

Characterization of Poly(*N*-(hydroxymethyl)methacrylamide-ATU) Hydrogels Synthesized by γ Radiation

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ABSTRACT: Poly(*N*-(hydroxymethyl)methacrylamide-1-allyl-2-thiourea), (poly(NHMMA-ATU)) hydrogels were synthesized by γ radiation, using ⁶⁰Co γ source at different radiation doses, to change the porosity and crosslinking density of the hydrogels. The percent of 1-allyl-2-thiourea (ATU) in the monomer mixture before the irradiation was varied between 2.5% and 10.0%, to increase the content of ATU, which was involved in some different applications in the hydrogels. Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), elemental analysis, and the swelling experiments were used to characterize the poly(NHMMA-ATU) hydrogels synthesized in this study. Characterization results of hydrogels showed that crosslinking density of the hydrogels was increased by the

increasing radiation dose and ATU content in the irradiated mixture. Swellability of these hydrogels was found to be high enough to allow the metal ions and biomolecules getting inside the hydrogels to interact with all active groups on/in the hydrogels in the adsorption applications. Equilibrium swelling ratio of the hydrogels at pH 0.5 is at least half of the equilibrium swelling ratio of the hydrogels at pH 7.0. Oscillatory swelling behavior of poly(NHMMA-ATU) hydrogels between pH 0.5 and pH 7.0 showed that the hydrogels are quite stable at different pH conditions. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 1657–1664, 2006

Key words: *N*-(hydroxymethyl)methacrylamide; 1-allyl-2-thiourea; hydrogels; irradiation; swelling

INTRODUCTION

Chelating polymeric ligands have been extensively studied by several authors and many reviews are available in the field.^{1–3} Recently, a great deal of interest has been observed in relation to the applicability of chelating agents for removal and separation of metal ions from heavy metal contaminated water and preconcentration of precious metal ions from different samples.^{4–6} Among many sorptive materials, various forms of synthetic polymers containing complexing molecules which are available at low cost have emerged as one of the most important matrices for the synthesis of new sorbents.^{7–9} In the recent years, instead of chelating resins, some hydrogels having different swelling ratio have been used for different applications.^{10,11} Hydrogels are special class of crosslinked polymers, and they can be prepared by different polymerization techniques. Using radiation technology, the polymerization procedure, the crosslinking structure, and also the crosslinking density of the hydro-

gels could be controlled easily.¹² Hydrogels are polymeric networks, which absorb and retain large amounts of water. Hydrogels having different ionizable and hydrogen bonding capacity, show different swelling behavior in the solution at different pH, temperature, and ionic strength. These behaviors supply some advantages to the hydrogels in different applications, especially in drug delivery systems.^{13–15} Because of their water-absorbing capacity, hydrogels are subject of investigation of researchers interested in fundamental aspects of swollen polymeric networks, and have also found widespread application in different technological areas, such as materials for contact lenses and protein separation, matrices for cell encapsulation, removal of metal ions, adsorption of textile dyes, and devices for the controlled release of drugs and proteins.^{16–21} The advantages of the hydrogels are easy to obtain with some different polymerization techniques, and interacting species with the active functional group on/in to the polymeric sorbent could be penetrated inside cavities of hydrogel by the swellability of the hydrogels. Recently, there has been a substantial interest in the use of radiation-induced graft copolymerization of functionalized monomer onto polymeric hydrogels, for chelating sorbent materials.^{22–25} In the present study, poly(*N*-(hydroxymethyl)methacrylamide-1-allyl-2-thio-

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urea) (poly(NHMMA-ATU)) hydrogels were synthesized by ^{60}Co γ -radiation source at different radiation doses and different composition of the two monomers, *N*-(Hydroxymethyl)methacrylamide (NHMMA) and 1-allyl-2 thiourea (ATU). Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), elemental analysis, and swelling experiments were used for the characterization of the hydrogels synthesized in this study.

EXPERIMENTAL

Materials

ATU and NHMMA were purchased from Aldrich (Milwaukee, WI) and used as-received. IR-grade KBr and NaNO_3 were obtained from Merck (Germany). All other chemicals were of reagent grade and were purchased from BDH (England). All chemicals were used as-received, without further purification.

Preparation of poly(NHMMA-ATU) hydrogels

About 1 mL of NHMMA-ATU-water ternary mixture containing different amount of the monomers and water was placed in polyvinyl chloride (PVC) straws of 3 mm diameter and irradiated using a ^{60}Co γ source (Russian-made PX- γ -30 Isslodovatelj; 1.97 kGy/h) at varying dose rates. Hydrogels were taken out from straws and washed several times with distilled water to remove all unreacted monomers and low-molecular-weight polymeric materials. These hydrogels were first dried in air and then in vacuum oven at 60°C for 5 days, and then stored in desiccators until use.

Characterization of poly(NHMMA-ATU) hydrogels

Water uptake of poly(NHMMA-ATU) hydrogels

Swelling ratio of the hydrogels was obtained using the following procedure to study the swellability of the hydrogels. About 0.1 g of dry hydrogels were placed into the beakers and 0.01M of acetate ($\text{NaCH}_3\text{COO}-\text{CH}_3\text{COOH}$) or phosphate ($\text{Na}_2\text{HPO}_4-\text{NaH}_2\text{PO}_4$) buffer solution at different pHs between 3.0 and 7.0 were added into the beakers. Then, the hydrogels were allowed to swell at room temperature, with occasional shaking. For the acidic solutions having a pH < 3.0, the pH was adjusted by nitric acid. The hydrogels were periodically removed and weighed to calculate the swellability of the hydrogels at different times. Swelling ratio was calculated by the following expression:

$$\text{Swelling Ratio (\%)} = [(W_{\text{swollen}} - W_{\text{dry}}) / W_{\text{dry}}] \times 100$$

Elemental analysis

Elemental analysis of poly(NHMMA-ATU) hydrogels was performed using an elemental analyzer (CHNS-932, Leco), for the determination of the amount of ATU content in the different hydrogels synthesized in this study, at different monomer mixture ratios and at different radiation doses. About 1.0–2.0 mg of sample was placed into the tin capsule and introduced inside the furnace of the elemental analyzer system and the percent content of C, H, N, and S were obtained. The content of ATU in the hydrogels was calculated from the percent content of sulfur existing only in the chemical structure of ATU.

FTIR spectra

FTIR spectra of the hydrogels synthesized at different monomer ratios and radiation doses were obtained using an FTIR spectrometer (Mattson 10000 FTIR Spectrometer, Unicam, UK). About 0.02 g of poly(NHMMA-ATU) hydrogels were dried in vacuum oven at 60°C for 5 days to remove all adsorbed water, and then, the powder form of the hydrogels were thoroughly mixed with 0.1 g of KBr, to obtain a homogeneous mixture. This mixture was pressed to form a tablet, and then, the FTIR spectra were recorded. In the second experiment, the synthesized hydrogels were placed in the sample pan of TGA instrument and heated up to the final degradation temperature (T_f) of each degradation peak obtained in TGA curves, such as, 190, 260, 325, and 500°C under nitrogen atmosphere, to examine the structural changes in the hydrogels, and then, cooled to the room temperature for each period. After the sample pan was cooled to the room temperature, the sample in the TGA pan was removed and FTIR spectra of the samples were recorded, following the aforementioned FTIR sample preparation procedure. These experiments were carried out to examine the structural change in the hydrogels at different temperatures under inert atmosphere and to characterize the hydrogel structure in detail.

TGA thermograms

TGA curves of poly(NHMMA-ATU) hydrogels obtained at different radiation doses and from mixture containing different monomer ratios were examined by a thermogravimetric analyzer system (TA Instruments, 2050) with thermal advantage control system. Briefly, about 5–10 mg of the samples were weighed. The sample pan was placed onto the balance in TGA and the temperature was increased from 30 to 800°C at a heating rate of 10°C/min under nitrogen atmosphere at 25 mL/min nitrogen flux. The mass of the sample pan was continuously recorded as a function

of the temperature. In a separate experiment, temperature of TGA sample pan was increased to the desired temperature, after the hydrogels are introduced in TGA pan, and then, the pan was cooled to room temperature, to examine the characterization of the heated hydrogels in FTIR.

Oscillatory swelling

The oscillatory swelling behavior of hydrogels at 25°C with pH alternating at 0.5 and 7.0 was investigated in 24 h intervals. For this purpose, 0.2 g of the hydrogels were placed in 20 mL of solution at pH 0.5. After 24 h swelling period, swollen hydrogels were taken out and weighed. The same hydrogels were placed into the second solution that has pH 7.0. This procedure was repeated at least five times to calculate the swelling at different pH, repeatedly.

RESULTS AND DISCUSSION

Characteristics of poly(NHMMA-ATU) hydrogels

The hydrogels prepared in this study are highly swellable. The swelling ratio is around 450% at pH 7.0, when the hydrogels having highest content of ATU were used in this study. The plain poly(NHMMA-ATU) hydrogels showed a homogeneous (obtained from scanning electron microscope images, data not shown) and highly open pore structure, which may lead to high internal surface area (meaning high adsorption capacity in the applications) with low diffusional resistance in the matrix. The swelling patterns of the hydrogels produced in this study by changing radiation doses and ATU content are shown in Figure 1. As shown in Figure 1(A), the swellability of the hydrogels is decreasing with increasing the irradiation doses for the monomer mixture. This is the case of the high density of the crosslinking in the hydrogel structure at high radiation doses [Fig. 1(A)]. As shown in Figure 1(A), the maximum swellability of the hydrogels is about 450%, obtained at 0.2 kGy dose for the hydrogels having the highest ATU content. However, the swellability of the hydrogels is around 100% at 1.40 kGy dose for the same monomer content mixture used for the hydrogels preparation. Swellability is high for the hydrogels produced at low radiation doses. At low radiation doses, the degree of crosslinking in the hydrogel is less, compared to the hydrogels obtained at high radiation doses. Low degrees of crosslinking in the hydrogels allow more water molecule to penetrate inside the hydrogels and swellability of hydrogels could be increased. In Figure 1(B), swelling behaviors of the hydrogels produced with mixtures containing 0, 2.5, 7.5, and 10% of ATU at 1.4 kGy radiation dose are shown. As seen from Figure 1(B), when the content of ATU in the irradiation mix-

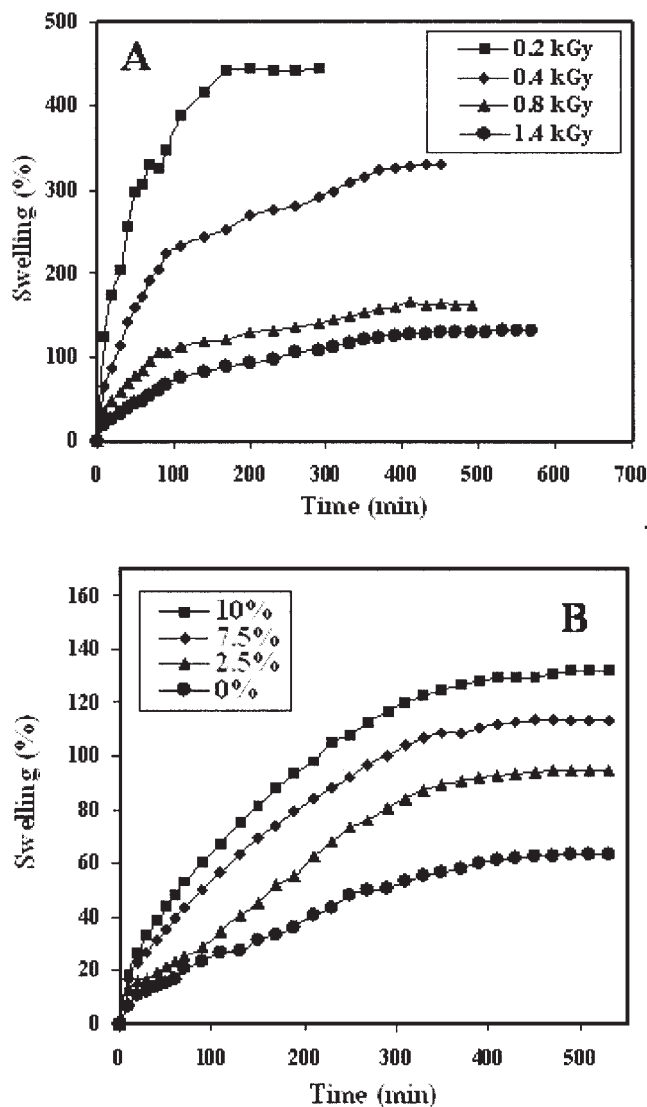


Figure 1 Swelling behavior of poly(NHMMA-ATU) hydrogels: (A) Swelling of poly(NHMMA-ATU) produced from 10% ATU containing mixture at different irradiation doses; (B) Swelling of poly(NHMMA-ATU) produced at different ATU contents at 1.4 kGy radiation dose.

ture was increased, the swelling ratio of the synthesized hydrogels also increased from 58% to 135%, with the increasing ATU content in the irradiation mixture from 0 to 10%. This shows that more ATU in the hydrogel structure provides higher swellability to the hydrogels.

To examine the effect of pH on the swellability of poly(NHMMA-ATU) hydrogels, swelling behaviors of the hydrogels produced at 0.8 kGy irradiation and 10% ATU in the irradiated mixture solution were examined at different pHs and were shown in Figure 2. Equilibrium swelling ratio of the hydrogels are almost the same between pH 2.0 and 8.0. Below the pH 2.0, swelling ratio of the hydrogels decreased dramatically and reached about half of the equilibrium swelling

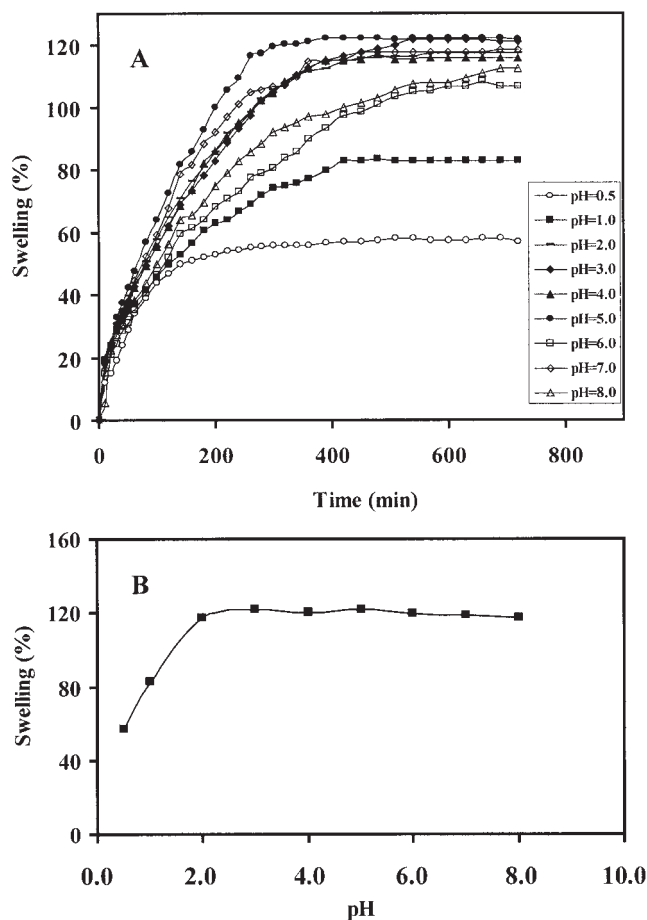


Figure 2 Swelling ratio of poly(NHMMA-ATU) at different pHs. (A) Swelling behavior with time; (B) Swelling equilibrium ratio at different pH values. Radiation dose: 0.8 kGy; ATU content in the irradiation mixture: 10%.

ratio of the hydrogels at pH 0.5, compared to the equilibrium swelling ratio of the hydrogels at high pHs. Decrease in equilibrium swelling ratio of the hydrogels at low pHs is because of the protonation of hydrogels. If the hydrogels had some charge on their interior surfaces, hydrogen bonding capacity of the hydrogels with free water molecules could be decreased and so, equilibrium swelling ratio was decreased. Equilibrium swelling ratio of hydrogels produced at 0.8 kGy irradiation and 10% ATU versus pH is shown in Figure 2(B), to follow the effect of pH on the swelling ratio of the hydrogels. As can be seen from Figure 2(B), when the pH was reduced (from 2.0 to 0.5), swelling ratio of the hydrogels decreased dramatically and reached almost half of the swelling ratio at pH 0.5, compared to the swelling ratio of the hydrogels at pH 2.0.

Elemental analysis results

After all hydrogels were dried in vacuum oven at 60°C for 5 days, elemental analysis of all hydrogels irradi-

ated at different doses and synthesized with different ATU content was carried out. From the nitrogen stoichiometry, and especially sulfur stoichiometry, of the hydrogels, percentage of ATU in the synthesized hydrogels was calculated [Figs. 3(A, B)]. In Figure 3(A), percent of ATU in the hydrogel was followed by changing the ATU percentage in the irradiation mixture. When the ATU percent in the irradiation mixture was increased, the percentage of ATU also increased and reached 4.6% at 10% of the ATU in the irradiation mixture at 0.4 kGy/h radiation dose. Effect of irradiation dose on the percentage of ATU in the hydrogel structure was also investigated [Fig. 3(B)]. When the 7.5% ATU containing monomer mixture was irradiated at different doses with the same irradiation source by changing the irradiation time, the ATU percentage increased and reached 6.45% ATU in the produced hydrogels at 1.4 kGy radiation doses. All of these results showed that by increasing irradiation dose and percentage of ATU in the irradiation monomer mixture, percentage of ATU in the synthesized hydrogels was increased.

FTIR spectra of poly(NHMMA-ATU)

For investigation of the production of poly(NHMMA-ATU) hydrogels, FTIR spectra of two monomers and

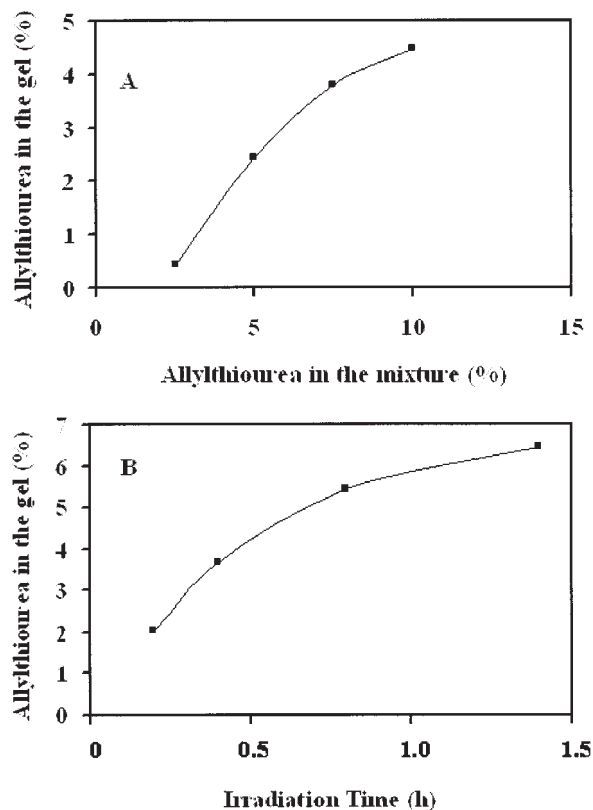


Figure 3 ATU content in the produced hydrogels: (A) Changing the ATU content in the polymerization mixture at 0.4 kGy; (B) Changing the irradiation dose for the hydrogel synthesis for 7.5% ATU.

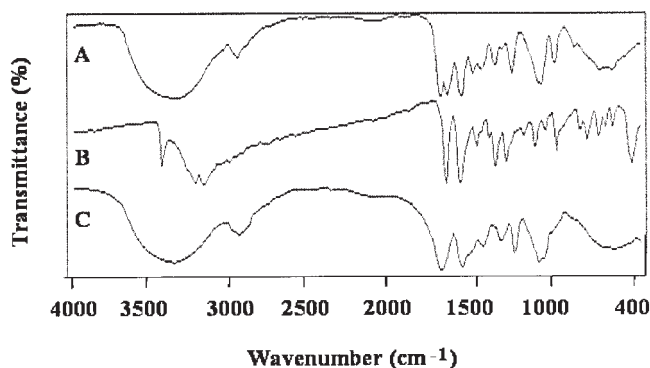


Figure 4 FTIR spectra of the monomer and hydrogels: (A) NHMMA; (B) ATU; (C) Hydrogel synthesized from monomer mixture containing 7.5% ATU. Irradiation dose: 1.4 kGy.

hydrogels were recorded. FTIR spectra of NHMMA, ATU, and poly(NHMMA-ATU) hydrogels are given in Figures 4(A)–4(C). The broad absorption band between 3100 and 3600 cm^{-1} corresponds to N–H and O–H stretching absorption bands of NHMMA [Fig. 4(A)]. The broadening of this band is due to the existence of intermolecular hydrogen bonding. The other absorption bands at 1687, 1636, and 1062 cm^{-1} characterize the existence of C=O, C=C, C–N, and C–O bonds. In the FTIR spectrum of ATU, characteristic absorption bands in the FTIR range are at 3439, 3270, 3231, 1640, 1542, and 447 cm^{-1} , representing asymmetric N–H vibration in NH_2 functional group, overtone band of NH_2 group, N–H vibration of –NH– group, C=C vibration, C=S, and SCN scissor absorption bands [Fig. 4(B)].²⁶ After the polymerization, mainly broad bands appeared on the FTIR spectrum of the polymer [Fig. 4(D)]. The adsorption band between 3050 and 3700 cm^{-1} is really broad in the hydrogel structure due to many functional groups from two different monomers having hydrogen bonding capability. C=C double bond onto the two different monomers disappeared after the polymerization and amide C=O vibration absorption band wavenumber shifted to high wavenumber value. This absorption band is broad compared to the amide C=O vibration absorption band wavenumber of free NHMMA. Also, absorption bands wavenumber of C=S shifted to short wavenumber value because of the hydrogen bonding via sulfur atom in ATU. The absorption band at 1062 cm^{-1} is dominant in the polymer structure. Mainly, this absorption band corresponds to C–O vibration onto the NHMMA. This is a reasonable effect because of the high content of NHMMA in the hydrogel. This will be discussed in the Elemental Analysis section. After the hydrogel samples are heated up to different temperatures (such as 190, 260, 325, and 500°C) under nitrogen atmosphere in the TGA pan, FTIR spectra were recorded from these samples after cooling the sample to the room temperature,

to get more information about the hydrogel structure. These temperatures were chosen by checking the degradation peaks in the TGA curves. After each degradation temperature, sample was cooled and FTIR spectrum was recorded in the separated experiments and given in Figure 5. In Figure 5(A), FTIR spectrum of the hydrogel obtained after heating the hydrogel up to 190°C was shown. In this spectrum, there was no significant change, compared to the original spectrum of the hydrogel. Only intensity of the absorption band at around 3370 cm^{-1} was found to be decreased because of the releasing of water molecules retained in the hydrogels, during normal drying processes at low temperature in vacuum oven. When the FTIR spectrum was recorded for the hydrogel after heating up to 260°C under the nitrogen atmosphere, the absorption bands at 1235, 1005, and 948 cm^{-1} disappeared and the others did not change [Fig. 5(B)]. These absorption bands were assigning to the absorption bands of free ATU retained in the hydrogels, even if the hydrogels were rinsed many times with water after the synthesis. The broad absorption band at 3370 cm^{-1} in the original spectrum of hydrogel [see Fig. 5(A)] was splitted to some absorption bands such as 3585, 3388, 3241, and 3100 cm^{-1} , when the temperature was increased up to 325°C [Fig. 5(C)]. This behavior might be because of the loosing of water from hydrogels. In this manner, hydrogen bonding capacity of the hydrogels decreased and free absorption bands of NH and NH_2 groups appeared in the spectrum. Also, absorption band wavenumber of amide C=O stretching shifted from 1665 to 1693 cm^{-1} because of water elimination and reduction in the intrahydrogen bonding capacity of hydrogels. However, the absorption band at 1154 cm^{-1} that corresponds to – NH_2 absorption band of ATU shifted to 1216 cm^{-1} . When the hydrogel was heated up to 500°C, all absorption bands of the original FTIR spectrum of the hydrogels almost disap-

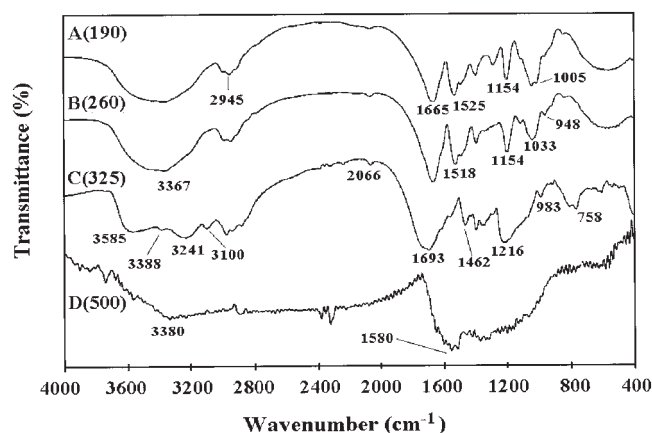


Figure 5 FTIR spectra of poly(NHMMA-ATU) synthesized from monomer mixture containing 7.5% ATU, after heated up to 190°C (A), 260°C (B), 325°C (C), and 500°C (D).

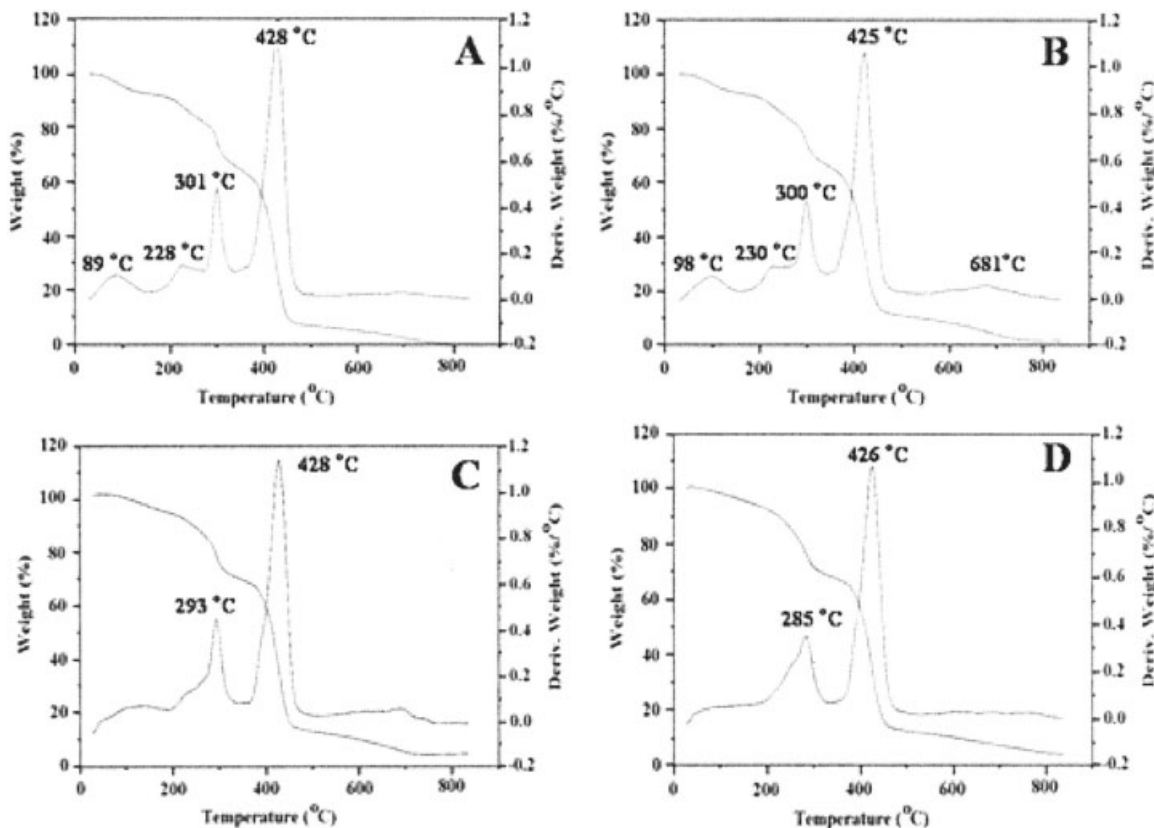


Figure 6 TGA and DTG curves of poly(NHMMA-ATU) hydrogels. Hydrogels synthesized from 7.5% ATU containing monomer mixture at 0.2 kGy (A), 0.4 kGy (B), 0.8 kGy (C), and 1.4 kGy (D).

peared and the structure of the hydrogels destroyed completely [Fig. 5(D)].

Characterization by TGA

To investigate the effect of the different radiation doses on the production of poly(NHMMA-ATU) hydrogels, TGA was performed. For the characterization of the stability of the polymeric hydrogels, TGA results were obtained for all types of polymeric hydrogels. TGA and derivative thermogravimetric (DTA) curves of the hydrogels are shown in Figure 6 with changing radiation doses. At low radiation doses, the conversion of the monomers to the poly(NHMMA-ATU) hydrogels was not completed and some higher-order oligomeric forms were retained in the hydrogels, even if the hydrogels were rinsed many times. In Figure 6(A), beside two main degradation peaks, two other peaks occurred from the degradation of higher-order oligomeric species. The main degradation peaks maxima observed at 301 and 428°C are because of the existence of two different monomers in the hydrogel structure. The other peaks on the DTA curve at 89 and 228°C characterize the water releasing process and oligomeric species degradation. When the radiation dose was increased from 0.2 to 1.4 kGy [Figs. 6(A–D)],

only two main degradation peaks remained and the other low-intensity peaks that correspond to the water releasing and oligomeric degradation disappeared because of the complete conversion of the all monomer to the hydrogels at high radiation doses.

Ionic strength effect on the equilibrium swelling ratio

The equilibrium swelling ratio was examined by changing the ionic strength between 1×10^{-3} and 2.5M in the swelling solution, using NaNO_3 at two different pHs, 0.5 and 7.0 (Fig. 7). At pH 0.5, equilibrium swelling ratio of the hydrogels increased (but not dramatically) to about 7.0% between 1×10^{-3} and 0.1M and then it decreased to about 5.0%, when the ionic strength reached 2.5M. At pH 7.0, the equilibrium swelling ratio remained unchanged between 1×10^{-3} and 0.1M ionic strength, but increased about 10.0% when the ionic strength reached 0.1M. All of these results showed that there was no critical increment when the ionic strength of the swelling solution changed in the wide range of 1×10^{-3} and 2.5M. This means that there was no high degree of the charged functional groups onto the hydrogels except very low pHs.

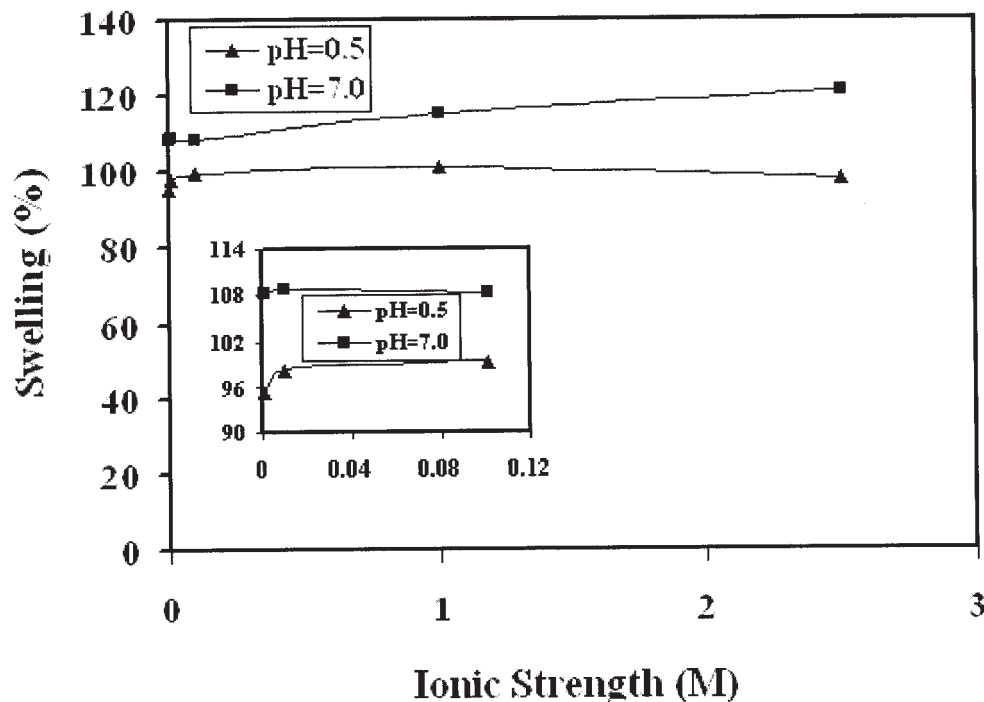


Figure 7 Swelling behavior of poly(NHMMA-ATU) hydrogels in different ionic strength solution at two different pH values. Irradiation dose: 1.4 kGy; ATU content in the irradiation mixture: 7.5%.

Oscillatory swelling behavior

The response of the hydrogels against swellability, by repeatedly changing the pH of the medium from 0.5 to 7.0, was examined and shown in Figure 8. For these experiments, the same hydrogel was replaced in to the solution at pH = 0.5 and kept the hydrogels in this

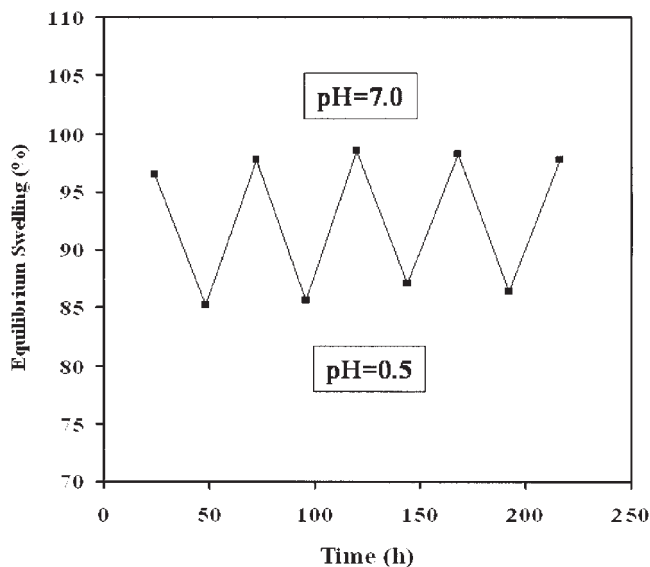


Figure 8 Oscillatory swelling behavior of poly(NHMMA-ATU) hydrogels at pH 0.5 and 7.0 in the 24 h intervals. Irradiation dose: 1.4 kGy; ATU content in the irradiation mixture: 7.5%.

solution for 24 h. After this period, hydrogels were taken out and weighed to find the equilibrium swelling ratio. Then, the same hydrogels were placed into the other solution having pH 7.0, for another 24 h. This process was repeated more than five times. In each case, equilibrium swelling ratios were found to be around 86% + 1% at pH = 0.5 and 97% + 1% at pH = 7.0. The results of these experiments showed that pH-sensitive poly(NHMMA-ATU) hydrogels are quite stable at different pH conditions, showing no structural change in the hydrogels resulted from harsh pH values. Also, the results confirm the reversibility of the swelling process.

CONCLUSIONS

In this communication, synthesis and characterization of poly(NHMMA-ATU) hydrogels synthesized by γ -radiation at different radiation doses and different monomer ratios in water solution was reported. At high radiation doses and also at high ATU content, rigid hydrogels containing high amount of ATU were managed to obtain. Thiourea-type functional group polymeric sorbent could be used for the selective recovery of precious metal ions beside the high concentration of the other metal ions, at low pH values. The hydrogels synthesized in this study have open pore structure to allow the metal ions and also biomolecules penetrate the internal cavities of the hydrogels and increased the adsorption capacity of the adsor-

bents on/in the hydrogels. It was also noted that hydrogels produced at high radiation doses had rigid and swellable structure for the adsorption applications even in the harsh conditions. The precious-metal-ion recovery from geological samples onto these hydrogels is currently under study.

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References

1. Sun, W.; Jiang, L.; Weng, J.; He, B.; Cen, D.; Shen, Z. *React Funct Polym* 2003, 55, 249.
2. Dasgupta, M.; Peori, M. B.; Kakkar, A. K. *Coord Chem Rev* 2002, 233–234, 223.
3. Salih, B. *J Appl Polym Sci* 2002, 83, 1406.
4. Ghoul, M.; Bacquet, M.; Morcellet, M. *Water Res* 2003, 37, 729.
5. Zougagh, M.; Garcia de Torres, A.; Cano Pavón, J. M. *Talanta* 2002, 56, 753.
6. El-Hag Ali, A.; Shawky, H. A.; Abd El Rehim, H. A.; Hegazy, E. A. *Eur Polym J* 2003, 39, 2337.
7. Pekel, N.; Salih, B.; Güven, O. *J Mol Catal B* 2003, 21, 273.
8. Roma-Luciw, R.; Sarraf, L.; Morcellet, M. *Eur Polym J* 2001, 37, 1741.
9. Chang, L.-Y.; Dawison, W.; Zhang, H.; Kelly, M. *Anal Chim Acta* 1998, 368, 243.
10. Kaşgöz, H.; Özgümüş, S.; Orbay, M. *Polymer* 2003, 44, 1785.
11. Li, W.; Zhao, H.; Teasdale, P. R.; Jhon, R. *Polymer* 2002, 43, 4803.
12. Safrany, A. *Radiat Phys Chem* 1999, 55, 121.
13. Kim, S. J.; Park, S. J.; Kim, S. I. *React Funct Polym* 2003, 55, 61.
14. Lee, W.; Shieh, C. *J Appl Polym Sci* 1999, 71, 221.
15. Akkaş, P.; Sari, P.; Şen, M.; Güven, O. *Radiat Phys Chem* 1999, 55, 717.
16. Hoffman, A. S. *Adv Drug Delivery Rev* 2002, 43, 3.
17. Jeong, B.; Bae, Y. H.; Kim, S. W. *Trans Soc Biomater* 2000, 1491.
18. Matthew, H. W.; Salley, S. O.; Peterson, W. D.; Klein, M. D. *Biotechnol Prog* 1993, 9, 510.
19. Hoch, G.; Chauhan, A.; Radke, C. J. *J Membr Sci* 2003, 214, 199.
20. Horvath, J.; Boschetti, E.; Guerrier, L.; Cooke, N. *J Chromatogr A* 1997, 678, 11.
21. Duran, S.; Şolpan, D.; Güven, O. *Nucl Instrum Methods Phys Res Sect B* 1999, 151, 196.
22. Pekel, N.; Savaş, H.; Güven, O. *Colloid Polym Sci* 2002, 280, 46.
23. Ören, S.; Çaykara, T.; Kantoglu, O.; Güven, O. *J Appl Polym Sci* 2000, 78, 2219.
24. Chauhan, G. S.; Guleria, L. K.; Mahajan, S. *Desalination* 2001, 141, 325.
25. Salih, B.; Pekel, N.; Guven, O. *J Appl Polym Sci* 2001, 82, 446.
26. Gambino, D.; Kremer, E.; Baran, E. J. *Spectrochim Acta Part A* 2002, 58, 3085.