

# HYDROGELS BASED ON (DIMETHYLAMINO)ETHYLACRYLATE (DMAEA) AND N,N'-DIMETHYLACRYLAMIDE (NNDMAAM): SYNTHESIS, CHARACTERIZATION, AND SWELLING BEHAVIOR

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## ABSTRACT

Hydrogels of 2-(dimethylamino)ethylacrylate (DMAEA) with N,N'-dimethyl acrylamide (NNDMAAm) were synthesized by solution free-radical polymerization at different feed mol ratios. These copolymers were completely water-insoluble. Polymers were characterized by elemental analysis, FT-IR spectroscopy, thermogravimetric analysis (TGA), and scanning electron microscopy (SEM).

The monomer reactivity ratios were determined by Kelen-Tüdös method. According to that, the monomer reactivity ratios for poly(DMAEA-co-NNDMAAm) were  $r_1 = 0.288$  ( $M_1 = \text{DMAEA}$ ) and  $r_2 = 1.460$  ( $M_2 = \text{NNDMAAm}$ ), ( $r_1 \times r_2 = 0.419$ ).

Low critical solution temperatures (LCST) values of hydrogels are around 60°C, which was significantly higher than that poly(NIPAAm) and increased with increasing of hydrophilic DMAEA unit content in the copolymers. The hydrogels achieved a water-absorption value of 188 g of water/g of dry polymer (xerogel) in distilled water. Effects of time, temperature, pH, salt concentration, cross-linking concentration, and solvent polarity on the water absorption were studied. Experimental results indicated that the copolymer poly(DMAEA-co-NNDMAAm) with a feed mol ratio 2:1 presents the best swelling properties.

**Key words:** Hydrogels, radical polymerization, swelling, stimuli-sensitive polymers.

## INTRODUCTION

Hydrogels are three-dimensional crosslinked hydrophilic polymeric structures that are able to swell in an aqueous environment<sup>[1-10]</sup>. 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<sup>[4]</sup>.

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<sup>[3]</sup>. Product of a large amount of research during the last two decades, hydrogels are now recognized as a well established class of polymers with widespread applications in agriculture, medicine, food industry, biotechnology, environmental sciences, among others. The structural feature of these materials dominates its surface properties, permselectivity and permeability, giving hydrogels with their unique, and interesting properties and the similarity of their physical properties to those of living tissue<sup>[11,12]</sup>.

Hydrogel properties mainly depend on the degree of crosslinking, the chemical composition of the polymeric chains, and the interaction of 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, alcohols and so on<sup>[5]</sup>.

In stimulus responsive hydrogels, the response of the functional group, depending on the type, changes according to the scale of external stimulus, such as pH, temperature, and salt concentration. These environmental variables are always found in controlled drug delivery, immobilized enzyme reactors, and separation processes<sup>[11-15]</sup>.

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<sup>[16]</sup>.

The poly(N-isopropylacrylamide), poly(NIPA), exhibits a sharp phase transition in water. Poly(NIPAAm) has a lower phase transition temperature at around 32°C. Several authors<sup>[11-15]</sup> have studied the collapse temperature in poly(NIPAAm) hydrogels and reported that while incorporation of a hydrophilic comonomer leads to a higher LCST, incorporation of a hydrophobic monomer decreases the critical temperature  $T_c$ . The reason for this sharp phase transition is a good balance between hydrophilic and hydrophobic interactions in the polymer<sup>[17]</sup>. 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 poly(NIPAAm) gels<sup>[18-31]</sup>. Raising the temperature of an aqueous poly(NIPAAm) 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. Thus, light scattering to detect the coil-to-globule transition<sup>[23]</sup>, turbidimetric measurements to achieve phase transition<sup>[24]</sup>, or

differential scanning calorimetry (DSC) to measure the transition heat<sup>[25]</sup> have been reported. The proposed application of these polymers is their use in the preparation of thermosensitive polymers (microsystems). As these devices are employed in real environments, the copolymers will have temperatures far in excess of their LCSTs (typically ca. 30°C for poly(NIPAAm)<sup>[18]</sup> in the course of their lifetimes. Thus, the thermal properties of the copolymers, especially the glass transition temperatures ( $T_g$ ) and the thermal decomposition were investigated

The network density of the polymeric gels is also an important factor that is responsible for controlled release of active molecules.

We have previously published<sup>[29-31]</sup> 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 stimulus as pH, temperature, ionic strength, and copolymer composition.

The aim of this paper is synthesize copolymers of 2-(dimethylamino)ethylacrylate with N,N'-dimethylacrylamide at different feed comonomer ratios with different amount of crosslinking reagent, and study the swelling effects of these hydrogel systems in twice distilled water at different pH, temperature, time, and salt concentration.

## EXPERIMENTAL

### Materials

2-(dimethylamino)ethylacrylate (DMAEA; Aldrich) was purified by distillation at 64°C and 12 mm Hg. All the other reagents were used as received.

Preparation of poly[2-(dimethylamino)ethylacrylate-co-2-NNDMAAm], poly(DMAEA-co-NNDMAAm).

Crosslinked poly(DMAEA-co-NNDMAAm) hydrogels, containing 25, 33, 50, 66, and 75 mol-% of DMAEA were prepared by free radical solution polymerization. NNDMAAm was dissolved in water, DMAEA, N,N-methylene-bis-acrylamide, MBA, and ammonium persulfate, APS, as crosslinking and initiator reagents respectively were added in the above NNDMAAm 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 x 20 mm, and vacuum dried until constant weight. Finally, the dried product was characterized and the swelling properties were determined.

The feed mole ratios of DMAEA and NNDMAAm are 1:1; 1:2; 2:1, 1:3, and 3:1. The total weight percentage of both monomers is 20%. The mol percentage of the cross-linking compared with the monomers is 4%. The mol percentage of the initiator compared with the monomers is 0.01%.

Nevertheless, the crosslinking reagent is part of the polymer chain it was not considered to calculate the N/C ratio. It is due to the amount is low and it

will not contribute significantly considering the experimental error.

*Hydrogel characterization*

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

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

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

*Swelling measurements*

Sample of poly(DMAEA-co-NNDMAAm) (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:

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

Absorbency is expressed in grams of liquid retained in the gel per grams of dry copolymer.  $W_2$  and  $W_1$  are the weights of the swollen gel and the dry poly(DMAEA-co-NNDMAAm), respectively.

*Effect of time, temperature, and pH on absorbency*

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

*Water retention capacity*

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. To investigate the variation in their weight, they were weighed at 1 h intervals.

**RESULTS AND DISCUSSION**

Stimulus-responsive hydrogels change their volume and elasticity in response to a change in liquid phase properties, such as temperature, pH, solvent composition, and ionic strength. Depending on the chemical composition of gels and liquid in experimental conditions the change in the swelling behavior can occur either continuously or non-continuously.

The relationship between the gels' swelling behavior and the copolymerization ratio were studied at different temperatures in solutions with various pH. The transition temperature of the crosslinked gels changed according to the feed monomer ratio used in copolymerization. The pH value of the solution strongly affected the swelling ratio.

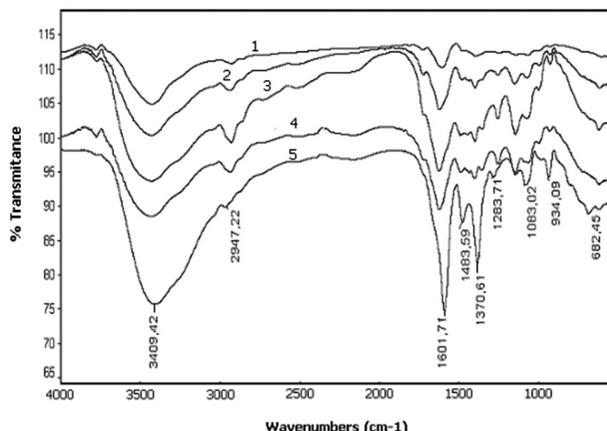
*Synthesis and characterization*

The yield for all copolymer systems was higher than that 90 % (see Table 1). Hydrogels are transparent, smooth, and maintain their shape in the swollen state.

**Table I.** Experimental conditions of the copolymerization reaction and yield poly(DMAEA-co-NNDMAAm) 4 mol-% MBA / 1 mol-% PSA. MBA:  $8.87 \times 10^{-4}$ , PSA:  $2.23 \times 10^{-4}$ .

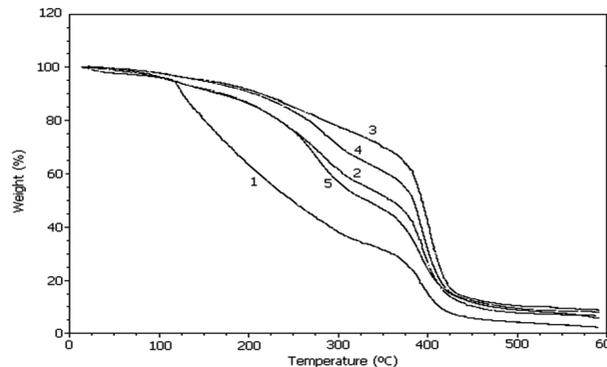
Polymer Sample No	Feed monomer ratio (in mol)	[DMAEA] (mol)	[NNDMAAm] (mol)	Yield (% w/w)
1	1:1	0.0111	0.0110	90.7
2	1:2	0.0074	0.0149	92.6
3	2:1	0.0147	0.0074	97.0
4	1:3	0.0055	0.0166	90.8
5	3:1	0.0166	0.0055	91.1

Figure 1 shows the FT-IR spectra of the copolymers poly(DMAEA-co-NNDMAAm), 1:1; 1:2, 2:1, 1:3, and 3:1 with 4 mol-% of MBA. The spectra show the typical absorption bands of both comonomers and the crosslinking reagent. Among the most characteristic absorption bands are the following (in  $\text{cm}^{-1}$ ): 3409 (N-H); 2947, 2810 (C-H stretching, aliphatic); 1601 (C=O vibration of the ester group); 1063 (N-H deformation of amide group).



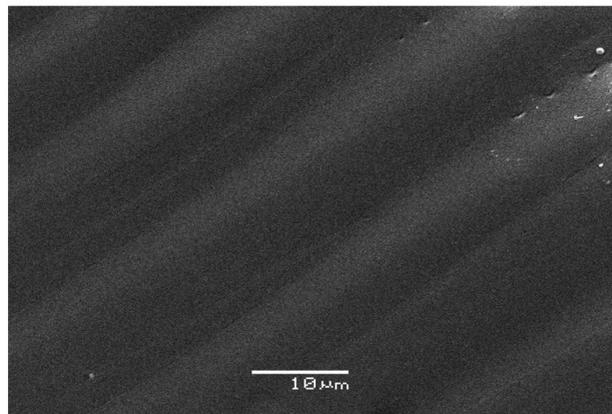
**Figure 1.** FTIR (KBr) spectra for poly(DMAEA-co-NNDMAAm) 1:1(2); 1:2(4); 2:1(5); and 1:3(3); 3:1(1) / 4 mol-% MBA.

The primary thermograms of all polymers show a typical sigmoidal shape. All the copolymers degrade in one step and they are stable until 200°C with a weight-loss lower than 10%. Polymer 1 shows a different behavior due to, probably the higher content of ester groups which is less stable (see Figure 2).



**Figure 2.** Thermal behavior of poly(DMAEA-co-NNDMAAm) 1:1(2); 1:2(4); 2:1(5); and 1:3(3); 3:1(1) / 4 mol-% MBA, heating rate:  $10^\circ\text{C min}^{-1}$  under  $\text{N}_2$ .

The typical scanning electron microscopy (SEM) of poly(DMAEA-co-NNDMAAm) 1:2 is shown in Figure 3, where the micrograph does not indicate a porous in the structure.



**Figure 3.** SEM micrographs of poly(DMAEA-co-NNDMAAm) 2:1 / 4 mol-% MBA (2000x).

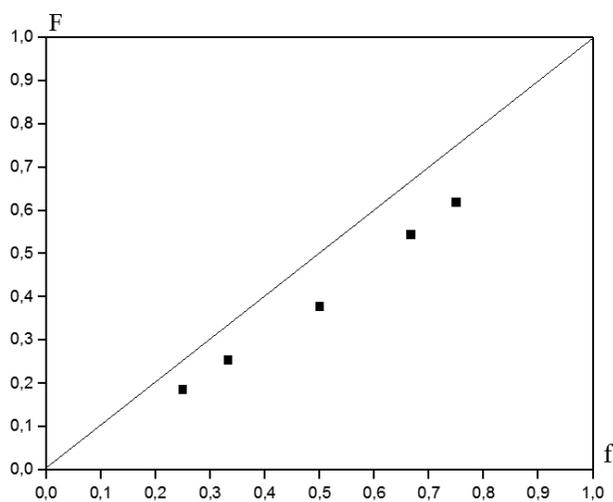
*Monomer reactivity ratios, (MRR)*

The monomer reactivity ratio values for the monomers NNDMAAm and

DMAEA were determined from the monomer feed ratios and the copolymer composition obtained at relatively low conversions, according to Kelen Tüdös (K-T) method.<sup>[24]</sup> Copolymer compositions were determined from elemental analysis data (see Table II). To determine the monomer reactivity ratios, a plot of monomer feed composition ( $M_1$ ) vs monomer composition in the copolymer ( $m_1$ ) (mol-%) for DMAEA is shown in Figure 4 for poly(DMAEA-co-NNDMAAm).

**Table II.** Elemental analysis, N/C relationship, and copolymer composition.

Initial load, M1:M2, (mol/mol)		Elemental Analysis:			
<b>M1:M2</b>	Copolymer ( <b>m1</b> )	Nitrogen	Carbon	Hydrogen	N/C Ratio
3:1	61.9	9.156	48.981	13.220	0.187
		<b>11.080</b>	<b>59.275</b>	<b>9.151</b>	<b>0.187</b>
2:1	54.3	9.432	49.225	12.735	0.192
		<b>11.382</b>	<b>59.404</b>	<b>9.151</b>	<b>0.192</b>
1:1	37.9	10.081	49.783	12.989	0.202
		<b>12.091</b>	<b>59.708</b>	<b>9.151</b>	<b>0.202</b>
1:2	25.3	10.840	51.184	13.529	0.212
		<b>12.701</b>	<b>59.969</b>	<b>9.151</b>	<b>0.212</b>
1:3	18.5	11.500	52.962	12.703	0.217
		<b>13.054</b>	<b>60.120</b>	<b>9.151</b>	<b>0.217</b>



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

The Kelen Tüdös equation (1) is symmetrically transformed into

$$G = r_1 \times F - r_2 \quad (1)$$

by introducing the new parameters  $x$ ,  $h$ , and  $\alpha = (F_{min} \times F_{max})^{0.5}$ , where  $F_{min}$  and  $F_{max}$  correspond to the smallest and largest fraction in the copolymer ( $F$ ) that are calculated, respectively (see Table 3).

The transformed variables are defined as :

$$h = G / (r_1 + r_2 / a) \quad x = F / (a + F)$$

The  $r_1$  and  $r_2$  values were also determined according to Equation (2):

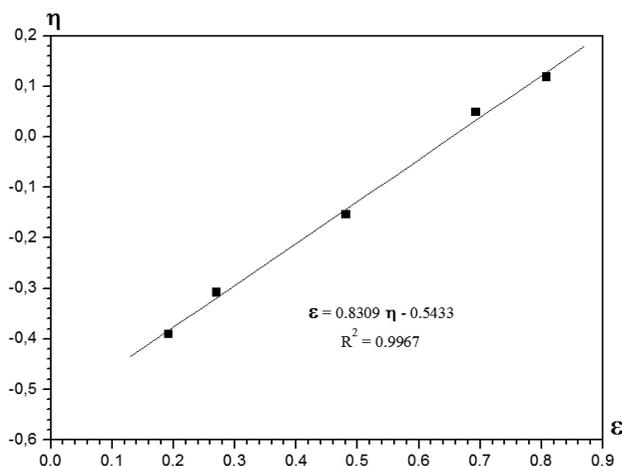
$$h = (r_1 + r_2 / a) \times x \quad (2)$$

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

The parameters  $x$ ,  $h$  and  $a$  have been previously defined:  $G = (m_1/m_2 - 1)/z$  and  $F = (m_1/m_2) / z^2$ ;  $z = \log(1 - d_1) / \log(1 - d_2)$ ;  $d_1 = d_2 y / X_0$ ;  $d_2 = \text{wt}\% (m + X_0) / (m + y) / 100$ ;  $m = m_2/m_1$ ;  $y = m_1/m_2$ ;  $X_0 = M_1/M_2$ ;  $\text{wt}\% = \text{conversion}$ ;  $m_1$  and  $m_2$  are the molecular weights of monomers 1 and 2 respectively;  $M_1$  and  $M_2$  = initial composition of monomers in mol,  $M_1 = (\text{DMAEA})$  and  $M_2 = (\text{NNDMAAm})$ ;  $m_1$  and  $m_2$  = correspond to the monomer composition in the copolymer for each monomer. The variable  $x$  can take any possible value in the 0 to 1 interval. A plot of  $hvs x$  gives a straight line, which on extrapolation to  $x = 0$  and  $x = 1$  gives  $-r_2/a$  and  $r_1$ , respectively (see Figure 5).

**Table III.** Reactivity ratios of DMAEA and NNDMAAm in poly(DMAEA-co-NNDMAAm) by Kelen Tüdös for high conversion method,  $m = 0.69233552$ ,  $a = 2.67967$ .

Charge	Copolym	conversion		y	d 1	d 2	z	F	G	e	h
		wt.-% <sup>(c)</sup>	Xo								
75.0	61.9	46.5	3.000	1.625	0.401	0.740	0.380	11.252	1.644	0.8077	0.1180
66.7	54.3	49.5	2.000	1.188	0.421	0.708	0.443	6.047	0.425	0.6929	0.0486
50.0	37.8	46.3	1.000	0.608	0.366	0.602	0.494	2.487	-0.794	0.4814	-0.1536
33.3	25.3	47.2	0.500	0.339	0.370	0.546	0.585	0.990	-1.131	0.2699	-0.3081
25.0	18.5	46.3	0.333	0.227	0.352	0.517	0.596	0.638	-1.296	0.1923	-0.3906



**Figure 5.** h vs x representation of the copolymerization parameters of poly(DMAEA-co-NNDMAAm) by K-T method.

According to these values, the monomer reactivity ratios for poly(AA-co-NNDMAAm) are the following:  $r_1 = 0.288$  and  $r_2 = 1.460$ , ( $r_1 \times r_2 = 0.419$ ). According to the results from the data, these copolymers would correspond to copolymers in random mainly.

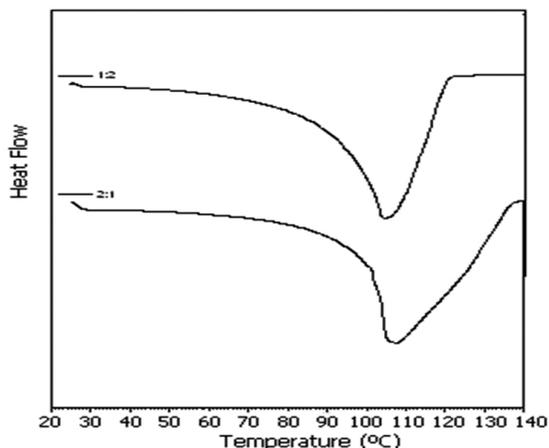
These results suggest for poly(DMAEA-co-NNDMAAm) system, that the chain growth reactions proceeds predominantly by the addition of DMAEA monomer to the  $\sim R$ -NNDMAAm macroradical, which NNDMAAm possess a higher tendency of homopropagation to the chain producing also copolymers in random

*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. Furthermore, thermosensitive hydrogels could be prepared by the free radical copolymerization of DMAEA and NNDMAAm in the presence of the cross-linking reagent MBA and initiator PSA.

LCST was determined by DSC and this temperature was determined at the point of the first slope where was starting the release of water from the hydrated hydrogel.

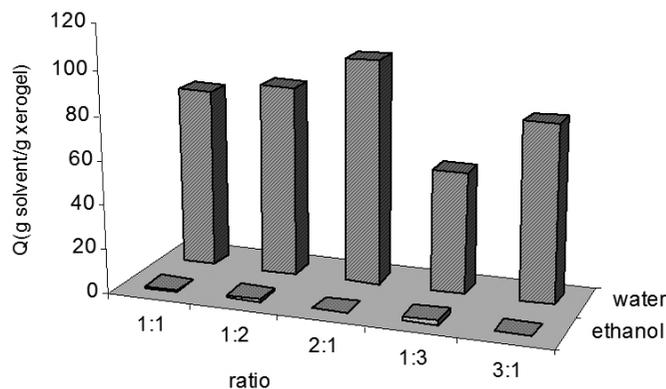
Poly(DMAEA-co-NNDMAAm) showed a LCST around 78°C, which was significantly higher than that poly(NIPAAm) (23). With an increase of hydrophilic DMAEA moiety in the copolymer, the LCST increased, see copolymers with initial feed composition 2:1 and 1:2 respectively, (see Figure 6). The LCST of copolymers comprising NIPAAm and other acrylamide derivatives have been reported to be between 0 and 65°C, and it is dependent on the hydrophobic-hydrophilic balance of their copolymers.



**Figure 6.** DSC thermograms of poly(DMAEA-co-NNDMAAm) show a LCST around 78 °C for a feed composition 2:1 and 57.6 °C for a ratio 1:2. Heating rate: 10 °C/min.

*Absorbency*

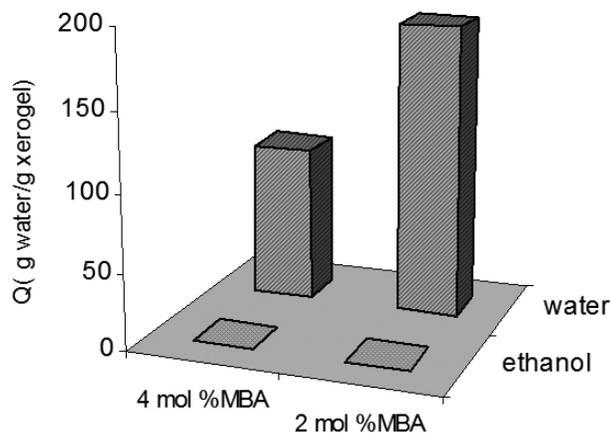
The absorbency of hydrogels in distilled water and ethanol for five feed mol ratios are shown in Figure 7. It is shown that the highest value is obtained with a polymer containing a ratio 2:1. This result is due to the gradual diffusion of water molecules into the network of the hydrogel and complete filling or occupation of the pre-existing or dynamically formed spaces in the polymer chains. The results with ethanol are included in order to compare with water, both highly hydrophilic.



**Figure 7.** Absorption (Q) of poly(DMAEA-co-NNDMAAm) 1:1 ; 1:2 ;2:1 ; 1:3 ; 3:1 / 4 mol % MBA in twice-distilled water and ethanol at room temperature.

Equilibrium swelling in water and ethanol of the ratio 2:1 at room temperature as a function of percent of MBA is shown in Figure 8.

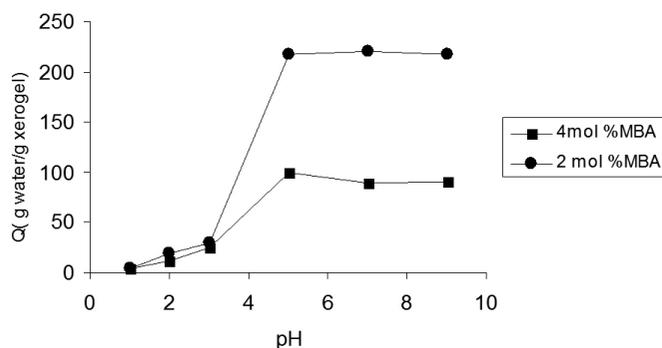
The absorbency of poly(DMAEA-co-NNDMAAm) 2:1 with 2 mol-% of MBA copolymer is higher than that other copolymers in twice-distilled water at room temperature. It is due to the higher amount of amine groups incorporated into the backbone. These strong amine groups adsorb significantly water molecules. In ethanol was not observed absorption.



**Figura 8.** Absorption (Q) of poly(DMAEA-co-NNDMAAm) corresponding to the ratio 2:1 / with 4 mol-% and 2 mol-% of MBA in twice-distilled water and ethanol at room temperature.

*Effect of pH on absorbency*

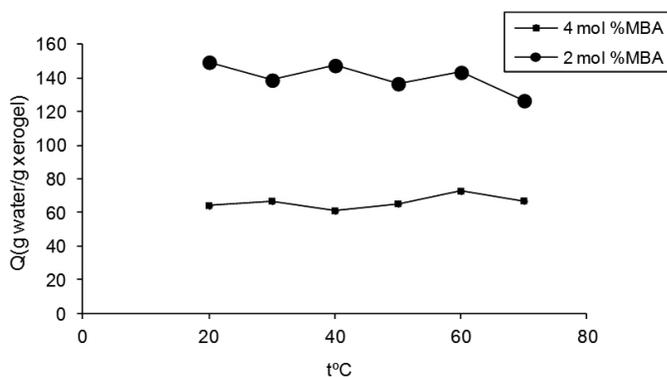
To investigate the influence of pH on the degree of gel swelling, the pH was adjusted with 1M HCl or 1M NaOH from pH 1 to pH 9. Figure 9 shows the effects of the solution pH values on the swelling behavior for all the studied copolymers. The water absorption curve shows an optimal value at pH 5 when the feed monomer ratio is 2:1 with 2 mol-% and 4 mol-% of MBA. At pH above 9, poly(DMAEA-co-NNDMAAm) maintains a high absorption capacity in the solution with a high basic concentration.



**Figure 9.** Absorption (Q) of poly (DMAEA-*co*-NNDMAAm) ratio 2:1 / 4 and 2 mol-% MBA in water at room temperature for pH 1, 3, 5, 7, and 9.

#### Effect of the temperature on absorbency

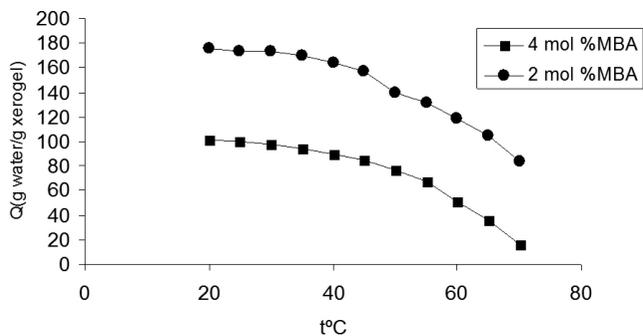
The effect of the temperature on the absorbency for poly(DMAEA-*co*-NNDMAAm) for 2:1 feed mol ratios is shown in Figure 10. This study was carried out with a contact time of 1 h for each temperature. It demonstrates that the absorbency does not change significantly as increases the temperature until 45°C and then increase sharply for ratio 2:1 with 2 mol-% of MBA; but ratio 2:1 with 4 mol-% MBA maintaining constant.



**Figure 10.** Absorption (Q) of poly(DMAEA-*co*-NNDMAAm) ratio 2:1 / 4 and 2 mol-% MBA at different temperatures.

#### Effect of the temperature on the maximum swelling degree

Figure 11 shows that the swelling degree decreases as the temperature increases for the three gels, and it is a characteristic behavior. At a higher temperature, the coil is contracted limiting the entrance of water in to the diffusion system.

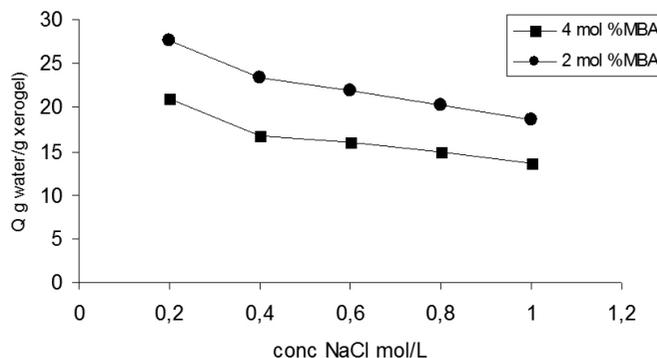


**Figure 11.** Water loss (Q) of poly(DMAEA-*co*-NNDMAAm) ratio 2:1 / 4 and 2 mol-% MBA at different temperatures for 24 hours.

#### Effect of NaCl solutions on absorbency

Figure 12 shows the effect of the solution's salt concentrations (NaCl) on the absorbency of the poly(DMAEA-*co*-NNDMAAm). The results indicate that

the absorbency of this polymer decreases with an increase in the concentration of the univalent salt solution at three different initial mol ratios. Additionally, the effects of ion hydration are remarkable at the lower ionic concentration (0.2 mol/L) and weak at the higher ionic concentration (0.4 mol/L).



**Figure 12.** Absorption (Q) of two polymers, poly(DMAEA-*co*-NNDMAAm) ratio 2:1 / 4 mol % and 2 mol-% MBA at room temperature from different concentrations of NaCl.

## CONCLUSIONS

A novel hydrogel of DMAEA and NNDMAAm was prepared in aqueous solution, and the swelling properties were studied. The experimental results show that poly(DMAEA-*co*-NNDMAAm) has a high absorbency not only in water but also in ethanol and salt solutions. The absorbency of these polymers decreased as the solvent's polarity decreased.

The effect of pH on the absorbency was studied. It was found that the absorbency of poly(DMAEA-*co*-NNDMAAm) 2:1 increased as the pH increased from 1 to 5. It was maintained practically constant from this pH to pH 9. It was found that the absorbency increased until 50°C for the copolymer more cross-linked, and then kept constant up to 70°C. This result implies that poly(DMAEA-*co*-NNDMAAm) can be used in a wide temperature range. The influence of the salt solutions on the absorbency was investigated, and the results indicate that absorbency is a decreasing function of the rising salt concentration.

## ACKNOWLEDGEMENTS

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