Synthesis and Characterization of Hydroxyethyl Methacrylate/Acrylamide Responsive Hydrogels

Horia M. Nizam El-Din,[1] Abdel Wahab M. El-Naggar[2]

[1]*Department of Polymer Chemistry, National Center for Radiation Research and Technology, P.O. Box 29, Nasr City, Cairo, Egypt*
[2]*Department of Radiation Chemistry, National Center for Radiation Research and Technology, P.O. Box 29, Nasr City, Cairo, Egypt*

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ABSTRACT: Hydrogels based on an aqueous solution of hydroxyethyl methacrylate (HEMA) and acrylamide (AM) in the presence of trithioglycolic acid (TTGA) were prepared under the effect of gamma irradiation. These hydrogels were characterized by IR spectroscopy and thermogravimetric analysis and investigated for temperature- and pH-responsive materials. It was found that TTGA is essential for the formation of HEMA/AM hydrogels at different compositions, in which the gel fraction depends on composition. A binary mixture of HEMA and AM at equal ratios was the critical composition that forms hydrogels, even in the presence of TTGA. The IR spectroscopic analysis showed that the formation of hydrogels depends on hydrogen bonding and crosslinking. The TGA investigations with respect to mass loss and the temperatures of the maximum value of the rate of reaction showed that HEMA/AM hydrogels possess higher thermal stability than that of pure HEMA and this stability increases with increasing ratio of the AM component. Also, it was observed that the temperature of the maximum value of the rate of thermal decomposition reaction depends on hydrogel composition. However, calculations of the activation energy showed that the hydrogel composed of 90% HEMA and 10% AM exhibits the highest thermal stability during the increasing or decreasing rate of reaction. Kinetic studies of swelling in water showed that HEMA/AM hydrogels displayed a temperature-responsive character within the temperature range 25–30°C, and showed a stepwise swelling behavior in the pH range 2–10, depending on composition. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 95: 1105–1115, 2005

Key words: hydrogels; activation energy; crosslinking; swelling; thermal properties

INTRODUCTION

Superabsorbent hydrogels have gained considerable attention in recent research work because of their wide industrial applications in the medical and pharmaceutical fields such as diapers or pads for surgical operations.[1–3] Considerable attention, however, has been focused on responsive hydrogels because of their applications for stimuli-sensitive drug delivery, in which they display changes in swelling character according to the external environments.[4] External effects include chemical signals, such as pH, and ionic medium or physical stimuli, such as temperature or electrical potential.[5] Poly(*N*-ispropylacrylamide) (PNIPAAm) is well known to exhibit a lower critical solution temperature (LCST) around 32°C in aqueous solution. However, poly(NIPAAm) hydrogels with crosslinked structure displayed a temperature-responsive character, in which they swell in water below and shrink above the LCST.[6–9] A substantial contribution has been reported by Shin et al.[10–12] on pH- and temperature-sensitive interpenetrating polymer network of (IPN) hydrogels, responsive properties, and drug-release behaviors under electric stimulus. Also, with respect to thermo- and pH-sensitive polymers, based on semi-IPN and comb-type graft hydrogels composed of alginate and poly(NIPAAm),[13,14] the graft polymerization or blending of chitosan and NIPAAm were prepared and characterized.[15]

The formation of hydrogels under the effect of gamma radiation is one of our interests because of the strong interaction between chains through covalent bonds, contrary to the physical form of hydrogels through weak interaction. In this regard, the radiation crosslinking and metal sorption of hydrogels based on poly(acrylic acid) with trithioglycolic acid or 2-mercaptobenzimidazol were investigated.[16,17] Recently, radiation crosslinking and dye sorption of hydrogels, based on 1-vinyl-2-pyrrolidone, hydroxyethyl methacrylate, and their copolymers, were investigated.[18] Hydroxyethyl methacrylate (HEMA) and acrylamide (AM) are hydrophilic monomers containing hydroxyl and amide groups giving a unique combination of

Correspondence to: H. Nizam El-Din (nizam_eldin@yahoo.com).

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properties. Therefore, in the present work, an attempt was made to prepare hydrogels based on different compositions of HEMA and AM in the presence of trithioglycolic acid under the effect of gamma radiation. Moreover, the swelling kinetics in water, temperature, and pH sensitivity of these hydrogels were studied.

EXPERIMENTAL

Materials

2-Hydroxyethyl methacrylate (HEMA) and acrylamide (AM) were laboratory-grade monomers, purchased from Merck (Schuchardt, Germany). Trithioglycolic acid (TTGA) was used without purification.

Preparation of HEMA/AM hydrogels

The hydrogels were prepared by dissolving separately 0.05 wt/vol % of TTGA (constant in all hydrogels) and the required ratio of AM monomer in the appropriate volume of distilled water. The mixture was then added to the required ratio of HEMA (wt/vol %) such that the total hydrogel solution was kept constant at 20 mL in test tubes. The tubes were then subjected to gamma radiation for different durations to obtain different doses (10–50 kGy), depending on a dose rate of 7.0 kGy h^{-1}. Gamma irradiation was carried out in the cobalt-60 cell facility of NCRRT.

Determination of gel fraction

Samples of the prepared hydrogels were accurately weighed (W_0) and then extracted with distilled water using a Soxhlet system for 24 h. After extraction, the samples were then removed and dried in a vacuum oven at 50°C until a constant weight was reached (W). The sol fraction was calculated according to the following equation:

$$\text{Sol fraction (\%)} = [(W_0 - W)/W_0] \times 100$$

$$\text{Gel fraction (\%)} = 100 - \text{Sol fraction (\%)}$$

IR spectroscopic analysis

The infrared spectra of the hydrogels of different compositions were performed on a Mattson 5000 FTIR spectrometer (Mattson Instruments, Madison, WI) over the range 500–4000 cm^{-1}. The samples for IR analysis were dried in a vacuum oven, ground to a very fine powder, mixed with a highly dried KBr powder (30 mg), and then pressed to transparent disks.

Thermogravimetric analysis (TGA)

TGA thermograms were carried out 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 such as activation energy and order of thermal decomposition reaction.

Swelling behavior of HEMA/AM hydrogels

Swelling studies were conducted on HEMA/AM hydrogels as a function of time, temperature, and pH of swelling medium. A known dry weight of insoluble hydrogel (W_d) was immersed in water for different times up to 48 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 percentage swelling was calculated according to the following equation:

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

The equilibrium water content (EWC) is defined as the ratio between the absorbed water and the weight of hydrogel at equilibrium swelling (ES) and was calculated from the following equation:

$$\text{EWC (\%)} = [(W_{ES} - W_d)/W_{ES}] \times 100$$

The responsive characters of HEMA/AM hydrogels were determined by investigating the swelling in different external environments. Pure HEMA and HEMA/AM hydrogels, at dry weight (W_d), were immersed in water at different temperatures (10–50°C) to an equilibrium time (Et) specific for each hydrogel and weighed (W_{Et}). The percentage swelling was calculated in terms of the change between W_{Et} and W_d with respect to W_d. The same procedure was followed to investigate the pH-responsive character of HEMA/AM hydrogels.

RESULTS AND DISCUSSION

Gamma radiation synthesis of HEMA/AM hydrogels

The formation of hydrogels based on individual AM or its mixture with HEMA at any composition or gamma irradiation dose was not possible, as shown by the preliminary experiments. However, when a small ratio of 0.05 wt/vol % of TTGA was used it was possible to form HEMA/AM hydrogels at different compositions, in which 50 wt/vol % of AM is the critical ratio. Beyond this ratio and up to 100 wt/vol % of AM it was also not possible to form hydrogels, even in the presence of TTGA under the effect of gamma irradiation.

TABLE I
Percentage Gel Fraction of Pure HEMA and HEMA/AM Hydrogels at Different Compositions Formed at Various Doses of Gamma Radiation

Hydrogel composition (%)	Gel fraction (%)			
	10 kGy	20 kGy	30 kGy	50 kGy
HEMA (100)	75.6	80.5	99.0	99.7
HEMA/AM (90/10)	60.0	94.0	96.6	97.0
HEMA/AM (72/25)	40.0	86.0	95.5	96.0
HEMA/AM (50/50)	30.5	75.0	87.0	88.0

Table I shows the gel fraction of pure HEMA and HEMA/AM hydrogels, at different compositions, formed at various doses of gamma radiation. It is clear that the gel fraction tends to decrease slightly with increasing content of AM ratio, up to 25 wt/vol % in the initial hydrogel solution, within the dose range 20–50 kGy of gamma radiation. A sudden decrease in gel fraction can be observed with increasing ratio of AM monomer to 50%, in which there was nearly no effect on the gel fraction by increasing the irradiation dose from 20 to 50 kGy. It seems that the low dose of 10 kGy scarcely has effect on the conversion of hydrogel solution to complete hydrogels, particularly for those compositions containing a higher ratio of AM monomer. In a previous work[18] on the synthesis of pure HEMA hydrogel, using water as a pure solvent and 0.05 wt/vol ratio of *N,N*-methylenebisacrylamide (MBAm) as a crosslinking agent followed by gamma irradiation to a dose of 10 kGy, a gel fraction of about 90% was obtained compared to 75.6%, as shown in Table I. Thus, it can be concluded that MBAm initiated the radiation crosslinking[19] of pure HEMA rather than that of the TTGA compound at such a low dose. This behavior can be attributed to the higher sensitivity of the carbon atom adjacent to the amide groups CO–NH_2 to form free radicals than the thio groups. However, the presence of TTGA is essential to form HEMA/AM hydrogels. Therefore, the formation of HEMA/AM hydrogels can be attributed to the free radicals formed on the macromolecules of HEMA and TTGA, which initiate polymerization and crosslinking rather than those formed on AM.

The irradiation of acrylates and methacrylate with electron beam or gamma radiation has been reported to lead to the formation of radicals, starting both polymerization and crosslinking.[19] On the other hand, the products of the radiolysis of water, present in appropriate quantities, will eventually participate in the formation of the hydrogels as follows[20]:

$$H_2O \xrightarrow{\text{radiation}} e_{aq}^{-}, OH^{\bullet}, H^{\bullet}, H_2O_2, H_2$$

The radiation chemical yields (*G*-value) of these primary reactive products are $G(e_{aq}^{-}) \approx G(OH) = 2.9 \times 10^{-7}$ mol/J, and $G(H) = 0.6 \times 10^{-7}$ mol/J.[21] Because no scavengers were used in the medium the probability is that these species create active sites on the hydrogel components to form crosslinking.

IR spectroscopic analysis

IR spectroscopic analysis was used to illustrate the type and nature of bonding and to confirm the effect of hydrogen bonding on radiation crosslinking of hydrogels. Figure 1 shows the IR spectra of pure HEMA and HEMA/AM hydrogels, formed from solutions of different compositions under the effect of a constant dose of 50 kGy of gamma radiation as an example. However, the intensities of the characteristic bands of the IR spectra of the hydrogels formed at various doses are summarized in Table II. It should be noted that the IR absorbance values are less than 1, whereas the samples for IR analysis were dried in a vacuum oven at 80°C for 2 h to exclude the effect of H-bonding to water in the sample. Also, it was observed that the different absorption bands did not change their position by increasing the dose from 20 to 50 kGy. An absorption band at 2950 cm^{-1} with a weak shoulder, attributed to C–H stretching, can be seen in the IR spectrum of pure HEMA hydrogel as in almost all organic compounds. The intensity of this band was found to increase with increasing ratio of AM monomer in the initial hydrogel solution, up to 25%, after which it tended to decrease at 50%, as shown in Table II.

A distinctive absorption band can be seen at 1730 cm^{-1}, which is attributed to C=O stretching. This band appeared as a sharp peak in the IR spectrum of pure HEMA, with a small shoulder in the IR spectrum of HEMA/AM (90/10) hydrogel, and split into two adjacent peaks in the IR spectra of HEMA/AM hydrogels composed of 25 and 50% AM. These findings may indicate that the C=O of the amide groups of AM or that along the chains of HEMA was not involved in the formation of HEMA/AM hydrogels.

Hydrogen bonding changes the position and appearance of the IR absorption bands attributed to OH stretching. The appearance of absorption bands at 3320, 3420, and 3520 cm^{-1} in the IR spectrum of pure HEMA hydrogel indicates the formation of hydrogen bonding between the hydroxyl groups. The IR spectra of HEMA/AM hydrogels, with increased AM contents, showed the appearance of a broad absorption, starting from 3225 cm^{-1} and sloping to 3593 cm^{-1}, which indicates that the formation of hydrogels is through hydrogen bonding in addition to the crosslinking of HEMA. The hydrogen bonding in this case may be formed between the hydroxyl groups of HEMA and the NH_2 of the amide groups of AM. The crosslinking of AM inside the hydrogels may be initi-

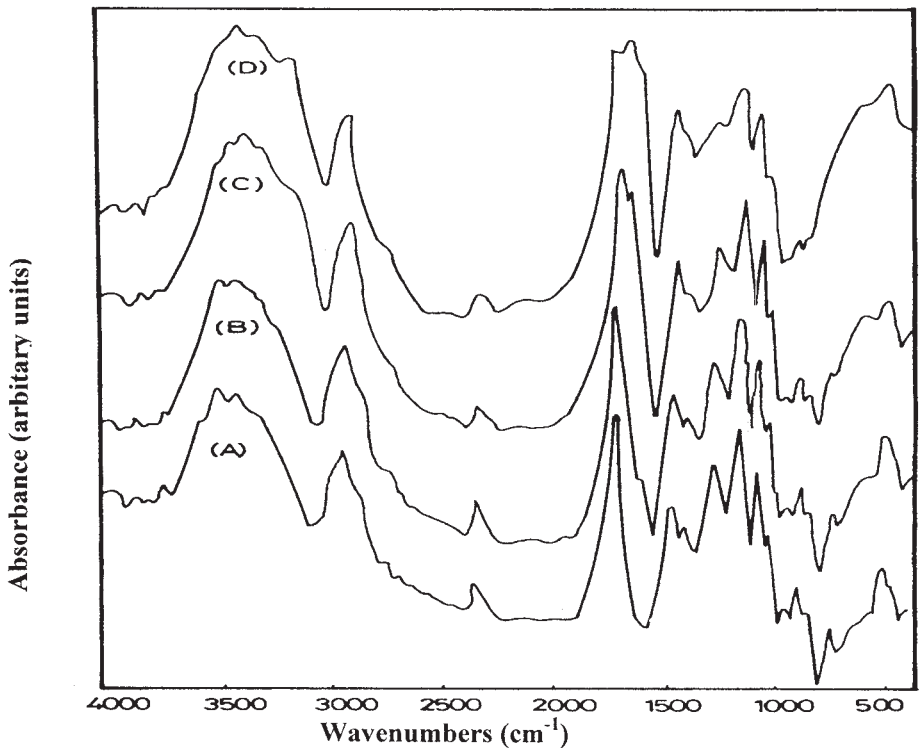

Figure 1 IR spectra of pure HEMA and HEMA/AM hydrogels at different compositions at a dose of 50 kGy of gamma radiation: (A) pure HEMA, (B) 90%/10%, (C) 75%/25%, (D) 50%/50%.

ated through the radicals formed on TTGA and the radiolysis products of water.

Characteristic peaks were observed at 1277 and 1461 cm^{-1}, which were attributed to the methyl and amide groups of HEMA and AM, respectively. These absorption bands also appeared in the IR spectra of HEMA/AM hydrogels. The distinctive adsorption band at 1075 cm^{-1} may be attributed to the C═S stretching of the TTGA compound and the intensity of this band was found to increase with increasing ratio of AM component, even though the ratio of TTGA is constant in the prepared solutions.

For the hydrogels formed at 20 kGy, the band ratios 1075/1277, 1075/1461, and 1075/1730 were found to be 0.986, 1.026, and 0.928 for pure HEMA; 0.989, 0.990, and 0.937 for HEMA/AM (90/10); 1.012, 1.030, and 0.955 for HEMA/AM (75/25); and 1.003, 0.994, and 0.936 for HEMA/AM (50/50), respectively. In this light, the band ratios suggest that the HEMA/AM ratio is constant, as it should be. Upon exposure to 50 kGy, the intensity of the different band ratios was found to decrease, regardless of the hydrogel composition, except the one at equal ratios of HEMA and AM, in which it was found to increase with dose. However, the previous band ratios were also found constant for all hydrogels. Also, the intensity of any band can be observed to increase with increasing ratio of AM component in the hydrogel solutions.

TABLE II
Intensity of Characteristic Absorption Bands of the IR Spectra of Pure HEMA and HEMA/AM hydrogels at Different Compositions Formed Under the Effect of Various Doses of Gamma Radiation

Hydrogel composition (%)	Irradiation dose (kGy)	Intensity of characteristic bands (cm^{-1})					
		1075	1277	1461	1730	2950	3320
HEMA (100)	20	0.5771	0.5852	0.5625	0.6220	0.6348	0.6715
	50	0.5657	0.5712	005468	0.6008	0.5059	0.6084
HEMA/AM (90/10)	20	0.6103	0.6173	0.6166	0.6513	0.6912	0.7074
	50	0.6013	0.6004	0.5839	0.6299	0.6089	0.6435
HEMA/AM (75/25)	20	0.8111	0.8107	0.7871	0.8443	0.8478	0.8723
	50	0.5849	0.5819	0.5721	0.6322	0.5960	0.6446
HEMA/AM (50/50)	20	0.5604	0.5587	0.5639	0.5988	0.5719	0.5978
	50	0.6947	0.6847	0.6973	0.6847	0.6906	0.7349

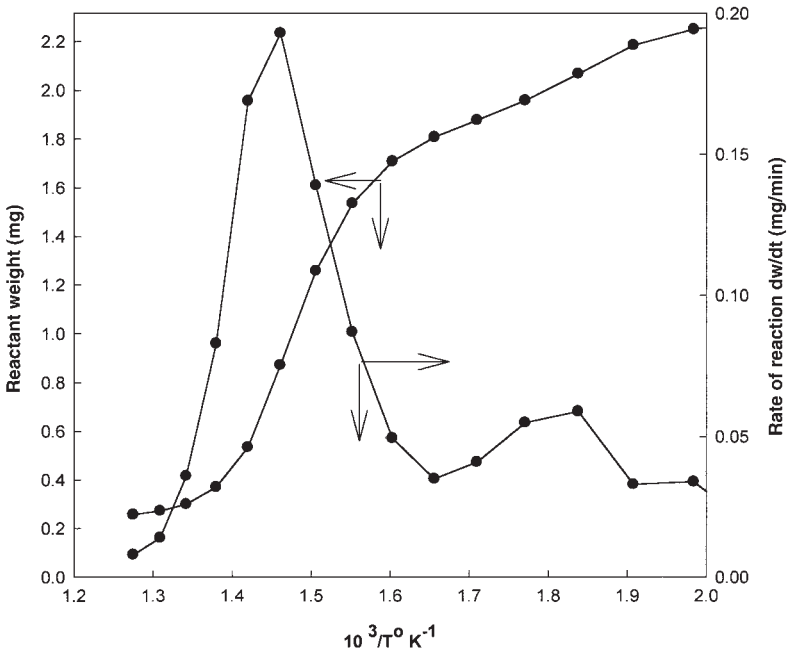

Figure 2 Rate of reaction (*dw/dt*) and residual reactants against $1/T$ for the hydrogel composed of HEMA/AM (50%/50%).

Thermal decomposition behavior

The calculated average complete dissociation energies for HEMA, AM, and TTGA were found to be 409.6, 414.4, and 417.5 kJ/mol on the basis of the reported dissociation energies for the different covalent bonds forming the polymer molecules.[22] Thus, it may concluded that TTGA and AM possess a higher theoretical thermal stability than that of HEMA and the formation of hydrogels with increased AM ratio will eventually result in hydrogels with higher thermal stability than that of pure HEMA. TGA was used to investigate experimentally the thermal stability of pure HEMA and HEMA/AM hydrogels, formed at a dose of 50 kGy of gamma radiation. Figure 2 shows the TGA thermograms and the rate of thermal decomposition reaction (*dw/dt*) against the reciprocal of the absolute temperature $1/T$ over the range 227–500°C for HEMA/AM (50/50) hydrogel formed at 50 kGy as an example for these kinds of curves. However, the percentages of weight loss at different decomposition temperatures for all hydrogels are summarized in Table III. Within the temperature heating range 300–500°C, the HEMA/AM hydrogels are thermally more stable (with less weight loss) than pure HEMA and this stability was found to decrease with increasing ratio of AM, contrary to the assumption based on theoretical calculations. Meanwhile, up to a heating temperature of 300 or 400°C, the weight loss of HEMA/AM hydrogels was found to constantly increase by a factor of about 1.5 or 1.3, respectively, with increasing ratio of AM from 10 to 25% and from 25 to 50%. Thus, it may be concluded that the decrease in thermal stability of hydrogels is nearly concomitant with increasing ratio of AM component.

The derivative of the rate of reaction (DTGA) curves for pure HEMA and HEMA/AM hydrogels containing 10 and 25% AM (not shown) showed that the thermal decomposition reaction goes through one

TABLE III
Weight Loss (%) at Different Decomposition Temperatures of HEMA/AM Hydrogels at Different Compositions Formed at a Constant Dose of Gamma Radiation of 30 kGy

Hydrogel composition (%)	Weight loss (%)					
	100°C	200°C	300°C	350°C	400°C	500°C
HEMA (100)	0.54	3.65	22.31	36.78	83.26	96.76
HEMA/AM (90/10)	0.04	4.42	8.76	14.13	30.66	96.44
HEMA/AM (75/25)	1.11	5.86	13.24	20.17	40.06	91.81
HEMA/AM (50/50)	0.2	6.23	20.69	30.81	49.03	88.94

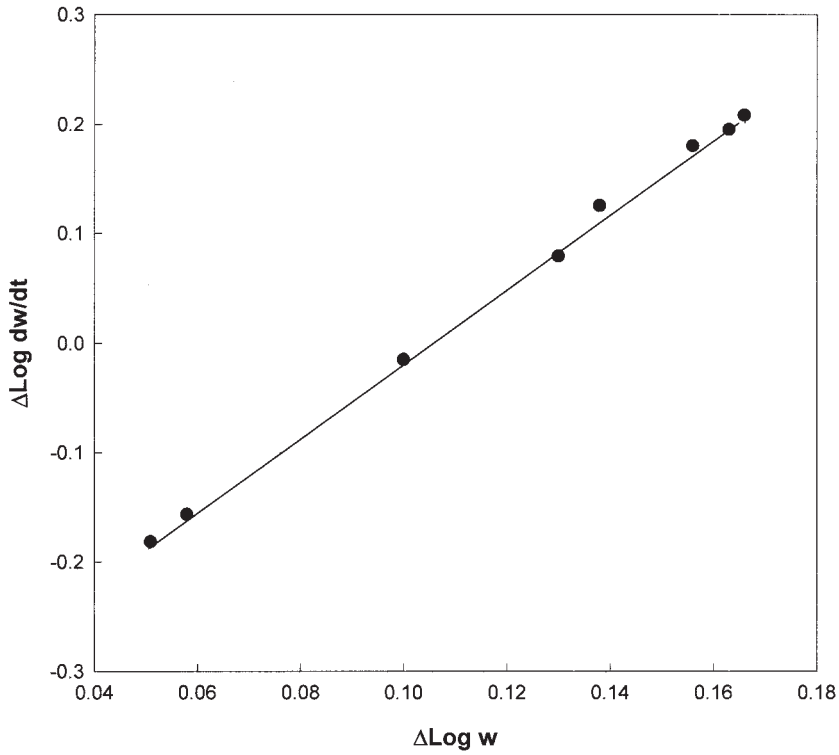

Figure 3 Plot of Δ log w against Δ log(dw/dt) for the thermal decomposition reaction within the high-temperature range for pure HEMA hydrogel formed at a dose of 50 kGy of gamma radiation.

maximum, whereas the DTGA of the hydrogel containing equal ratios of HEMA and AM goes through two maxima, as shown in Figure 2. However, the temperatures of the maximum value of the rate of thermal decomposition reaction for HEMA/AM (50/50) was found to occur at 271 and 411°C, corresponding to the two maxima shown in Figure 2. The percentage weight loss at the temperatures of the maximum value of the rate of reaction for pure HEMA and HEMA/AM hydrogels containing 10, 25, and 50% AM was found to be 69.6, 69.9, 79.9, and 64.7%, respectively. On the basis of these findings, it is difficult to determine the thermal stability of these hydrogels.

The thermal stability was further confirmed by determining the kinetic parameters of the thermal decomposition reactions. A method based on the rate of reaction proposed by Anderson and Freeman[23] was used, in which the quantities Δ log(dw/dt) and Δ log w, corresponding to a constant small difference of Δ($1/T$) over the entire course of the initial TGA curve, were first determined. The Anderson–Freeman equation, which relates these quantities, is given as

$$\Delta \log(dw/dt) = n\Delta \log w - (E^*/2.303)\,\Delta(1/T)$$

where dw/dt is the rate of the thermal decomposition reaction (mg min^{-1}), w is the reactant mass (mg), R is the gas constant (J mol^{-1} K^{-1}), E^* is the activation energy (J mol^{-1}), and n is the order of reaction. When Δ log(dw/dt) is plotted against Δ log w, it gives a straight line of slope n and the intercept gives the activation energy E^*. The procedure and application of this method have been described elsewhere.[24] When Δ log(dw/dt) was plotted against Δ log w for the present hydrogels over the entire range of temperatures, the data points did not fall on a straight line, except in the case of pure HEMA within the high-temperature range (Fig. 3). Therefore, on the basis of the Anderson–Freeman equation, the thermal decomposition of these hydrogels does not depend on the residual mass but on temperature and follows a zero-order reaction. In this case, log(dw/dt) is plotted against $1/T$ and the slope is equal to $E^*/2.303R$, from which the activation energy can be calculated, as shown in Figures 4–7. The calculated activation energies of the thermal decomposition reactions of the hydrogels are summarized in Table IV. It should be noted that the values in stages 1 and 2 represent the activation energies during the increasing and decreasing passing the first maximum, whereas those in stages 3 and 4 represent the activation energies corresponding to the second maximum. It is clear that the thermal decomposition reaction of HEMA/AM hydrogels goes through a stepwise process during the increasing rate of reaction until it reaches the maximum and then goes through one step

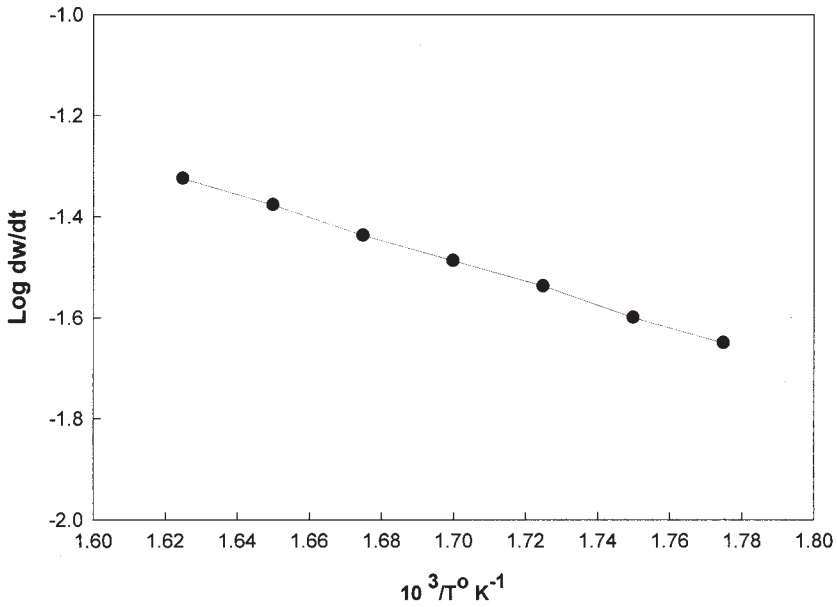

Figure 4 Temperature dependency of the logarithm of *dw/dt* of the thermal decomposition reaction within the low-temperature range for pure HEMA hydrogel formed at a dose of 50 kGy of gamma radiation.

during the decreasing rate of reaction. As shown in Table IV, the activation energy of HEMA/AM hydrogels was found to decrease with increasing ratio of AM component up to 50% during the increasing or decreasing rate of reaction. However, during the decreasing rate of reaction (i.e., within the high-temperature range), the activation energy was found to suddenly increase at a ratio of 10% of AM and then decreased substantially with increasing ratio of AM up to 50%. However, HEMA/AM hydrogels still possessed higher a thermal stability than that of pure HEMA.

Equilibrium swelling of HEMA/AM hydrogels

The swelling kinetics in water at 25°C of pure HEMA and HEMA/AM hydrogels at different compositions, formed at a dose of 50 kGy of gamma radiation, is

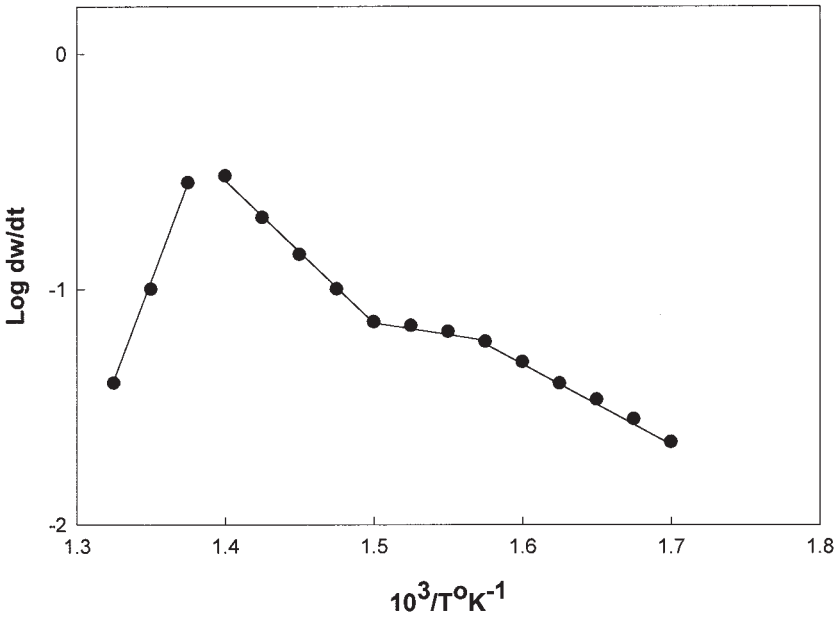

Figure 5 Temperature dependency of the logarithm of *dw/dt* of the thermal decomposition reaction for HEMA/AM (90%/10%) hydrogel formed at a dose of 50 kGy of gamma radiation.

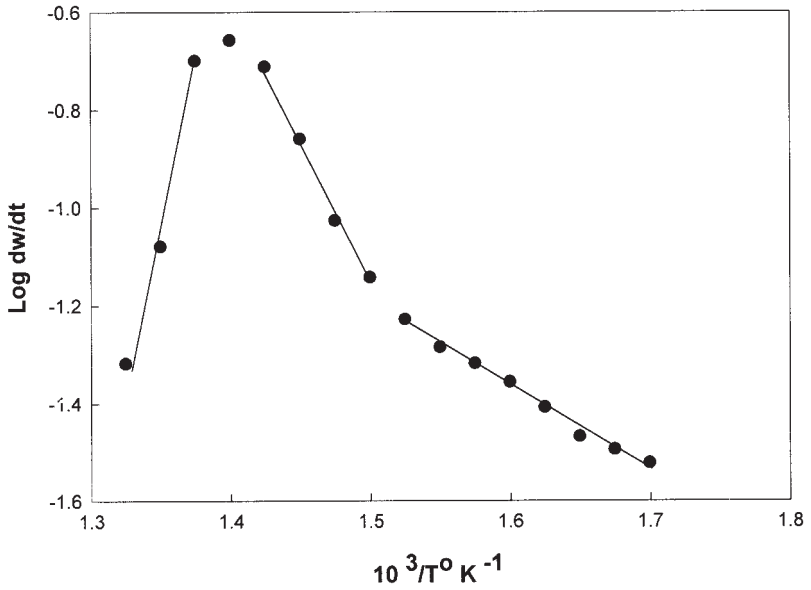

Figure 6 Temperature dependency of the logarithm of *dw/dt* of the thermal decomposition reaction for HEMA/AM (75%/25%) hydrogel formed at a dose of 50 kGy of gamma radiation.

shown in Figure 8. It can be seen that the percentage swelling of all hydrogels increases linearly within the initial time of swelling and then reaches the equilibrium state, depending on the composition of hydrogels. Also, the percentage swelling was found to increase with increasing ratio of AM component, in

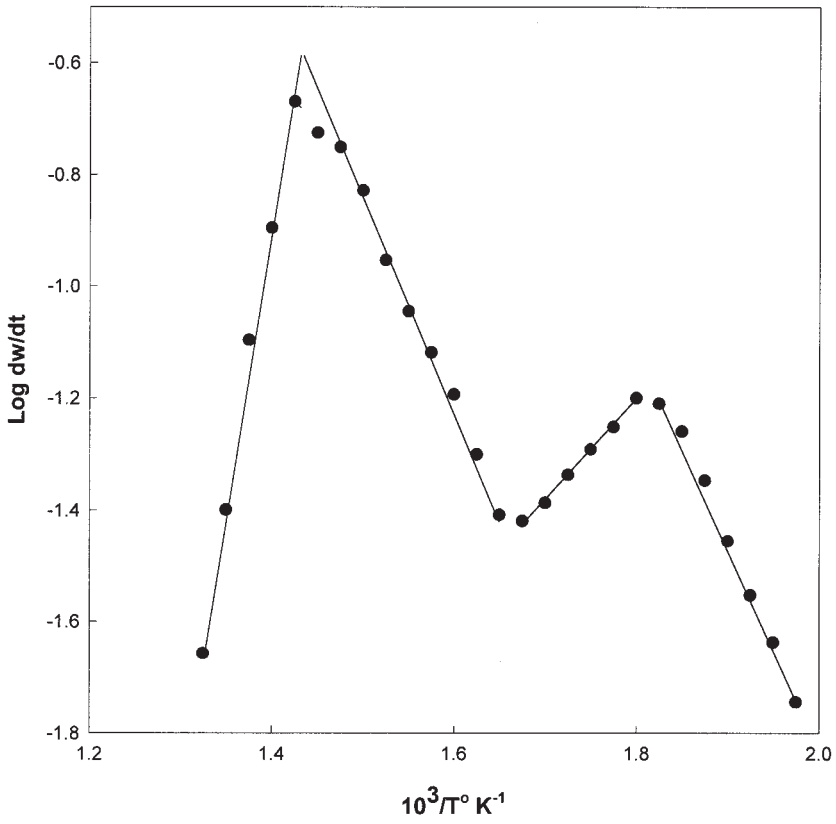

Figure 7 Temperature dependency of the logarithm of *dw/dt* of the thermal decomposition reaction for HEMA/AM (50%/50%) hydrogel formed at a dose of 50 kGy of gamma radiation.

TABLE IV
Activation Energy and Order of the Thermal Decomposition Reaction of Pure HEMA/AM Hydrogels at Different Compositions Formed at a Dose of 50 kGy of Gamma Radiation

Hydrogel composition (%)	Activation energy (kJ/mol)			
	Stage 1	Stage 2	Stage 3	Stage 4
HEMA (100)	41.0 (zero-order) 290–352°C	271.9 (1.4 order) 352–440°C	Non	Non
HEMA/AM (90/10)	98.9 (zero-order) 315–441°C	344.7 (zero-order) 441–487°C	Non	Non
HEMA/AM (75/25)	77.2 (zero-order) 290–441°C	219.9 (zero-order) 441–482°C	Non	Non
HEMA/AM (50/50)	74.9 (zero-order) 233–275°C	34.8 (zero-order) 275–324°C	68.9 (zero-order) 324–417°C	199.5 (zero-order) 417–482°C

which pure HEMA showed the lowest swelling behavior in water, whereas pure HEMA and HEMA/AM (90/10) hydrogels reached the equilibrium state after 24 h. The hydrogels containing 25 and 50% of AM reached the equilibrium state after 6 h. The difference in swelling kinetics may result from the difference in hydrophilicity of HEMA and AM, even though both components are hydrophilic in nature, whereas the higher swelling is attributed to the strong hydration of HEMA and AM in the hydrogels. The calculated initial rate of swelling was found to be 1.5×10^{-5}, 2.5×10^{-3}, 6.3×10^{-3}, and 16.3×10^{-3} g water/g gel min^{-1} for pure HEMA, HEMA/AM (90/10), HEMA/AM (75/25), and HEMA/AM (50/50) hydrogels, respectively.

Equilibrium water content (EWC), an important quantitative factor to represent the water absorbed rather than the percentage swelling, is defined as the mass of absorbed water at equilibrium with respect to the mass of swollen gel at equilibrium. The EWC values for pure

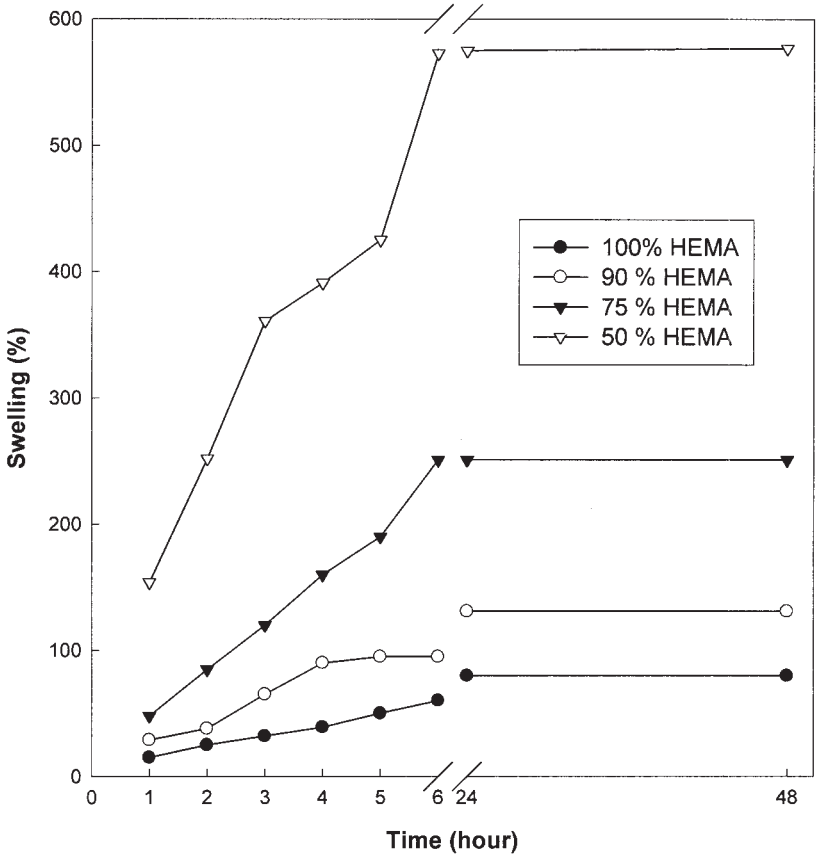

Figure 8 Swelling kinetics in water of pure HEMA and HEMA/AM hydrogels formed at a dose of 50 kGy of gamma radiation at 25°C.

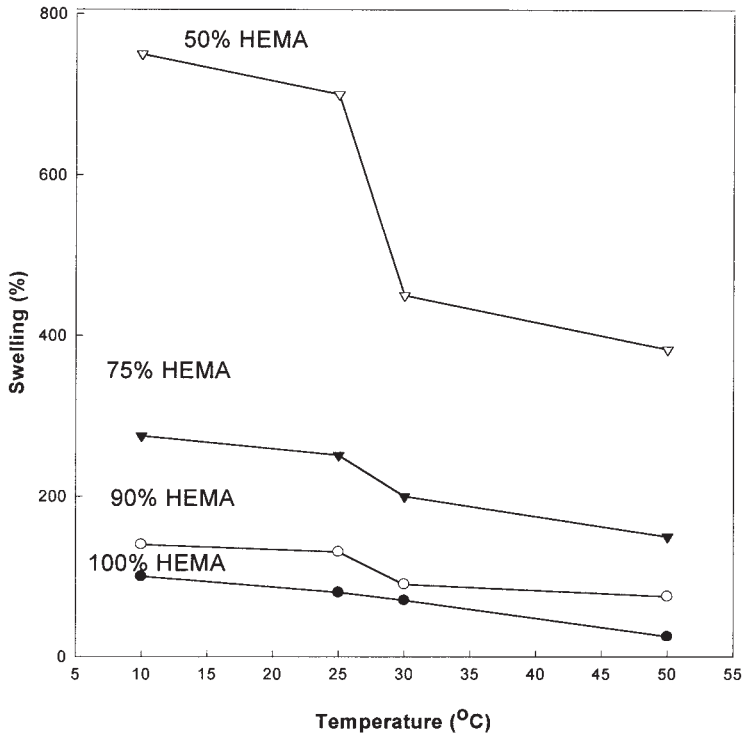

Figure 9 Swelling in water as a function of temperature of pure HEMA and HEMA/AM hydrogels at different compositions formed at a dose of 50 kGy of gamma radiation.

HEMA and HEMA/AM hydrogels, having 10.25 and 50% AM equilibrated at 25°C, was found to be 0.444, 0.567, 0.715, and 0.852, respectively. The EWC value of pure HEMA is comparable to that of living tissues, whereas those of HEMA/AM hydrogels exhibited fluid contents greater than that for living tissues by 60%.[25]

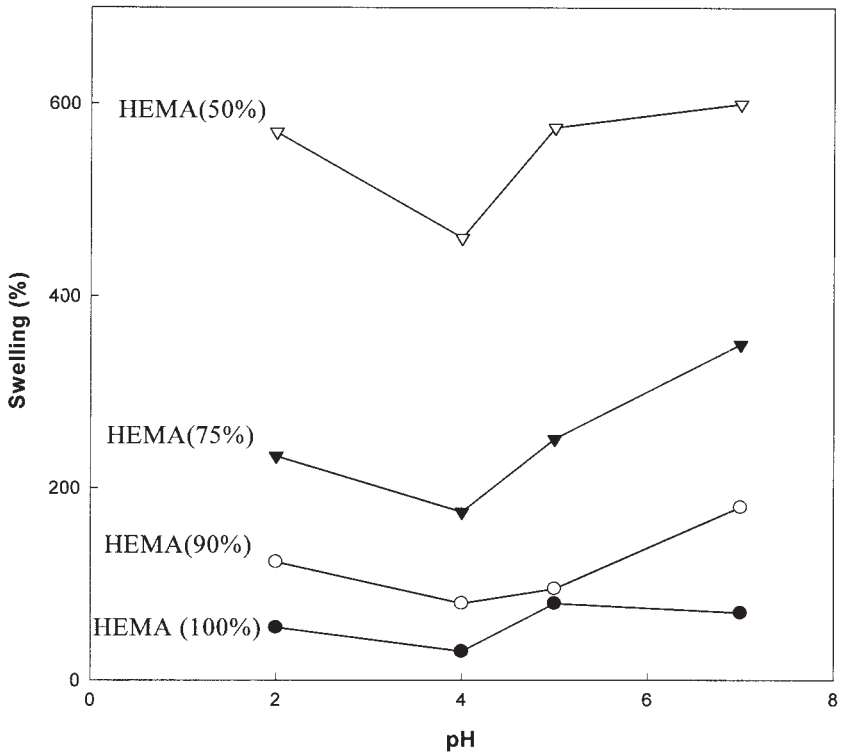

Figure 10 Swelling dependency on pH of pure HEMA and HEMA/AM hydrogels at different compositions formed at a dose of 50 kGy of gamma radiation at 25°C.

Temperature and pH-responsive characters of HEMA/AM hydrogels

The swelling behavior of pure HEMA and HEMA/AM hydrogels was investigated as a function of temperature, as shown in Figure 9. Whereas pure HEMA has no temperature sensitivity, HEMA/AM hydrogels displayed changes in the percentage swelling over the temperature range 25–30°C. This sensitivity was found to increase with increasing AM content. Thus, it can be concluded that the temperature 25°C is the lower critical solution temperature (LCST) for these hydrogels showing negative-sensitive systems, in which they shrink by heating above the LCST.[15] The calculated EWC at 30°C for pure HEMA, HEMA/AM having 10, 25, and 50% of AM, was found to be 0.412, 0.667, and 0.818, respectively. Usually, LCST behavior is driven by changes in water bonding accompanied by interchain bonding enhancement. Neither HEMA (Fig. 9) nor AM polymers have LCST and thus no hydrogels, based on individual AM or its mixture with HEMA at any composition under the effect of gamma irradiation, were formed except in the presence of TTGA. Therefore, it could be expected that the temperature sensitivity of HEMA/AM is a result of the formation of hydrophobic interchain bonding by copolymerization between TTGA and AM or HEMA, and this bonding will eventually increase with increasing AM ratio, as shown in Figure 9.

Figure 10 shows the swelling dependency on pH in water of pure HEMA and HEMA/AM hydrogels at different compositions formed at a dose of 50 kGy of gamma radiation. It should be noted that the hydrogel samples were immersed in different buffer solutions at 25°C for the equilibrium times specific for each hydrogel before measuring the swelling in the pH range. The stepwise swelling behavior can be observed, in which the swelling was shown to decrease at pH 5 and then tended to continuously increase within the pH range of 7–10 (not shown). At low pH values, the carboxylates of the combined TTGA in the networks were not ionized, whereas as the pH increased they became ionized with the formation of carboxylate salts. This phenomenon results in the development of an electrostatic repulsion in the network, thus causing the hydrogels to swell.

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