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Synthesis and Characterization of Hydrogels Based on Gamma Radiation Copolymerization of N-isopropylacrylamide and Ethylene Glycol Dimethacrylate Monomers

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Hydrogels based essentially on N-isopropylacrylamide (NIPAAm) and different ratios of ethylene glycol dimethacrylate (EGDMA) monomer were synthesized by gamma radiation copolymerization. The thermal decomposition behavior of NIPAAm/EGDMA hydrogels was determined by thermogravimetric analysis (TGA). The effect of temperature and pH on the swelling behavior was also studied. The results showed that the ratio of EGDMA in the comonomer feeding solution has a great effect on the yield product, gel fraction and water content in the final hydrogel. In this regard, it was observed that the increase of EGDMA ratio decreased these properties. The TGA study showed that all the compositions of NIPAAm/EGDMA hydrogels displayed higher thermal stability than the hydrogel based on pure PNIPAAm hydrogel. The swelling kinetics in water showed that pure PNIPAAm and NIPAAm/EGDMA hydrogels reached equilibrium after 6 h. However, NIPAAm/EGDMA hydrogels show swelling in water lower than pure PNIPAAm. The results showed that the swelling character of pure PNIPAAm and NIPAAm/EGDMA hydrogels was affected by the change in temperature within the temperature range 25–40°C, and showed a reversible change in swelling in the pH range 4–7 depending on composition.

Keywords: gamma irradiation; crosslinking; thermal stability; responsive hydrogels

1 Introduction

The synthesis of responsive hydrogels by ionizing radiation has special technical advantages, not only the interaction between chains through covalent bonds, but also the polymerization and crosslinking occurs through free radicals in the absence of initiators or crosslinking agents. In this respect, oral delivery of insulin using pH-sensitive hydrogels based on poly(vinyl alcohol) grafted acrylic acid/methacrylic acid prepared by gamma irradiation was investigated (1). For selective permeation of metal ions, pH-sensitive gel membranes based on poly(ocryloyl-L-proline methyl ester)-graft-poly (acrylic acid) synthesized by gamma irradiation was applied (2). The electro-activity of responsive hydrogels based on acrylic acid and vinyl sulfonic acid prepared by gamma irradiation was studied (3). Recently, the same authors studied the swelling behavior in response to the environmental conditions such as pH and ionic strength of hydrogels based on gamma radiation induced copolymerization of 2-acrylamide-2-methyl propane sulfonic acid and acrylic acid (4). Meanwhile, the swelling behavior of acrylic acid hydrogels prepared by gamma irradiation in aqueous solutions was investigated (5). In previous studies, hydrogels based on poly (vinyl alcohol)/acrylamide (6), hydroxyethyl methacrylate/acrylamide (HEMA/AM) (7) and poly (vinyl alcohol)/sodium alginate (8) have been synthesized by gamma and electron beam irradiation.

Among the thermosensitive hydrogels, poly (N-isopropylacrylamide) (PNIPAAm) is well known to be the best example due to its lower critical solution temperature (LCST) behavior around 32°C. In this case, expansion of the polymer hydrogel due to hydration in water occurs when the temperature is below its LCST and becomes compact due to dehydration when heated up above LCST (9, 10). However, the synthesis of PNIPAAm hydrogels, so far, in the literature was concerned with chemical initiation. In this regard, it has been reported that PNIPAAm displayed thermosensitive character and pH-sensitivity behavior when composed with sodium alginate (11, 12). In addition, the kinetics of swelling and shrinkage of poly (N-isopropylacrylamide) hydrogels at different temperatures (13) and drug targeting responsive polymers based on poly(N-isopropylacrylamide) (14) have

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been studied. Few authors were interested in the preparation of responsive hydrogels based on N-isopropylacrylamide by ionizing radiation. In this regard, temperature responsive hydrogels based on the photo grafting method of acrylic acid and N-isopropylacrylamide binary monomers onto periodic acid oxidized cellulose were prepared (15).

Even though, PNIPAAm hydrogels have recently been of increasing interest in the field of responsive materials, they have poor stability especially after swelling, which limits their applications. This advantage was improved by dispersing nano-sized PNIPAAm gel in ethylcellulose to obtain thermosensitive controlled-release systems (16). Also, a non-woven composite was prepared by grafting a thermosensitive hydrogel on another substrate having good mechanical properties (17). Therefore, the present work was undertaken to prepare stable thermosensitive hydrogels in aqueous solutions based essentially on NIPAAm and different ratios of ethylene glycol dimethacrylate (EGDMA) by gamma radiation copolymerization. The effect of temperature and pH on the swelling character NIPAAm/EGDMA hydrogels was studied. Also, the structure and thermal stability of the prepared hydrogels was studied by IR spectroscopy and thermogravimetric analysis.

2 Experimental

2.1 *Materials*

N-isopropylacrylamide monomer (NIPAAm) used in this study was of laboratory grade chemicals purchased from Aldrich Chemical Co. (Milwaukee, WI), and used as received. Ethylene glycol dimethacrylate monomer was a laboratory grade chemical and was purchased from Merck, Germany.

2.2 *Preparation of NIPAAm/EGDMA Hydrogels*

The hydrogels were prepared by dissolving separate different ratios of NIPAAm and EGDMA monomers in distilled water and methanol, respectively. The monomer solutions were then mixed with continuous stirring until complete miscibility was achieved. The ratio of NIPAAm and EGDMA in the mixture can be 92/8, 90/10, 85/15 and 80/20. The mixtures were then poured into test tubes and subjected to gamma irradiation. Prior to irradiation, the solutions were made free from oxygen by purging nitrogen gas for 5 min. Irradiation to the required doses was carried out in a ^{60}Co gamma cell (made in Russia) facility of the National Center for Radiation Research and Technology, Cairo, Egypt at a dose rate of 3.63 kGy/ h^{-1}.

2.3 *Determination of Gel Fraction*

Samples of the prepared hydrogels were accurately weighed (W_o) and then extracted with distilled water using a Soxhlet system and then dried in a vacuum oven at 80°C to a constant weight (W_1). The gel fraction is calculated according to the following equation:

$$\text{Gel fraction (\%)} = 100 - \{[(W_o - W_1)/W_o] \times 100\}$$

2.4 *Thermogravimetric Analysis (TGA)*

The TGA thermograms were performed on a Shimadzu–50 instrument (Kyoto, Japan) at a heating rate of 10°C/min under flowing nitrogen (20 ml/min) from room temperature to 500°C. The primary TGA thermograms were used to determine the kinetic parameters of the thermal decomposition reaction.

2.5 *Swelling Studies of NIPAAm/EGDMA Hydrogels*

Swelling studies were conducted on NIPAAm/EGDMA hydrogels as a function of time, temperature, and pH of the swelling medium. A known dry weight of insoluble hydrogel (W_d) was immersed in water for different intervals of time durations up to 24 h at 25°C. After each time, the sample was removed and blotted on filter paper to remove excess water and weighed (W_s), in which the degree of swelling is calculated according to the following equation:

$$\text{Degree of swelling (\%)} = [(W_s - W_d)/W_d] \times 100$$

The swelling character of NIPAAm/EGDMA hydrogels in different external environments was also studied. A weight (W_e) of equilibrated pure PNIPAAm and NIPAAm/EGDMA hydrogels is immersed in water at different temperatures (10–50°C) and then weighed (W_c). The degree of swelling is calculated in terms of the change between W_c and W_e with respect to W_e. The same procedure was followed to investigate the swelling character of NIPAAm/EGDMA hydrogels at different pH values.

3 Results and Discussion

3.1 *Radiation Synthesis of NIPAAm/EGDMA Hydrogels*

In the present work, EGDMA monomer was used to form polymer chains inside the network structure of PNIPAAm monomer under the effect of gamma irradiation. This is because NIPAAm and EGDMA may provide a combination of properties based on the known thermosensitive character of PNIPAAm. Preliminary experiments showed that approximately complete gelation of NIPAAm and NIPAAm/EGDMA comonomer mixtures were obtained at a dose of 20 kGy of gamma irradiation. However, the gelation of NIPAAm/EGDMA was greatly affected by the ratio of H_2O/MeOH in the initial feeding solutions, in which a solvent of equal ratios is the suitable mixture for complete gel formation. Meanwhile, the yield product, content of combined water and gel fraction was markedly affected

Table 1. Effect of total solvent volume on the gel fraction, yield product and combined water content of hydrogels prepared by gamma irradiation at a dose of 20 kGy

Total solvent volume (ml)	Gel fraction (%)	Yield product (g)	Combined water (%)
5	89	0.6328	13.3
6	79	0.3242	11.5
10	53	0.2336	6.7

Composition of comonomer feeding solutions is NIPAAm/EGDMA (86/14%).

by the total volume of solvents even equal ratios of H_2O and MeOH were used as shown in Table 1.

Figure 1 shows the effect of the mole fraction of the EGDMA monomer in the initial feeding solutions on the gel fraction, yield product and content of combined water of NIPAAm/EGDMA copolymer hydrogels formed at a constant dose of 20 kGy of gamma irradiation. It can be seen that the increase of EGDMA mole fraction in the feeding solutions causes a slight decrease in the total gel fraction and yield product. However, the increase of EGDMA mole fraction up to 14% cause a great drop in the content of combined water from 32.5% for pure PNIPAAm to 13.3% for the hydrogel prepared from feeding solution containing 14% of EGDMA as shown in the inset figure. The decrease in gel fraction observed by increasing the ratio of the difunctional EGDMA monomer may be explained as due to the relatively higher G-value of NIPAAm than the EGDMA monomer. Also, it may be explained based on the reactivity ratio of NIPAAm and EGDMA monomers during copolymerization. The reactivity ratios of NIPAAm and EGDMA monomers are reported to be 0.47 ± 0.13 and 0.32, respectively (15).

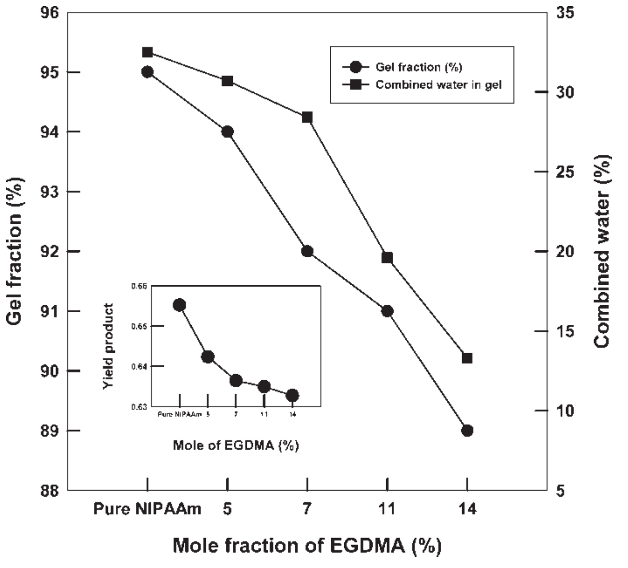

Fig. 1. Effect of EGDMA mole fraction on gel fraction, combined water and yield product content of NIPAAm/EGDMA hydrogels formed by gamma irradiation at a dose of 20 kGy.

The mechanism of formation of the network structure of NIPAAm/EGDMA copolymer hydrogels may be proposed to occur through two steps: (1) Both NIPAAm and EGDMA monomers contain unsaturation C═C double bonds, which absorb gamma radiation resulting in the formation of free radicals. In addition, the radiolysis products of water as reported in the early stage of radiation chemistry (shown below) would increase the concentration of free radicals on both monomers (18) (2). The crosslinking proceeds, in which two polymer radicals of PNIPAAm and PEGDMA with "n" and "m" repeat units, respectively combine to form a crosslinked points after which a network structure is formed as shown in Figure 2.

$$H_2O \quad \text{Gamma irradiation} \rightarrow e^-_{aq}, OH^\bullet, H^\bullet, H_2O_2, H_2$$

3.2 Thermal Decomposition Behavior

The average complete dissociation energies for PNIPAAm and PEGDMA, based on the reported theoretical dissociation energies of the different covalent bonds forming the polymer molecules are calculated to be 403.4 and 443.9 kJ/mole, respectively (19). Thus, it may be expected that the formation of copolymer hydrogels with increased EGDMA ratio will eventually result in hydrogels with higher thermal stability than a pure NIPAAm polymer hydrogel. It was intended to produce hydrogels based essentially on NIPAAm and relatively low rations of EGDMA for two reasons; firstly, to make use of the thermosensitive character of PNIPAAm and secondly, to strengthen the mechanical and thermal properties of the final hydrogel by PEGDMA. This is because PNIPAAm has poor mechanical strength, particularly after swelling, which limits its application (17). Therefore, thermogravimetric analysis (TGA) was used to investigate the thermal stability.

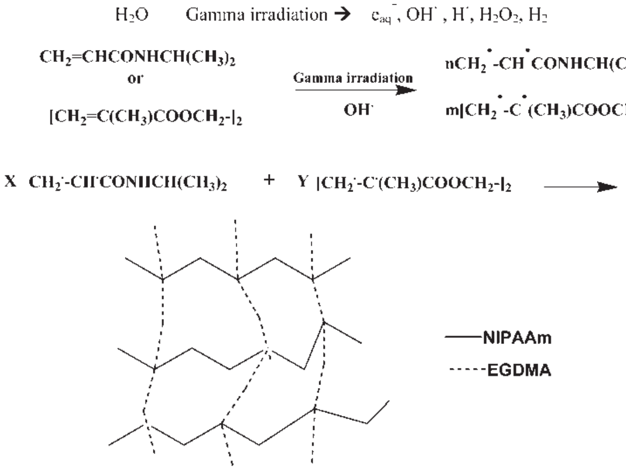

Fig. 2. Radiation synthesis of NIPAAm/EGDMA network hydrogels.

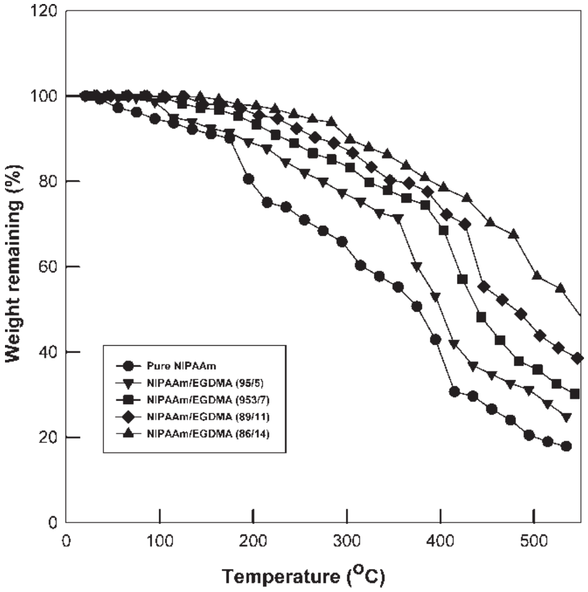

Fig. 3. Initial TGA thermograms for pure PNIPAAm and NIPAAm/EGDMA hydrogels at different ratios formed by gamma irradiation at a dose of 20 kGy.

Figure 3 shows the initial TGA thermograms of hydrogels prepared at a constant dose of 20 kGy of gamma irradiation of solutions based on pure NIPAAm and different ratios of NIPAAm and EGDMA monomers. In addition, the percentage weight loss at different heating temperatures for all the hydrogels is summarized in Table 2. Overall, the heating temperatures were from 200°C up to 500°C, the hydrogel of pure NIPAAm displayed the lowest thermal stability (with high weight loss) compared to NIPAAm/EGDMA copolymer hydrogels. In addition, the thermal stability of NIPAAm/EGDMA hydrogels increases with increasing the ratio of EGDMA in the initial feeding solutions. Within the heating temperature range of 300–400°C, in which the major decomposition occurs, the weight loss of NIPAAm/EGDMA hydrogels is constantly higher than the NIPAAm/EGDMA copolymer hydrogels by two times. In this respect, by increasing the ratio of EGDMA from 11 to 14%, the weight loss, at the heating temperature 350°C, was decreased from 13% to 10%, respectively compared to 45% for the hydrogel based on pure NIPAAm.

Table 2. Weight loss at different heating temperatures and temperatures of a maximum rate of reaction for different hydrogels prepared by gamma irradiation at a dose of 20 kGy based on NIPAAm and EGDMA monomers

Hydrogel feeding composition (%)	Weight loss (%) 200°C	250°C	300°C	350°C	400°C	Tmax (°C)
Pure NIPAAm	19.45	29.07	34.16	44.79	63.19	355
NIPAAm/EGDMA (95/5)	10.70	17.96	22.64	28.56	46.82	375
NIPAAm/EGDMA (93/7)	6.66	11.00	16.77	22.09	31.51	384
NIPAAm/EGDMA (89/11)	4.51	7.60	13.32	19.75	27.77	387
NIPAAm/EGDMA (86/14)	2.33	4.30	10.22	13.74	21.51	403

The derivative of the TGA curves (rate of reaction) for either pure PNIPAAm and NIPAAm/EGDMA hydrogels showed single stage decomposition indicating the non-occurrence of phase separation and the copolymerization of EGDMA with NIPAAm as shown in Figure 4. The temperatures at which the maximum values of the rate of reaction (T_{max}) occur are shown in Table 2.

Based on the thermal decomposition study, it can be conclude that the thermal stability of NIPAAm/EGDMA hydrogels is much higher than that of pure PNIPAAm hydrogel. Thus, the copolymerization of NIPAAm with EGDMA increases the thermal stability of the final hydrogel. However, the thermal stability increases with increasing the ratio of EGDMA in the initial feeding solutions suggesting that the composition of the final hydrogels is relevant to the composition of the initial feeding solutions. These findings are in accordance with previous work on semi-interpenetration and comb-type graft hydrogels composed of alginate and poly (N-isopropylacrylamide) (12). It was reported that the thermal stability of semi-interpenetration and comb-type graft hydrogels decreases in comparison with alginate and the hydrogel based on pure PNIPAAm displayed the lowest thermal stability.

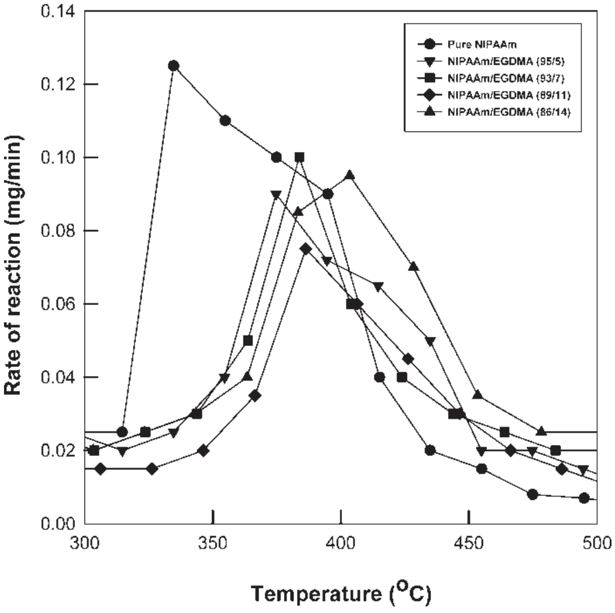

Fig. 4. Rate of reaction curves for pure PNIPAAm and NIPAAm/EGDMA hydrogels at different ratios formed by gamma irradiation at a dose of 20 kGy.

3.3 Effect of Temperature on the Swelling Behavior of NIPAAm/EGDMA Hydrogels

The swelling behavior of NIPAAm/EGDMA hydrogels was investigated as a function of temperature as shown in Figure 5. It can be seen that al the hydrogels had a significant change in the degree of swelling over the temperature range between 25 and 40°C. When the ratio of EGDMA in the feeding solution was increased, the degree of swelling of hydrogels within this range of temperature decreases. PNIPAAm in water exhibited a reversible phase transition in response to small temperature changes around 32°C (20). The sensitivity of PNIPAAm is due to the dissociation of ordered water molecules surrounding the hydrophobic N-isopropyl groups (12). As a result, NIPAAm/EGDMA hydrogels underwent a volume phase transition in water around the LCST of PNIPAAm.

3.4 Swelling-Deswelling Kinetics of NIPAAm/EGDMA Hydrogels

Figure 6 shows the swelling kinetics in water (pH = 7) at 25°C for pure PNIPAAm and NIPAAm/EGDMA hydrogels at different compositions formed at a dose of 20 kGy of gamma irradiation. It can be seen that the degree of swelling of all the hydrogels increases substantially within the initial time of swelling up to 6 h, at which time the equilibrium state is reached. The degree of swelling at equilibrium for all the hydrogels is in the range of 500–850%. As the ratio of EGDMA in the feeding solution is increased, the degrees of crosslinking of hydrogels decrease as shown in Figure 1. Therefore, NIPAAm/EGDMA hydrogels based on higher ratios of EGDMA has the highest degree of swelling. NIPAAm/EGDMA hydrogels form complexes composed of acrylate groups in EGDMA and amino groups in PNIPAAm. Thus, these complexes will eventually capture the hydrophilic groups producing a tight and ionic bonded structure.

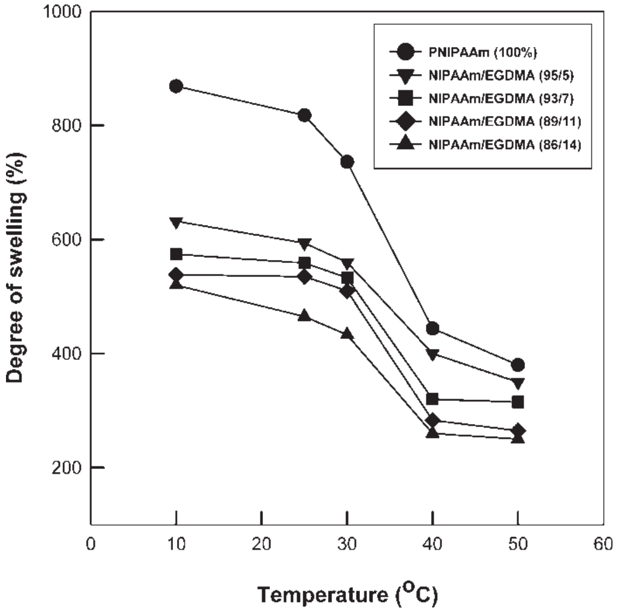

Fig. 5. Effect of temperature on the degree of swelling in water (at pH = 7) for hydrogels based on pure PNIPAAm and NIPAAm/EGDMA at different ratios formed by gamma irradiation at a dose of 20 kGy.

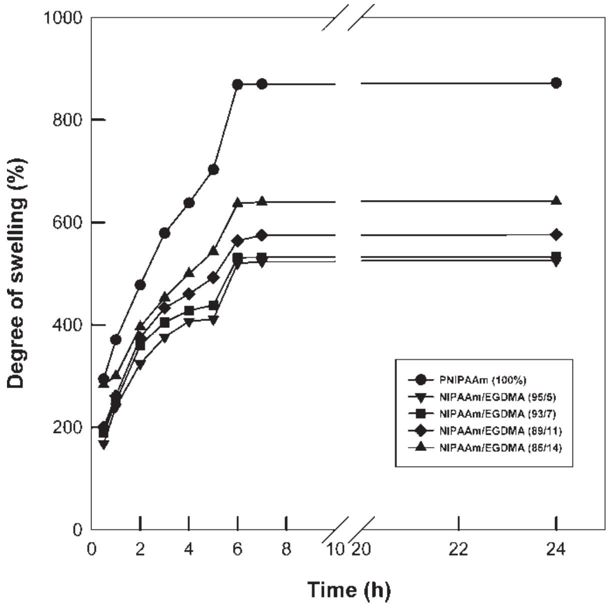

Fig. 6. Swelling kinetics in water at 25°C (pH = 7) for hydrogels based on pure PNIPAAm and PNIPAAm/EGDMA formed by gamma irradiation at a dose of 20 kGy.

Equilibrium water content (EWC) is an important quantitative factor to represent the water absorbed rather than the degree of swelling and it is defined as the ration between the mass of absorbed water at equilibrium and the mass of swollen gel at equilibrium. The values of EWC for pure PNIPAAm and NIPAAm/EGDMA hydrogels prepared from initial feeding solutions containing 5, 7, 11, 14% of EGDM equilibrated at 25°C is calculated to be 0.8969, 0.8387, 0.8413, 0.8507 and 0.8649, respectively. The EWC values of pure PNIPAAm and NIPAAm/EGDMA hydrogels (0.8969–0.8649) are greater than the percentage content of living tissues. The NIPAAm/EGDMA hydrogels exhibited fluid contents greater than that for living tissues by 60% (21).

Figure 7 shows the deswelling kinetics of pure PNIPAAm and NIPAAm/EGDMA hydrogels previously equilibrated at 25°C by elevating the temperature to 40°C. It is clear that all the hydrogels show a rapid dramatic deswelling with response to temperature changes. In addition, the rate of deswelling is dependent on the hydrogel initial feeding solution composition, in which the rate of deswelling decreases with increasing the ratio of EGDMA. This behavior is due to the differences in gel structure, in which as the ratio of EGDMA increases in the feeding solutions, the gel fraction decreases. Thus, it can be conclude that 40°C is the lower critical solution temperature (LCST) for those hydrogels, in

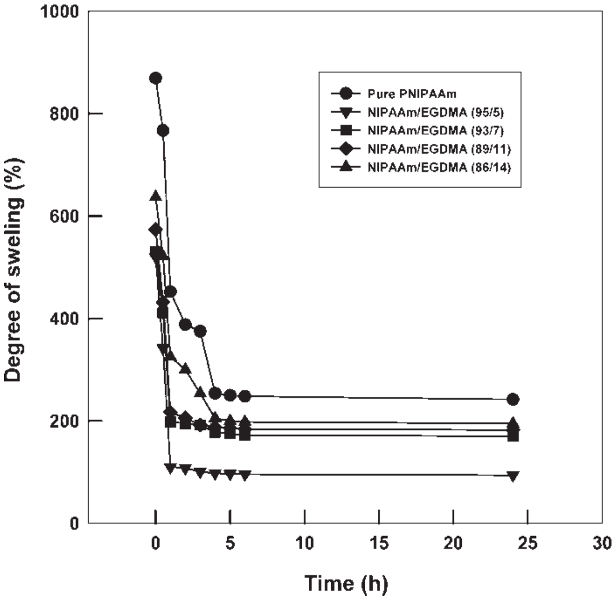

Fig. 7. Deswelling kinetics in water at 40°C from the equilibrium swelling at 25°C for hydrogels based on pure PNIPAAm and NIPAAm/EGDMA at different ratios formed by gamma irradiation at a dose of 20 kGy.

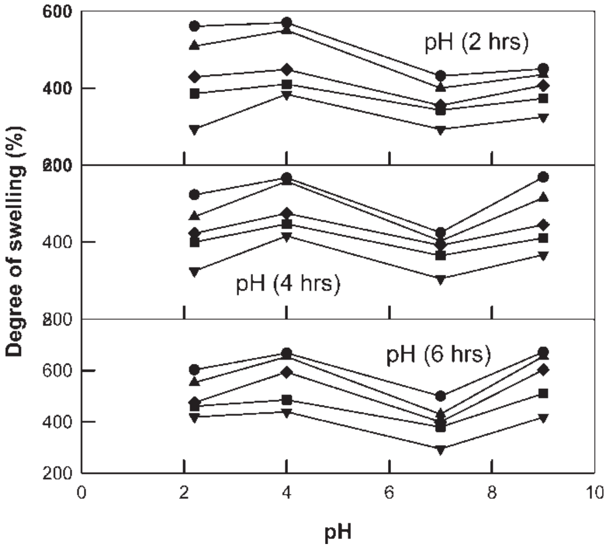

Fig. 8. Effect of pH on the swelling character in water at 25°C for different hydrogels formed by gamma irradiation at a dose of 20 kGy. (●) pure PNIPAAm, (▼) NIPAAm/EGDMA (95/5), (■) NIPAAm/EGDMA (93/7), (◆) NIPAAm/EGDMA (89/11), (▲) NIPAAm/EGDMA (86/14).

which they shrink by heating above the LCST. In aqueous solution, the chains hydrate to form expanded structures when the temperature is below the LCST but become compact by dehydration when heated up above LCST. Therefore, it would be expect that the temperature sensitivity of NIPAAm/EGDMA is due to the formation of hydrophobic inter-chain bonding and/or interpenetrating polymer network between NIPAAm and EGDMA and these bonding will decrease with increasing EGDMA ratios.

3.5 Effect of pH on the Swelling Characters of NIPAAm/EGDMA Hydrogels

Figure 8 shows the relationship between the degree of swelling in water and pH values for NIPAAm/EGDMA hydrogels prepared from feeding solutions at different ratios formed at a dose of 20 kGy of gamma irradiation. It should be noted that the hydrogel samples were immersed in different buffer solutions at 25°C for the equilibrium state time. The pH sensitive swelling behavior can be observed, in which the swelling is shown to increase by increasing the pH value from 2 to 4, and then suddenly decreases at pH 7. Furthermore, a slight increase in the degree of swelling can be observed by increasing the pH values from 7 to 9. All the hydrogels of either pure PNIPAAm or NIPAAm/EGDMA exhibit this oscillatory swelling behavior against the change in the pH range from low to high values. The degree of swelling of the NIPAAm/EGDMA hydrogels prepared from initial feeding solutions containing EGDMA ratios of 5, 7, 11 and 14% was decreased by 2.4, 1.7 and 1.3 times (based on the values at pH 4) by increasing the pH value from 4 to 7 after a swelling time of 2 h, respectively. Meanwhile, after a swelling time of 6 h, the decrease in the degree of swelling of the same hydrogels was found to be 2, 1.4 and 1.2 times, respectively. Thus, it can be seen that the pH-sensitivity decreases with increasing the EGDMA ratios in the initial feeding solutions of the hydrogels, whereas this sensitivity increases with increasing time of swelling.

4 Conclusions

This work was undertaken to explore the formation of hydrogels based comonomer mixtures composed mainly on N-isopropylacrylamide (NIPAAm) and different ratios up to 14% of ethylene glycol dimethacrylate (EGDMA) under the effect of gamma irradiation. Also, investigate the effect of EGDMA on the established temperature-responsive character of NIPAAm. Even though, the increase of the ratio of EGDMA in the initial feeding solution was accompanied by a decrease in the gel fraction of the final hydrogels, it improves the thermal durability of the hydrogel products. The results showed that the presence of EGDMA does not affect the equilibrium swelling in water or the deswelling from equilibrium. However, the results showed clearly that the equilibrium swelling of the hydrogel NIPAAm is much higher than the hydrogels based on different composition of NIPAAm and EGDMA. Meanwhile, the hydrogels based on NIPAAm/EGDMA showed the temperature-responsive similar to the behavior of hydrogels based on individual NIPAAm.

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