rate of 10 °C/min. DSC measurements were carried to determine the glass transition temperature (T_g) of the copolymer.

The elemental analyses were carried out using a 1108 FISON CE analyzer (Italy).

Swelling measurements

The sample of poly(DMAEA-*co*-AMPS) (0.5 g) was immersed in 400 mL of distilled water for 12 h until equilibrium was reached at room temperature. The weight of the swollen gel was measured after the excess surface solution was removed by filter paper. Then, the swollen gel was weighed. The absorbency was calculated by using the following equation [37, 38]:

$$Q = (W_2 - W_1)/W_1$$

Absorbency (Q) is expressed in grams of liquid retained in the gel per grams of dry copolymer. W_2 and W_1 correspond to the weight of the swollen gel and the dry xerogel, respectively.

Effect of time, temperature, and pH on absorbency

The methods were the same as used for the swelling measurement in twice distilled water, saline solution, and ethanol. The pH values of the solution were adjusted with dilute HCl or NaOH.

Water retention capacity

The hydrogels were placed in twice-distilled water for 12 h. The swollen gels that reached equilibrium in water were drained in nylon bags for 1 h, then the gels and the bags were put into an oven and heated at constant temperature. The change of weight was controlled at 1 h interval.

Results and discussion

Synthesis and characterization

Copolymerization reactions were performed by solution radical polymerization [36, 39] at different feed monomer compositions, while maintaining constant the total amount of comonomers (0.022 mol). The copolymerization reaction in the presence of a cross-linking reagent as MBA, will lead not only to branching but also to a cross-linked structure. Branches from one polymer molecule will be capable of reacting with those of another polymer molecule. Cross-linking reaction involves two polymer chains that have been joined together by a branch.

The yield for the all copolymer systems was higher than that 85% (see Table 1). Hydrogels are transparent, smooth, and maintain their shape in the swollen state. As can see, four copolymers show a yield higher than that 96%. Therefore, it should be not very important the presence of an eventual homopolymer.

Respect to the copolymerization mechanism, it corresponds to a characteristic free radical polymerization, where the AMPS macro radical would present a higher reactivity than that DMAEA macro radical producing random copolymers with a copolymer composition richest in the AMPS moiety (see Table 3).

Figure 1 shows the FT-IR spectra of the five copolymers poly(DMAEA-*co*-AMPS). The FT-IR spectra of five hydrogels are similar. Each spectrum shows a broad band in the range of 3,100–3,700 cm^{-1}, which is attributed to the typical absorption band of the comonomers and the cross-linking reagent. Others most characteristic absorption bands present in all copolymers are the following (in cm^{-1}): 2,940, 2,810 (C–H stretching, aliphatic), 1,750, 1,690 (C=O, ester group); 1,643, 1,550 (N–H deformation of amide group), 1,219, 1,034 (stretching SO_3, S=O from sulfonic acid group).

Table 1 Experimental conditions of the copolymerization reaction and yield

Polymer sample no	Feed monomer ratio (in mol)	[DMAEA] (mol)	[AMPS] (mol)	[MBA] (mol)	[PSA] (mol)	Yield (%)
1	(1:1)	0.0111	0.0111	8.87×10^{-5}	2.22×10^{-5}	84.0
2	(1:2)	0.0074	0.0148	8.87×10^{-5}	2.22×10^{-5}	99.9
3	(1:3)	0.0055	0.0166	8.87×10^{-5}	2.22×10^{-5}	96.9
4	(2:1)	0.0148	0.0074	8.87×10^{-5}	2.22×10^{-5}	99.9
5	(3:1)	0.0166	0.0055	8.87×10^{-5}	2.22×10^{-5}	98.0

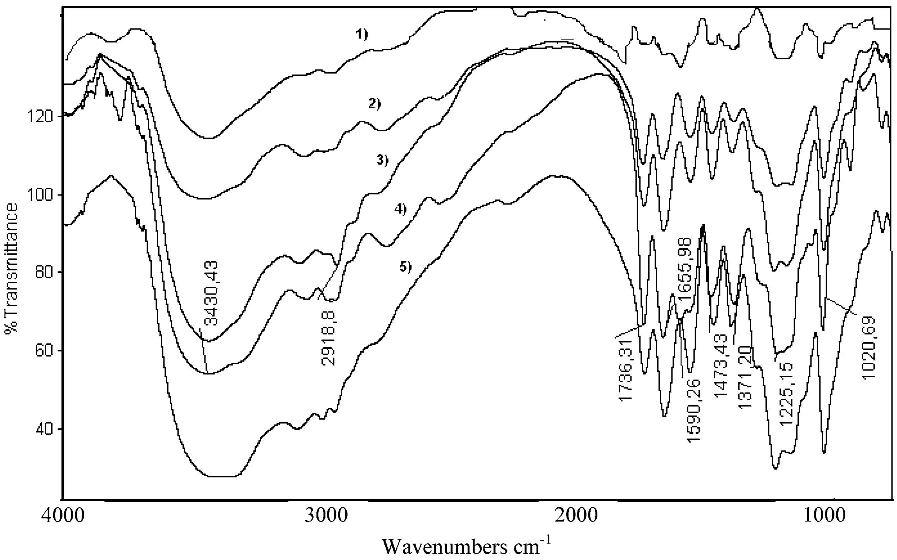


Fig. 1 FTIR (KBr) spectra for poly(DMAEA-*co*-AMPS) for feed monomer composition 1:1(1); 1:2(2); 1:3(3); 2:1(4); 3:1(5)/4 mol% MBA, respectively

The thermograms of all polymers show a typical sygmoidal shape. All the copolymers are degraded in one step and they are stable until 250 °C with a weight-loss lower than that 10% at 254 °C (see Fig. 2).

The values of the thermal decomposition temperature (TDTs) are shown in Table 2.

The copolymer thermal decomposition starts at around 200 °C. The samples are not completely decomposed up to 550 °C, there is a residual weight lower than 20%. It is not possible achieve a complete thermal behaviour due to the equipment work up to this temperature.

Table 2 shows the values of thermal $T_{10\%}$ and $T_{50\%,}$ the lowest TDT value corresponds to copolymer 5 which has a higher content of DMAEA monomer unit.

The typical micrograph by scanning electron microscopy (SEM) of the poly(DMAEA-*co*-AMPS) 1:3/4 mol% MBA is shown in Fig. 3. This copolymer corresponds to that with the highest water absorption properties. The micrograph shows a smooth surface morphology.

The monomer reactivity ratio values for the monomers DMAEA and AMPS were determined from the monomer feed ratios and the copolymer composition obtained at relatively low conversions according to Kelen–Tüdös (K–T) method [40]. Copolymer composition were determined from elemental analysis data (see Table 3). To determine the monomer reactivity ratios, a plot of monomer feed composition (M_1) versus monomer composition in the copolymer (m_1) (mol%) for DMAEA is shown in Fig. 4 for poly(DMAEA-*co*-AMPS).

The Kelen–Tüdös equation [1] is symmetrically transformed into:

$$G = r_1 \times F - r_2 \tag{1}$$

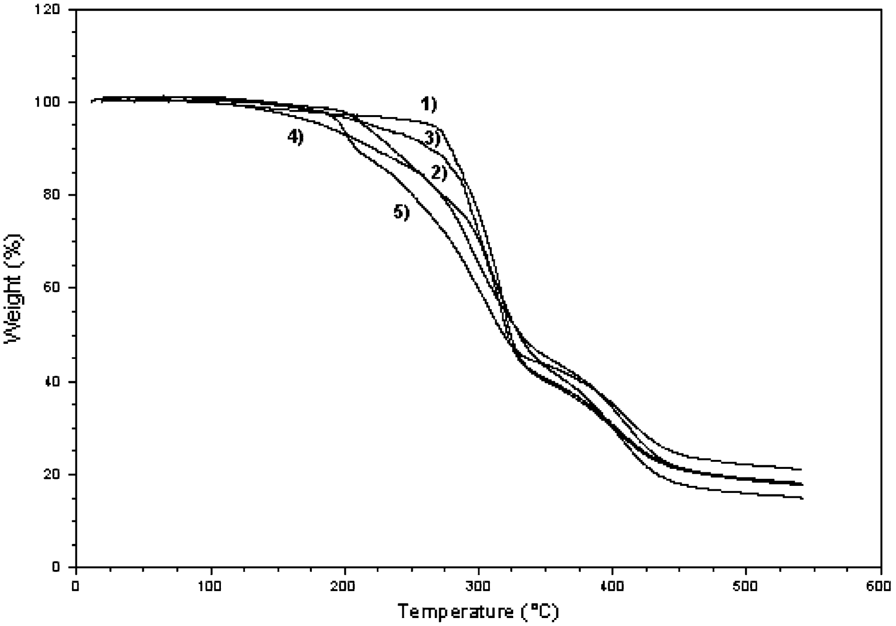


Fig. 2 Thermal behavior of poly(DMAEA-*co*-AMPS) for monomer feed composition 1:1(1); 1:2(2); 1:3(3); 2:1(4); 3:1(5)/4 mol% MBA, respectively, heating rate: 10 °C min^{-1} under N_2

Table 2 Thermal decomposition temperature (TDTs) of the copolymers

Polymer sample No	Feed monomer ratio	$T^{a}_{10\%}$ (°C)	$T^{b}_{50\%}$ (°C)
1	(1:1)	293	342
2	(1:2)	247	327
3	(1:3)	275	330
4	(2:1)	242	325
5	(3:1)	218	320

[a] At this temperature the weight loss was 10%

[b] At this temperature the weight loss was 50%

by introducing the new parameters ξ, η, and $\alpha = (F_{\min} \times F_{\max})^{0.5}$, where $F_{\min}$ and $F_{\max}$ corresponds to the smallest and largest fraction in the copolymer (F) that are calculated respectively (see Table 4).

The transformed variables are defined as :

$$\eta = G/(r_1 + r_2/\alpha)\ \xi = F/(\alpha + F)$$

The r_1 and r_2 values were also determined according to Eq. 2:

$$\eta = (r_1 + r_2/\alpha)\xi \tag{2}$$

where, η and ξ are mathematical functions of the monomer molar ratios in the feed and in the copolymer, respectively, α is an arbitrary denominator with any positive value, which produces a more homogeneous distribution of data along η–ξ axes.

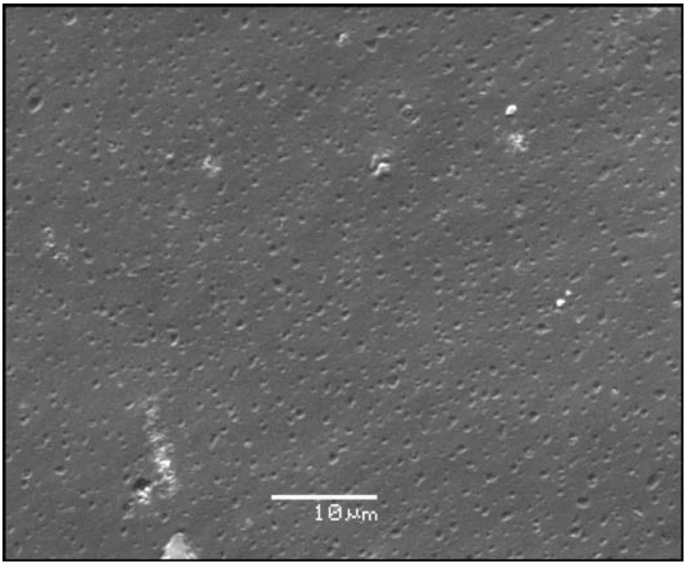


Fig. 3 SEM micrographs of poly(DMAEA-*co*-AMPS) 1:3/4 mol% MBA (2,000×). Monomer reactivity ratios (MRR)

Table 3 Elemental analysis, S/C ratio, and copolymer composition results

M1, (DMAEA) (mol%) in the feed	Copolymer composition M1 (mol%)	Elemental analysis[a]				S/C ratio
		Sulfur	Carbon	Hydrogen	Nitrogen	
3.0:1.0	52.61	8.668 (8.755)	47.966 (48.447)	10.592 (7.550)	8.292 (8.071)	0.1807 (0.1807)
2.0:1.0	43.90	10.096 (10.041)	47.193 (46.938)	9.914 (7.315)	8.283 (7.820)	0.2139 (0.2139)
1.0:1.0	26.44	12.525 (12.392)	44.653 (44.180)	8.718 (6.885)	8.194 (7.360)	0.2805 (0.2805)
1.0:2.0	17.53	12.689 (13.488)	40.354 (42.894)	8.597 (6.685)	7.290 (7.146)	0.3144 (0.3145)
1.0:3.0	11.90	15.111 (14.149)	44.981 (42.118)	9.508 (6.564)	7.942 (7.017)	0.3359 (0.3359)

[a] In brackets: Calculated values

The parameters ξ, η, and α have been previously defined: $G = (m_1/m_2 - 1)/z$ and $F = (m_1/m_2)/z^2$; $z = \log(1 - \delta_1)/\log(1 - \delta_2)$; $\delta_1 = \delta_2 y/X_o$; $\delta_2 = \mathrm{wt}\%(\mu + X_o)/(\mu + y)/100$; $\mu = \mu_2/\mu_1$; $y = m_1/m_2$, $X_o = M_1/M_2$, wt% = conversion, μ_1 and μ_2 are the molecular weights of monomers 1 and 2, respectively. M_1 and M_2 = initial composition of monomers in mol, M_1 = DMAEA and M_2 = AMPS, m_1 and m_2 = correspond to the monomer composition in the copolymer for each monomer.

The variable ξ can take any possible value in the 0–1 interval. A plot of η versus ξ gives a straight line, which on extrapolation to $\xi = 0$ and $\xi = 1$ gives $-r_2/\alpha$ and r_1, respectively (see Fig. 5).

According to these values, the monomer reactivity ratios for poly(DMAEA-*co*-AMPS) are the following: $r_1 = 0.125$ and $r_2 = 2.85$, ($r_1 \times r_2 = 0.356$). In general,

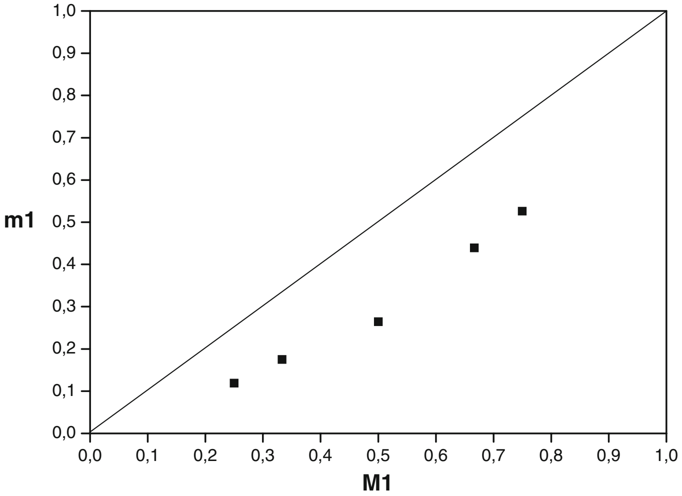


Fig. 4 Relationship of M1 in the feed (M1) and in the copolymer (m1)

Table 4 Reactivity ratios of DMAEA and AMPS in poly(DMAEA-*co*-AMPS) byKelen–Tüdös method for high conversion method, $\mu = 1.4473$, $\alpha = 6.3815$

M_1^a	m_1^b	wt^c	Xo	Y	δ_1	δ_2	z	F	G	ξ	η
75.0	52.6	49.5	3.000	1.110	0.318	0.860	0.195	29.27	0.566	0.8210	0.0159
66.7	43.9	50.5	2.000	0.781	0.305	0.781	0.240	13.55	0.905	0.6799	0.0454
50.0	26.4	42.8	1.000	0.359	0.209	0.580	0.269	4.95	2.377	0.4369	0.2098
33.3	17.5	50.5	0.500	0.213	0.252	0.592	0.323	2.034	2.436	0.2417	0.2894
25.0	11.9	50.5	0.333	0.135	0.230	0.568	0.312	1.391	2.766	0.1790	0.3571

* Values outside of range

[a] Monomer composition in the feed mol%

[b] Copolymer composition of M_1 in mol%

[c] Conversion

these results suggest for poly(DMAEA-*co*-AMPS) system, that the chain growth reactions proceeds predominantly by the addition of DMAEA monomer to the ~R-AMPS$^\bullet$ macro radical, where AMPS possess a higher tendency of incorporation to the polymer chain yielding also statistical copolymers.

Glass transition temperature

The glass transition temperature was estimated from the trace of this second run. In all cases to determine the glass transition temperature, Tg, of the samples, the criterion of Tg at Δcp/2 was adopted.

DSC thermograms of the poly(DMAEA-*co*-AMPS) (curve a–e) are illustrated in Fig. 6. The initial deflection is proportional to the sample heat capacity. The Tg of poly(DMAEA-*co*-AMPS) ranges between 98.8 and 103 °C. The Tg for hydrogels

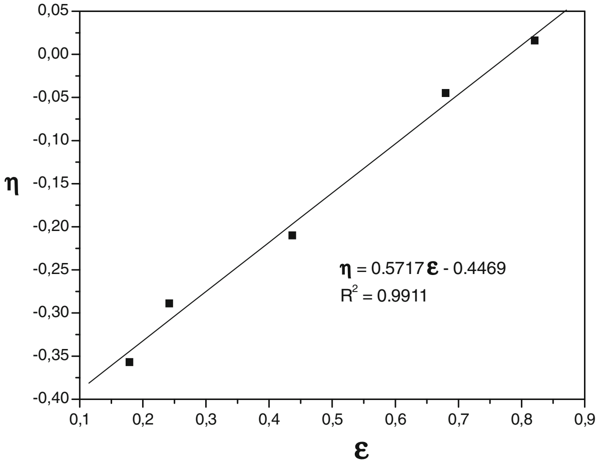


Fig. 5 η versus ξ representation of the copolymerization parameters of poly(DMAEA-*co*-AMPS) by K–T method

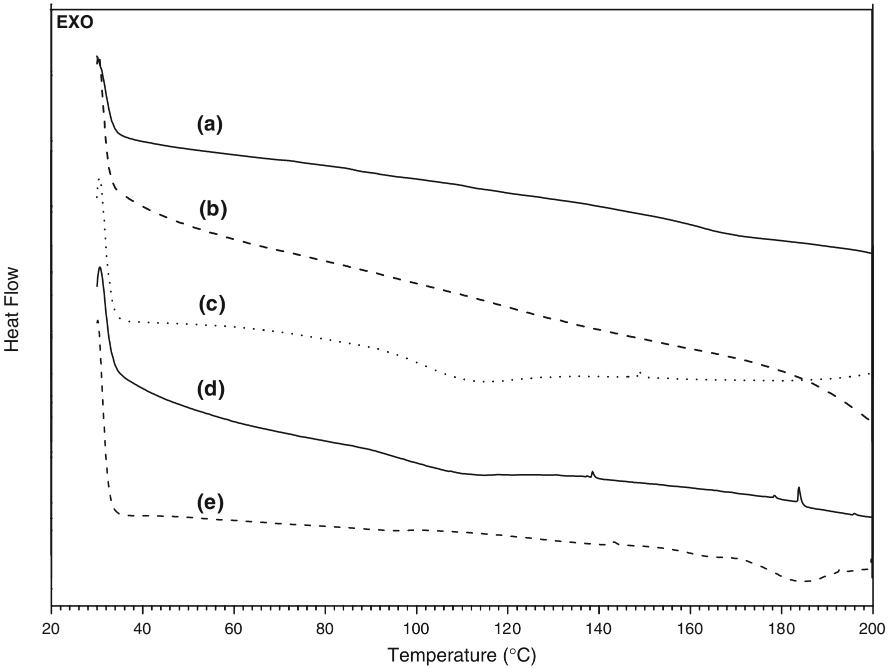


Fig. 6 DSC Thermograms of poly(DMAEA-*co*-AMPS) for monomer feed composition 1:1(a); 1:2(b); 1:3(c); 2:1(d); 3:1(e)/4 mol% MBA, respectively. Heating rate: 10 °C/min

shows a decrease with increasing comonomer of DMAEA contents, for example, see copolymer c, 2:1 and copolymer d, 3:1, 103.3 °C, and 98.8 °C respectively. The same behavior for the ΔCp/2 is observed in these copolymers (ΔCp = 0.368 J/g K;

ΔCp = 0.119 J/g K, respectively). An increasing amount of DMAEA slightly increases the Tg of the copolymer. For DMAEA content lower than 50 mol%, DSC showed no significant phase transition. The copolymer shows a single Tg indicating the formation of random copolymers. The Tg of PNIPAAm is 145 °C.

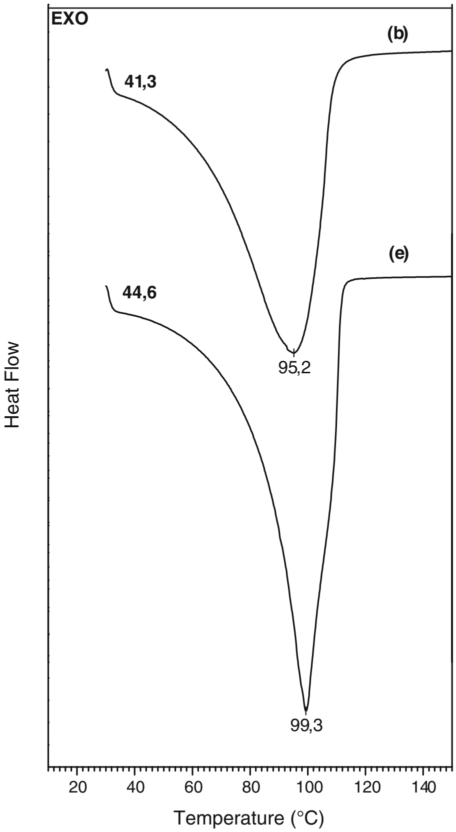
Low Critical Solution Temperature (LCST)

It is found that aqueous solutions of these copolymers exhibited a lower critical solution temperature (LCST), depending on their chemical composition followed by coacervate formation above the LCST.

The poly(DMAEA-*co*-AMPS) showed a LCST around 42 °C, which was significantly higher than that of poly(NIPAAm).

With an increase of DMAEA in the polymer, the transition phase temperature decreased due to the decrease of the hydrophilic balance, see Fig. 7. The LSCT increased with an Increasing of AMPS hydrophilic component in the copolymer, see copolymers b (1:2) and e (1:3), respectively.

Fig. 7 DSC Thermograms of poly(DMAEA-*co*-AMPS) show a LCST around 42 °C. Feed monomer composition 1:2(a) and 1:3(b), respectively. Heating rate: 10 °C/min



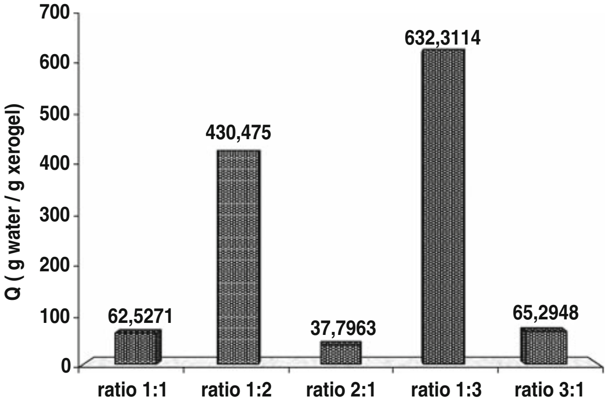


Fig. 8 Absorption (Q) of poly(DMAEA-*co*-AMPS) for feed monomer composition 1:1; 1:2;1:3; 2:1; 3:1/ 4 mol% MBA in twice-distilled water at room temperature

Absorbency

The absorbency of hydrogels in twice distilled water for five feed mol ratios are shown in Fig. 8. They show that of poly(DMAEA-*co*-AMPS) 1:2 is higher than that the other copolymers in twice-distilled water. This result is due to the gradual diffusion of water molecules into the network of the hydrogel and the complete filling or occupation of the pre-existing or dynamically formed spaces in the polymer chains. Nevertheless, the comonomer ratio 1:3 does not present suitable properties of hydrogel.

The absorbency of poly(DMAEA-*co*-AMPS)1:2/3 mol% MBA is higher than those other two copolymers in twice-distilled water as well as ethanol at room temperature. It is shown in Fig. 9. It is due to the smaller amount of cross-linking incorporated into the backbone. This increases the space for the water molecules.

Effect of pH on absorbency

To investigate the influence of pH on the degree of gel swelling, the pH was adjusted with 1 M HCl or 1 M NaOH from pH 1 to pH 9. Figure 10 shows the effects of the solutions' pH values on the swelling behavior for all the studied copolymers. The absorption curve shows an optimal value at pH 7 when the feed monomer ratio is 1:2. The absorbency increases from pH 1 to pH 7. At higher pH the absorbency decreased slowly.

Effect of the temperature on absorbency

The effect of the temperature on the absorbency and water loss for poly(DMAEA-*co*-AMPS) for these feed mol ratios is shown in Figs. 11 and 12. It demonstrates that the absorbency increase as increases the temperature until 55 °C, and water loss is not significant.

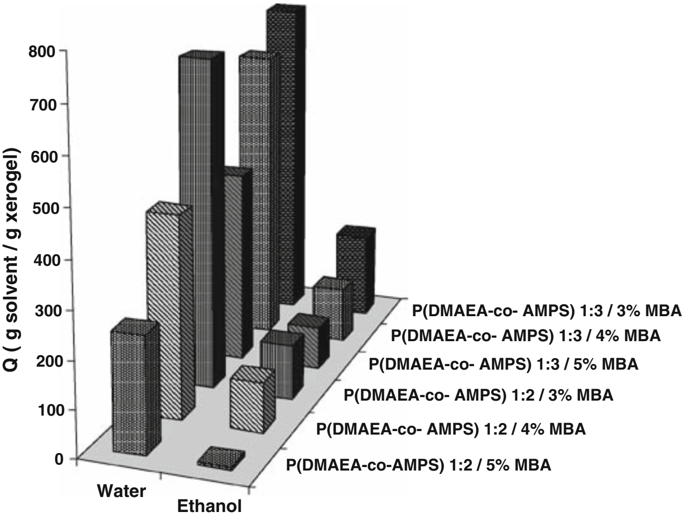


Fig. 9 Absorption (Q) of poly(DMAEA-*co*-AMPS) for feed monomer composition 1:2/5 mol% MBA(—▲—), 4 mol% MBA(—■—), 3 mol% MBA(—◆—) and 1:3/5 mol% MBA(—●—), 4 mol% MBA (—*—) in twice-distilled water and ethanol at room temperature

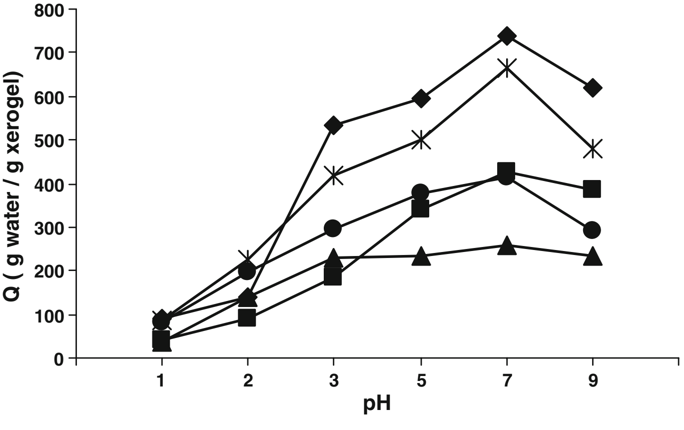


Fig. 10 Absorption (Q) of poly(DMAEA-*co*-AMPS) for feed monomer composition 1:2/5 mol% MBA(—▲—), 4 mol% MBA(—■—), 3 mol% MBA(—◆—) and 1:3/5 mol% MBA (—●—), 4 mol% MBA (—*—) in water at room temperature for pH 1, 2, 3, 5, 7, and 9

Effect of salt solutions on absorbency

Figure 13 shows the effect of the solution's salt concentrations on the absorbency of the poly(DMAEA-*co*-AMPS). It indicates that this polymer's absorbency in presence of the different NaCl concentrations depends on the copolymer composition. Thus, for initial mol concentration 1:2 it is observed a decrease until 0.6 M and finally it is maintained stable.

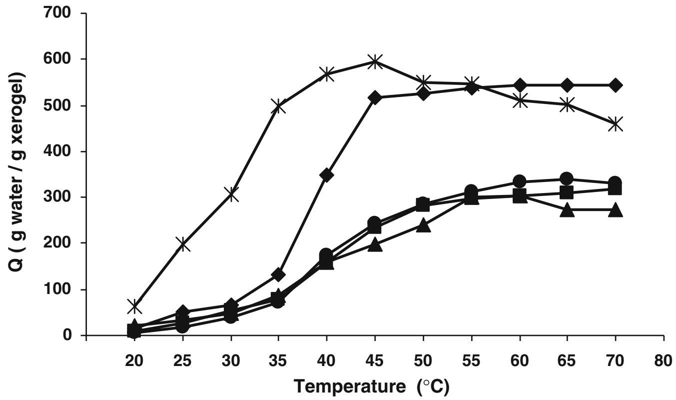


Fig. 11 Absorption (Q) of poly(DMAEA-*co*-AMPS) for feed monomer composition 1:2/5 mol% MBA(—▲—), 4 mol% MBA(—■—), 3 mol% MBA(—◆—) and 1:3/5 mol% MBA (—●—), 4 mol% MBA(—*—) at different temperatures

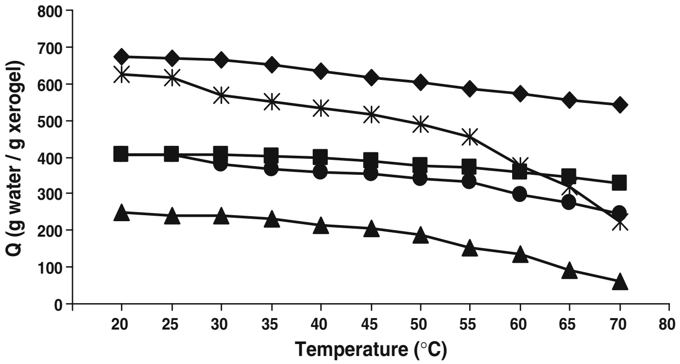


Fig. 12 Water loss (Q) of poly(DMAEA-*co*-AMPS) for feed monomer composition 1:2/5 mol% MBA(—▲—), 4 mol% MBA(—■—), 3 mol% MBA(—◆—), and 1:3/5 mol% MBA (—●—), 4 mol% MBA (—*—) at different temperatures

Conclusions

Hydrogels of DMAEA and AMPS were prepared in aqueous solution and the swelling properties were studied. The monomer reactivity ratios for poly(DMAEA-*co*-AMPS) were $r_1 = 0.125$ and $r_2 = 2.85$, ($r_1 \times r_2 = 0.356$). These results suggested that the chain growth reactions proceeds predominantly by the addition of DMAEA monomer to the $\sim$R-AMPS$^\bullet$ macroradical. AMPS possess a higher tendency of incorporation to the polymer chain yielding also statistical copolymers. Poly(DMAEA-*co*-AMPS) showed a higher absorbency in water with respect to ethanol and salt solutions. The absorbency of these polymers decreases as the solvent's polarity decreases.

The effects of pH on the absorbency were studied. It was found that the absorbency of poly(DMAEA-*co*-AMPS) 1:2 increased as the pH increased until 7

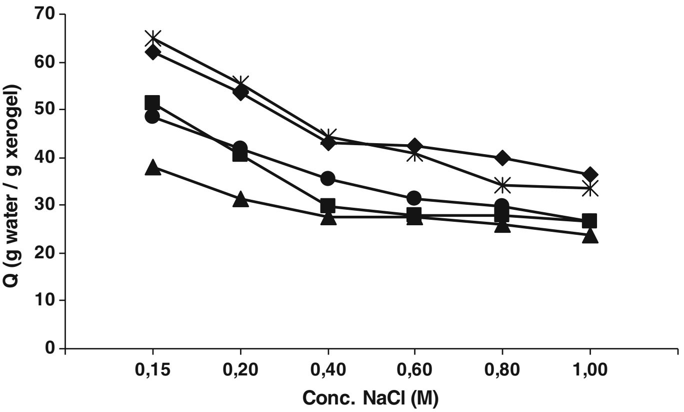


Fig. 13 Absorption (Q) of poly(DMAEA-*co*-AMPS) for feed monomer composition 1:2/5 mol% MBA(—▲—), 4 mol% MBA(—■—), 3 mol% MBA(—◆—) and 1:3/5 mol% MBA(—●—), 4 mol% MBA (—*—) at room temperature from different concentrations of NaCl

and then slightly decreased at higher pH. The absorbency at pH 7 is still up to 706 g water/g xerogel.

The absorbency increased as increased the temperature. These results implies that poly(DMAEA-*co*-AMPS) can be used in a wide temperature range. The influence of the salt solutions on the absorbency was investigated and the results indicated that absorbency is a variable function of the rising salt concentration.

The copolymer shows a single Tg indicating the formation of random copolymers. The Tg for the poly(DMAEA-*co*-AMPS) showed a decreases with increasing comonomer of DMAEA contents. Aqueous solutions of the copolymers showed lower critical solution temperature behavior (LCST). The temperature transition phases of the aqueous solutions of these copolymer increased with increasing of hydrophilic comonomer AMPS content. The LSCT was higher than that poly(NIPAAm) [24] at room temperature and thus, these polymers are suitable as precursor polymers for the preparation of hydrogels for the development of temperature- and pH-responsive switching devices through the sensitive gels with different properties.

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