The effect of PEG(400)DA crosslinking agent on swelling behaviour of acrylamide-maleic acid hydrogels

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Summary

Acrylamide (AAm)-maleic acid (MA) hydrogels with different monomer ratios were prepared in an aqueous solution by radical polymerization using a new crosslinking agent, polyethyleneglycol (400) diacrylate (PEG (400) DA) and also using N, N'-methylenebisacrylamide (NMBA) for comparison purpose. The hydrogels were characterized by acid group content and FTIR spectroscopy. Their swelling and deswelling behavior were studied as a function of maleic acid content, pH and crosslinking agent. Incorporation of MA in hydrogels significantly increased their swelling ability and their equilibrium degree of swelling (EDS) values changed between 100-269 g water/g polymer in water while AAm polymers swollen less (22-23 g water/g polymer). The AAm hydrogels showed Fickian type diffusion but the all AAm-MA hydrogels showed non-Fickian type behavior. Their swelling degree increased with the increase of pH of the external medium and an instantaneous increase was observed near a pH value of 7.0. The use of PEG (400) DA instead of NMBA as a crosslinking agent also increased the swelling rate and capacity of the gel. The swelling constant (K) and the diffusion coefficient (D) of hydrogels were also increased. The swelling-deswelling cycles in acidic-basic solutions showed that they could be used as pH responsive gels without any decrease in swelling capacity.

Introduction

Hydrogels are three dimensionally crosslinked polymeric structures capable of swelling in water and retaining a large volume of water in their swollen state [1, 2]. Depending upon the type of the monomers incorporated into the gels, they may demonstrate a large volume transition and associated phase transition as a function of physical and chemical variables, such as temperature [3, 4], pH [5, 6] and ionic

strength [7] as well as electric and magnetic fields [8] and thus are known as "stimuli-responsive" polymers. Temperature and pH have been the most common used solution variables in the typical physiological, biological and chemical systems [9]. Hydrogels are used extensively in medicine and pharmacy as drug delivery systems, contact lenses, catheters, wound dressings and biosensors [10-12]. Especially pH sensitive hydrogels have a variety of novel applications including site-specific drug delivery [13] and immobilized enzyme systems [14].

The hydrogels of acrylamide and its copolymers with different monomers exhibit a very high capability to absorb water and possess good biocompatibility. The biocompatibility and nontoxicity of maleic acid have promoted its use in the synthesis of pH responsive hydrogels [15]. In preceding publications, the acrylamide-maleic acid (AAm-MA) hydrogels by radical polymerization were prepared by using small amount of MA and different crosslinking agent such as N, N'-methylenebisacryamide (NMBA), 1,4-butanedioldimethacrylate and tri-methylolpropanetriacrylate [15-18]. In this work, the series of AAm-MA hydrogels with higher MA ratios were prepared by using polyethyleneglycol (400) diacrylate (PEG (400) DA) having higher molecular weight and more flexible chain structure compared with those of given in the literature [15-18], for the first time. Their swelling-deswelling behaviors were investigated depending upon MA content, pH and also crosslinking agent. The results were compared with corresponding data obtained by using NMBA as a crosslinking agent.

Experimental

Chemicals and instruments

Acrylamide (AAm), N, N'-methylenebisacrylamide (NMBA), potassium persulfate ($K_2S_2O_8$) and N,N,N',N'-tetramethylethylene diamine (TEMED) were Merck "for synthesis". Maleic acid (MA) was supplied by Fluka Chemicals and polyethyleneglycol (400) diacrylate (PEG (400) DA) having molecular weight of 508 g/mol was kindly supplied by Sartomer Chemicals (SR-344). All of the other reagents used were "extra pure" chemicals. Bidistilled water was used for the polymerization reactions.

The FT-IR spectra of dried polymers were obtained by Digilab, Excalibur-FTS 3000 MX model instrument with the ATR technique.

Preparation of hydrogels

Hydrogels composed of AAm and MA were prepared by free radical solution polymerization in the presence of PEG (400) DA and also NMBA as a crosslinking agent, where the molar amount of crosslinking agent is same for all compositions. The amounts of materials used are given in Table 1. Prior to polymerization, dried nitrogen was bubbled into the monomer/solvent/crosslinker mixtures for 10 minutes to remove the oxygen dissolved in the reaction mixture. $K_2S_2O_8$ and TEMED were added into the mixture as an initiator and an activator, respectively, which was then transferred to cylindrical vials, sealed and left at 80 °C for 8 hrs. The resulting hydrogels were recovered, cut into pieces and then washed repeatedly with water up to 6 days to remove unreacted monomers and then dried in vacuum at the ambient temperature.

Table 1. Feed compositions of AAm-MA hydrogels.

Polymer	AAm (g)	MA (g)	NMBA (g)	PEG(400)DA (ml)	$K_2S_2O_8$ (mg)	TEMED (ml)	Water (ml)
PP-00	1.00	0.00	-	0.033	6	0.25	10
PP-10	0.90	0.10	-	0.033	6	0.25	10
PP-25	0.75	0.25	-	0.033	6	0.25	10
PP-50	0.50	0.50	-	0.033	6	0.25	10
PN-00	1.00	0.00	0.01	-	6	0.25	10
PN-10	0.90	0.10	0.01	-	6	0.25	10
PN-25	0.75	0.25	0.01	-	6	0.25	10
PN-50	0.50	0.50	0.01	-	6	0.25	10

PP ; the hydrogel prepared by using PEG (400) DA
PN ; the hydrogel prepared by using NMBA
The numbers represent the percentage amount of MA used

Determination of carboxylic acid group content (acid value, AV)

The polymers (50 mg) grinded were swollen in distilled water (25 ml, neutralized against phenolphthalein indicator) and titrated with NaOH (0.1N). The results are given in Table 2 as mmol/g dry polymer.

Determination of amounts of unreacted monomers

The total amounts of unreacted monomers were determined in the washing water by the bromate-bromide method [19]. The amount of MA incorporated in gel was calculated from carboxylic acid content.

Swelling studies

The polymers were swollen in distilled water for 72 hrs and the degree of swelling was determined gravimetrically. The amounts of water absorbed by polymers under equilibrium conditions, named as equilibrium degree of swelling (EDS), are given in Table 2.

For the pH dependent swelling studies, the preweighed dry gels were placed in various buffer solutions with different pH values of 2.7, 5.3, 6.5, 7.0, 8.0 and 9.5. KHphtalate/HCl, KHphtalate/NaOH, KH_2PO_4/NaOH and $NaHCO_3$/NaOH buffer solutions were used for the desired pH values. Ionic strength of all buffer solutions was adjusted to 0.03M. The swollen gels were taken out of solution at regular time intervals, wiped superficially with a filter paper, weighed and replaced in the same solution to ensure a state of equilibrium swelling. The swelling degree, F (the amount of water absorbed per g polymer) was calculated from the following expression of:

$$F \text{ (g water/g polymer)} = (W_s - W_p)/W_p, \tag{1}$$

where W_s and W_p are the weights of swollen and dry polymer, respectively.

Swelling-deswelling studies

The dry polymers were initially placed in an alkaline buffer solution at a pH value of 8.0 and allowed to attain the equilibrium swelling. Later, the swollen gels were

removed from this solution and placed in an acidic buffer solution at a pH value of 2.7 until they deswelled to reach a constant weight. The deswollen polymers were again kept in a solution at a pH value of 8.0 to attain the equilibrium swelling again. These cycles were repeated for several times.

Results and discussion

Preparation of hydrogels

AAm-MA hydrogels were prepared with different mol ratios of AAm/MA (see Table 1) by free radical polymerization in an aqueous solution using PEG (400) DA and also NMBA as a crosslinking agents. The amount of MA in hydrogels was determined by analyzing carboxylic acid group content of the polymers and free monomer from water extractions. The analysis of water extractions also showed that there was no monomer unreacted other than MA. The MA content of gel and the gelation percentage of MA (MA mol amount in gel/MA mol amount in feed), given in Table 2, show that the MA ratio in gels increased with the increasing of MA ratio in feeds while the gelation percentage of MA was decreased. As expected from the reactivity ratios of MA (r_{MA}=0.0) and AAm (r_{AAm}=2.2) [20], the carboxylic acid groups prevented the MA from reacting, to some extent, due to the steric hindrances and repulsive forces between ionic groups. As a result, the incorporation of the MA into the gel structure took place with a maximum value of only 47% (mole) of MA in feed under the current experimental conditions. On the other hand, in preceding publications, there is no knowledge about the percentage gelation of MA in AAm-MA hydrogels prepared at high MA/AAm ratios [15] and it is also supposed that the MA gelation is 100% in AAm-MA hydrogels prepared at low MA ratios [17]. The carboxylic acid group contents (acid value) of polymers increased with the increasing of MA content in feeds, as expected (see Table 2). But there is no clear difference in acid value of hydrogels by changing of molecular structure of crosslinking agent. The acid values of PP-25 and PN-25 hydrogels are almost the same. On the other hand,

Table 2. The properties of AAm-MA hydrogels.

Polymer	Mol % MA		Gelation of MA	AV[a]	EDS[b]
	In feed	In gel	(mol %)	(mmol/g)	(g water/g polymer)
PP-00	0	0	-	0.03	23 ± 0.2
PP-10	6.47	3.04	47.0	0.81	103 ± 1.0
PP-25	15.38	6.15	40.0	1.61	178 ± 1.8
PP-50	38.05	11.41	39.0	2.75	139 ± 1.4
PN-00	0	0	-	0.03	22 ± 0.2
PN-10	6.47	2.73	42.2	0.76	100 ± 1.0
PN-25	15.38	6.16	40.1	1.67	179 ± 1.8
PN-50	38.05	13.08	34.4	3.40	269 ± 2.7

[a] Acid Value
[b] Equilibrium Degree of Swelling (in distilled water).
PP ; the hydrogel prepared by using PEG (400) DA
PN ; the hydrogel prepared by using NMBA

PN-00 and PP-00 had an acid value of about 0.03 mmol/g, although they did not have maleic acid units in polymer matrix. This is probably due to the hydrolysis of acrylamide units under experimental conditions. The FT-IR spectrum analysis results of these polymers also support the existence of hydrolysis of acrylamide group during polymerization reaction of PN-00 and PP-00.

In Figure 1, the FT-IR spectra of crosslinked polyacrylamides exhibit the characteristic absorption peaks of polyacrylamide; 1650-1660 cm^{-1} (strong), 1608 cm^{-1} (weak) and 1350-1370 cm^{-1} (weak), indicating the C=O, N-H bending and C-N stretching, respectively, which are the characteristics of the –CONH$_2$ group [21, 22]. An additional peak was also observed at around 1720 cm^{-1} due to the carboxylic acid groups [23]. This additional peak shows that a parallel hydrolysis reaction of acrylamide occurred during the polymerization reaction. In the spectra of AAm-MA hydrogels obtained with PEG (400) DA, in addition to the characteristic peaks of polyacrylamide, the absorption peaks of maleic acid were also observed at 1716 cm^{-1}, 1453 cm^{-1} and 938 cm^{-1} for the C=O stretching, C-O stretching and O-H bending of the –COOH group, respectively.
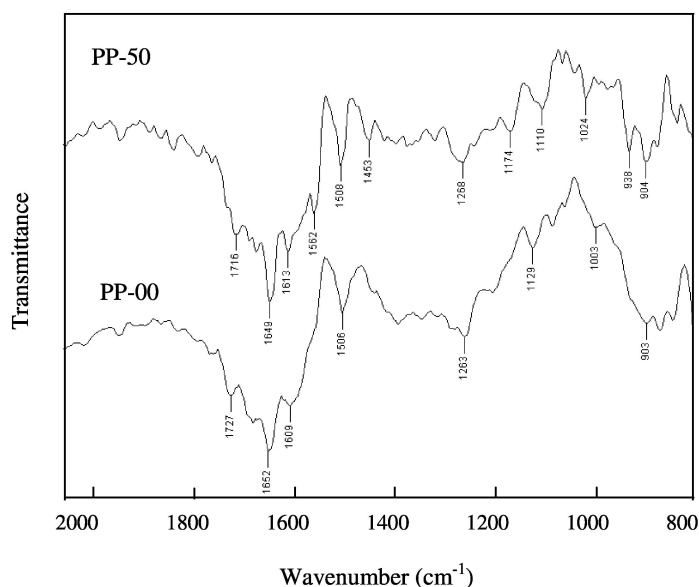

Figure 1. The FT-IR spectra of PP-00 and PP-50 hydrogels.

Swelling studies

For the purpose of observing the swelling behavior of polymers in water, polymers were left in distilled water at ambient temperature for a sufficiently long time (see below). It is known that swelling degree increases with time up to a certain point and then it becomes constant. This value of swelling degree is named the "equilibrium degree of swelling" (EDS). As expected, the EDS of polymers, given in Table 2, show that the AAm-MA hydrogels have increasingly higher swelling degrees compared to PN-00 and PP-00, with the increase of the hydrophilic (-COOH) group amount in polymers.

Swelling isotherms of hydrogels at pH value of 6.5 are depicted in Figure 2. The swelling rate of polymers changed with their carboxylic acid group content and also with the type of crosslinking agent used in polymerization. The polymers having higher carboxylic acid group content have higher swelling degree. It is interesting to see that PN-10, PP-10, PN-25 and PP-25 polymers swelled faster than those of the PN-50 and PP-50 polymers and they reached the equilibrium within shorter times.

PN-50 and PP-50 polymers have slower swelling rates, with a longer swelling time but they reach higher swelling degrees in equilibrium. It is also seen from Figure 2 that PP-50 polymer swelled faster than the PN-50 polymer.

The PN-00, PP-00, PN-25 and PP-25 polymers were kept in a buffer solution of a pH value of 7.0 at ambient temperature for determining the effect of crosslinking agent on the swelling behavior of polymers. PN-00 and PP-00 polymers have the same acid value of 0.03 mmol/g (see Table 2) but the PP-00 polymer had higher EDS and its swelling rate was faster than that of PN-00 polymer, as seen in Figure 3. The same behavior was also observed for MA containing polymers of PP-25 and PN-25. The acid values and crosslinking densities of these polymers were almost the same but the PP-25 polymer had higher EDS, as well as faster swelling ability than that of PN-25 polymer. This must be due to the structure of crosslinking agent (PEG (400) DA) that has a longer and more flexible chain structure than that of NMBA. Flexibility of the PEG (400) DA segment of the gel increases the swelling rate. Its longer chain length provides a larger space amongst acrylamide chains. As a result; water diffuses into the gel structure more easily and with higher amounts providing a higher EDS value.
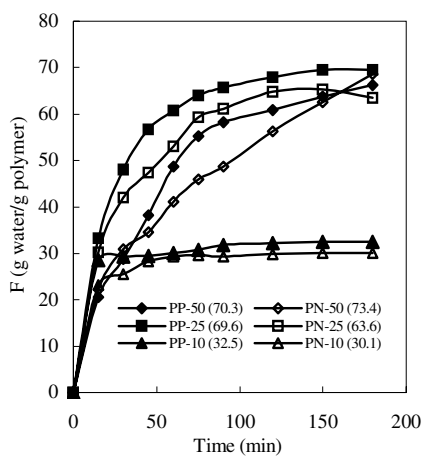

Figure 2. The swelling isotherms of AAm-MA hydrogels at pH=6.5 (The values in parentheses are the EDS values for the corresponding hydrogels).
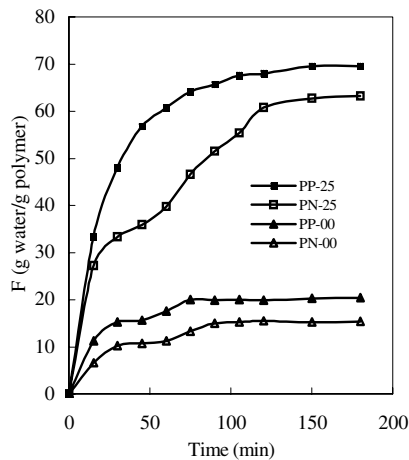
Figure 3. The swelling isotherms of AAm-MA and PAAm hydrogels at pH=7.0.

Diffusion

When a glassy hydrogel is immersed in water, water diffuses into the polymer matrix, and polymer network swells. The following equation (2) was used to determine the nature of the diffusion process:

$$F = (W_s - W_p) / W_p = Kt^n \qquad (2)$$

where t is the time, K and n are swelling constant and swelling exponent, respectively. For disk shaped samples, as it is known, n is 0.5 if the swelling is by Fickian diffusion mechanism, n is between 0.5 and 1.0 for non-Fickian or anomalous diffusion, n is 1.0 for case-II diffusion and n is greater than 1 for supercase-II diffusion. The above equation is applied to the initial stages of swelling and the plot of lnF vs lnt yields straight lines up to almost a 60% increase in mass of the hydrogel.

Figure 4 represents the plot of lnF versus lnt for AAm-MA hydrogels in the swelling media at pH 6.5 and 25 °C. The values of n and K, as calculated from the slopes and intercepts of the straight lines, have been shown in Table 3. It is shown that the values of the diffusional exponent range of AAm-MA hydrogels are generally between 0.57 and 0.88. The number to the determine type of diffusion (n) was found to be over 0.5. It can be said that the diffusion of water into AAm-MA hydrogel systems had non-Fickian character, while AAm hydrogels show Fickian type diffusion (see Table 3). It is interesting that the K values of polymers obtained by using PEG (400) DA are higher than those of the corresponding NMBA polymers. Also, the K value of PP-25 polymer is higher than that of PN-25 polymer, although they have almost the same acid value. This phenomenon confirms the effect of crosslinking agent on the swelling properties of hydrogels as described above.
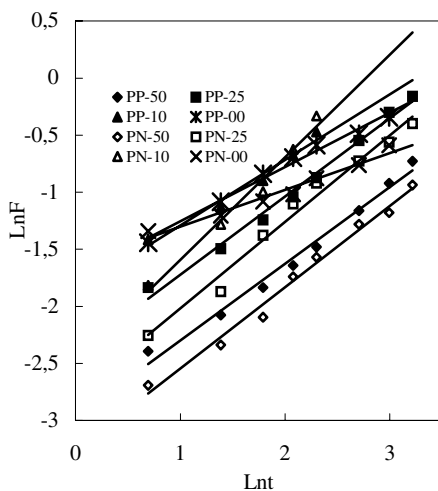

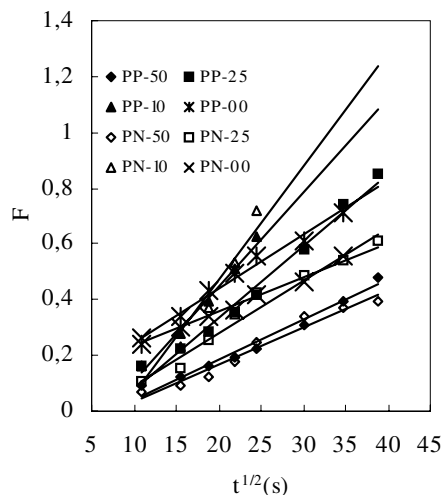Figure 4. Swelling kinetic curves of AAm-MA hydrogels at pH=6.5.

Figure 5. Diffusion curves (F vs $t^{1/2}$) of AAm-MA hydrogels in buffer solution at pH=6.5.

Figure 5 shows the F value versus $t^{1/2}$ diagrams obtained at 25 °C for the AAm-MA hydrogels. The diffusion coefficients were calculated from the slope of the lines by using the following equation (3):

$$F = 4(Dt/\pi r^2)^{1/2} \tag{3}$$

where D is diffusion coefficient ($cm^2.s^{-1}$), t and r are the time (s) and the radius (cm) of polymer sample, respectively. The values of diffusion coefficients calculated from the slope of the lines are listed in Table 3. It may be seen from Table 3 that the D values varied from 9×10^{-6} to 68×10^{-6} $cm^2.s^{-1}$. Diffusion coefficients of PEG (400) DA

polymers showed a linear decrease with the corresponding acid value (acid value of polymers are given in Table 2). It is interesting that PP-25 polymer has the higher diffusion coefficient than that of PN-25 polymer, although they have almost the same acid value. It is also seen in Figure 3 that, the PP-25 polymer swells faster than the PN-25 polymer. It is supposed that this increase in swelling rate of PP-25 polymer results from the use of PEG (400) DA in the formation of the polymer matrix. The values of the diffusion coefficients confirm this fact.

Table 3. Swelling exponents (n), swelling constants (K) and diffusion coefficients (D) of AAm-MA hydrogels.

Polymer	n	$Kx10^2$	$Dx10^6$ $(cm^2.s^{-1})$
PP-00	0.46	18.1	21
PP-10	0.57	15.5	68
PP-25	0.68	9.0	41
PP-50	0.69	4.9	18
PN-00	0.31	19.9	9
PN-10	0.88	8.4	55
PN-25	0.76	6.2	29
PN-50	0.66	4.3	17

PP ; the hydrogel prepared by using PEG (400) DA
PN ; the hydrogel prepared by using NMBA
The numbers represent the percentage amount of MA used

pH dependent swelling behaviour

The hydrogels containing hydrophilic groups especially carboxylic acid groups can show different swelling behaviour in different pH values. In order to observe this effect, hydrogels were kept in different pH buffer solutions with constant ionic strength and their swelling degrees were determined until the equilibrium was reached. As expected, the preliminary experiments showed that the swelling degree of polymers increased with decreasing the ionic strength of medium. The swelling experiments were carried out in solution with a low ionic strength (0.03 M).
Polymers were first kept in a buffer solution at a pH value of 2.7 and the swelling degrees were determined at various time intervals as described in Experimental part. The swelling isotherms of polymers at the pH value of 2.7 are given in Figure 6. It is seen that the PP-50 polymer had the lowest swelling degree while the PP-10 polymer had the highest one. It is known that the carboxylic acid groups cannot ionize well in acidic solutions, thus; the polymer having more carboxylic groups swells less. At low pH values, carboxylic acid groups exhibit hydrophobic character due to their low ionization [15] and the lack of repulsive interactions among the ionized carboxylic acid groups results in shrinking of the gels with respect to their conformation under the pH values which are lower than its pK_{a2} value (pK_{a2}=6,06) [24]. Within this content, Meaurio and coworkers [25] demonstrated, in acidic solutions, the occurrence of hydrogen bonding between carboxyl groups within the polyacrylic acid units in acrylic acid-N, N isopropylacrylamide gels and also involving carboxyl groups with amide groups by DSC technique. Hydrogen bond interaction between amide and

carboxyl groups was also detected by means of a solid-state NMR [26] and it was stated that these types of interactions tend to make the hydrogel structure more compact, effectively acting as a form of crosslinking hence their swelling ability was reduced. PP-50 polymer, which has the highest carboxylic acid groups behaved like a relatively hydrophobic polymer and had the lowest swelling degree in this acidic solution.
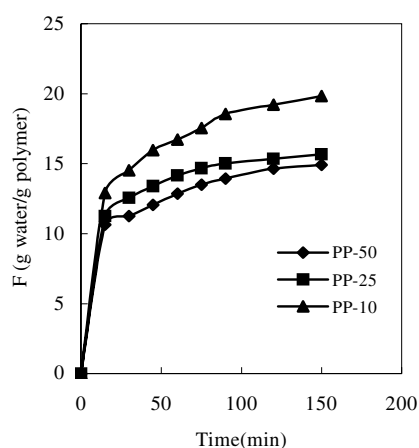

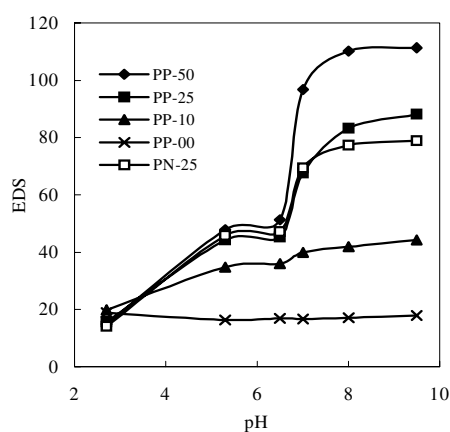Figure 6. The swelling isotherms of AAm-MA hydrogels crosslinked by PEG (400) DA (pH=2.7).

Figure 7. EDS values of AAm-MA hydrogels as a function of pH.

The effect of increasing the pH of the external medium on swelling is shown in Figure 7. PP-00 polymer did not show any change in its EDS values with the increasing of pH and hence it has a pH-independent swelling behaviour. But the EDS values of copolymers containing MA increase with the pH of the external solution and this pH-dependent swelling behaviour originates from the ionizable (hydrophilic) units in the polymer matrix. The carboxylic acid groups were weakly ionized at a pH value of 5.3 and the increase in swelling degree was dependent on the increase of MA content of the polymers. As a result, PP-50 polymer has the highest water uptake at this pH value, while the increase of carboxylic acid group content exhibits negative effect on swelling degree in low pH value, which is 2.7 for the current experimental study. This effect must be due to, a major part, the enhancement of intramolecular hydrogen bonding with the increasing of carboxylic acid content as mentioned above. The increase in the swelling degree of copolymers is rather accelerated near the pH value of 7.0, which may be due to the complete ionization of all acidic groups of maleic acid around this pH value [27]; where $pH > pK_{a2}$. This ionization causes an increase not only in the osmotic swelling pressure but also in the extent of chain relaxation process resulting from the increasing of ionic repulsion. The effect of crosslinking agent on the EDS values of polymers at different pH values is shown in Figure 7. There is no difference between EDS values of PP-25 and PN-25 polymers at low pH at which ionization is low and hydrogen bonding interaction is high. But at high pH, it is observed that the EDS value of PP-25 is higher than that of PN-25.

Swelling-deswelling cycles of hydrogels

The polymers were initially kept in an alkaline buffer solution of a pH value of 8.0 and allowed to swell to their equilibrium value. Later, the swollen polymers were taken out and were placed in an acidic solution of a pH value of 2.7 until equilibrium was reached (12 hours). The EDS of polymers was determined as described earlier for each cycle. The swelling-deswelling cycles of polymers obtained by using PEG (400) DA are given in Figure 8. In these cycles, the polymers showed a swelling-deswelling behaviour periodically without any decrease in the absorption capacity.
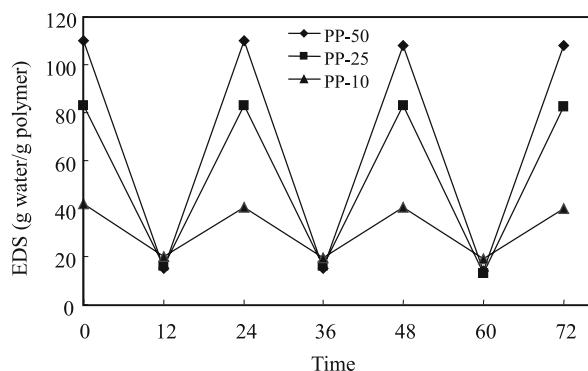

Figure 8. The swelling-deswelling behavior of AAm-MA hydrogels crosslinked by PEG (400) DA as a function of pH values alternating between 2.7 and 8.0 (lower and upper EDS values in Figure correspond to pH values of 2.7 and 8.0, respectively).

Conclusion

The copolymerization of AAm with MA in the presence of crosslinking agent having long chain structure yielded a pH responsive gel carrying carboxylic acid functionality. The equilibrium degree of swelling for copolymers increased with the increasing of MA content but swelling rate decreased. Replacement of classical crosslinking agent (NMBA) with one having more elastic and long chain structure (PEG (400) DA) resulted in an increase in swelling rate and swelling capacity of the hdyrogels. Swelling constant (K) and diffusion coefficient (D) of the AAm-MA hydrogels decreased with an increase in their acid group content, and swelling behaviour also changed from Fickian to non-Fickian type diffusion which indicates the relations of the structure-chain relaxation behaviour of the gels. In acidic-basic solutions, the hydrogels had swelling-deswelling properties, which remained constant for several cycles, without any decrease in their swelling capacity.

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