

Preparation and Characterization of Novel Poly(glycidyl methacrylate) Beads Carrying Amidoxime Groups

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ABSTRACT: Poly(glycidyl methacrylate) (PGMA) beads with an average size of 350 μm were synthesized by suspension polymerization technique. The PGMA beads were first modified with iminodiacetonitrile (IDAN). Then, the IDAN-modified beads were subsequently modified by hydroxylamine. The IDAN modification and the conversion of the nitrile groups to amidoxime were followed by FT-IR spectroscopy. The surface morphology and thermal behav-

ior of the PGMA and its modified forms were also characterized by scanning electron microscopy and thermogravimetric analysis techniques, further confirming modification and amidoximation. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 2126–2131, 2007

Key words: microspheres; poly(glycidyl methacrylate); suspension; amidoximation

INTRODUCTION

In recent years, the effective treatment of metal ions from an aqueous solution has received much attention because of their toxicities in relatively low concentration and tendency to bioaccumulate.^{1,2} Many publications concentrated on metal ion recovery using chelating polymers, because they are reusable and are easy to handle; as well they have higher adsorption capacities and efficiencies.^{3,4} Therefore, numerous studies have either introduced low-molecular-mass ligands to various synthetic^{5–7} and natural polymeric matrices,^{8–10} or synthesized a copolymer containing conventional chelating vinyl monomer to form a chelating resin.^{11–13}

Previous studies¹⁴ prepared a chelating vinyl monomer, glycidyl methacrylate–iminodiacetic acid (GMA-IDA), via an epoxy group reaction of GMA with IDA. This monomer has the hydrophilic nature of hydroxyl and iminodiacetate groups and has an adequate affinity to metal ions.⁷ Many types of adsorbents were also developed and used for the recovery of uranium from seawater and aqueous media.^{15–18} Among them, amidoxime group carrying adsorbents were shown to be the most effective for recovery of uranium from seawater and aqueous media.^{18–21} Lin and coworkers observed that the amidoxime-chelating resins were useful for recovering

uranium from seawater and enrichment or separation of noble metal ions from aqueous systems.²² To the best of our knowledge, although a great deal of research has been conducted on the amidoxime group carrying adsorbents, poly(glycidyl methacrylate) (PGMA) beads with surface-grafted chains carrying two amidoxime groups per repeating unit have not been reported in the literature.

The objective of this study is to report the results on the synthesis of PGMA beads by suspension polymerization technique, modification of PGMA beads with iminodiacetonitrile (IDAN) and conversion of two adjacent pendant nitrile groups into amidoximes. In FT-IR spectroscopy studies, the conversion was ascertained from the change in the characteristic peak intensities. Thermal analysis and surface morphology studies were also performed to determine changes in the thermal behavior and on surface appearance of the PGMA and its modified forms.

EXPERIMENTAL

Materials

Glycidyl methacrylate (GMA, Aldrich, Milwaukee, WI) and ethylene glycol dimethacrylate (EGDMA, Aldrich) were purified by passing through active alumina. Benzoyl peroxide (BPO, Merck, Darmstadt, Germany) and poly(*N*-vinyl-2-pyrrolidone) (PVP, $M_w = 55,000$ g/mol, Aldrich) and tricalcium phosphate (TCP, Merck) were utilized as the initiator and stabilizers, respectively. Iminodiacetonitrile (IDAN, Aldrich) and hydroxylamine hydrochloride ($\text{NH}_2\text{OH HCl}$, Aldrich) were used as received. Distilled water was used in all experiments.

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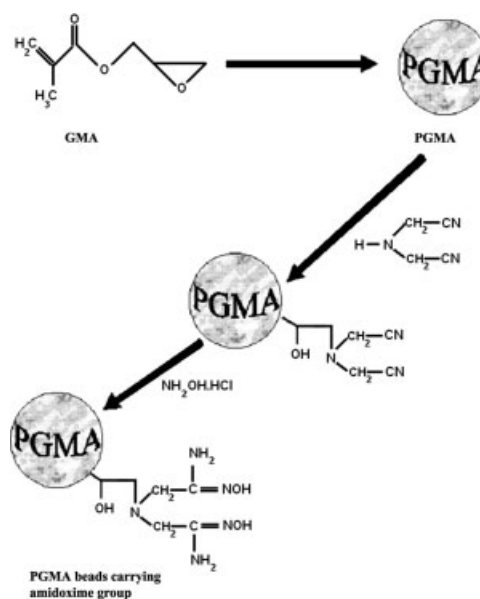
Preparation of PGMA beads

A typical procedure for the preparation of PGMA beads is exemplified later and shown in Scheme 1. The dispersion medium was prepared by dissolving 1 g of PVP and 1 g of TCP in 50 mL of deionized water. On the other hand, 0.14 g BPO was dissolved within the monomer phase comprised of 2 mL GMA and 0.15 mL EGDMA. This solution was then transferred into the dispersion medium contained in a mechanically stirred glass polymerization reactor which was in a thermostatic water bath. The suspension was sealed and stirred at 400 rpm, at room temperature, for 15 min for complete mixing of the two phases. Then, the reactor temperature was raised and kept at 70°C for 2 h. At the end of period, the temperature was increased to 85°C and the polymerization was completed after 2 h. A washing procedure was applied after polymerization, to remove the diluents and any unreacted monomer from the product. The polymer beads were filtered and resuspended within ethyl alcohol. The new dispersion was stirred for about 2 h at room temperature and the beads were isolated by decanting the liquid part. The beads were washed twice with ethyl alcohol, and then three times with deionized water using the same procedure. The washed beads were dried in a vacuum oven at 50°C for 24 h. The average size and size distribution of the PGMA beads were determined by screen analysis performed by using Tyler Standard Sieves. The PGMA beads with an average size of 350 μm were obtained.

Modification of PGMA beads

The preparation of PGMA beads with surface-grafted chains carrying two pendant amidoxime groups per monomeric unit consisted of two steps: (1) modification of epoxy groups with IDAN and (2) amidoximation reaction of nitrile groups. First, the PGMA beads were immersed in 0.425M IDAN in ethanol solution. The reaction was performed at 80°C. During the modification reaction of epoxy group with IDAN, samples were taken from the reaction vessel at certain time intervals, and binding of IDAN groups onto the epoxy group of PGMA was followed by determining the changes in $\text{C}\equiv\text{N}$ bonds of polymer from respective FT-IR spectra. After grafting of IDAN groups, the remaining unreacted epoxide groups were hydrolyzed with dilute HCl (10 mL, 0.1M) solution for 2 h at 80°C. Subsequently, IDAN-modified PGMA beads were washed with methanol and then dried at 50°C in a vacuum oven.

Second, the modified PGMA beads obtained were reacted with the methanol solution of hydroxylamine hydrochloride–sodium hydroxide (1 : 1 in $\text{NH}_2\text{OH}\cdot\text{HCl}\text{--NaOH}$) at 80°C. Similarly, as mentioned earlier, the conversion to amidoxime structure was also



Scheme 1 Schematic preparation of poly(glycidyl methacrylate) beads carrying amidoxime group.

followed by determining the changes in $\text{C}\equiv\text{N}$ bonds of polymer from respective FT-IR spectra. After amidoximation reaction was complete, the amidoximated PGMA beads taken from reaction vessel were washed with distilled water and then dried at 50°C in a vacuum oven.

Characterization of PGMA beads and its modified forms

To characterize PGMA beads and their modified forms, a detailed FT-IR analysis was made. FT-IR spectra of these beads were taken by using Nicolet 520 FT-IR Spectrometer. The dry beads [about (0.1 g)] were thoroughly mixed with KBr (0.1 g), IR grade, Merck] and pressed into a pellet form, and the spectrum was then recorded. Surface morphology of the unmodified and modified PGMA beads were determined by a scanning electron microscope (SEM; JEOL, JSM-6360 LV, Tokyo, Japan). PGMA beads were coated with a thin layer of gold in vacuum and photographed in the electron microscope at 30 \times and 3000 \times magnifications. Thermal analysis was performed by utilizing TA instrument 2050 thermogravimetric analyzer (TGA). All tests were conducted in a N_2 purge (25 mL/min), using sample weights of 5–10 mg over a temperature range 20–600°C at a scan rate of 10°C/min. Dynamic mass loss curves and their derivatives were obtained.

RESULTS AND DISCUSSION

A novel PGMA beads with surface-grafted chains carrying two amidoxime groups per repeating unit

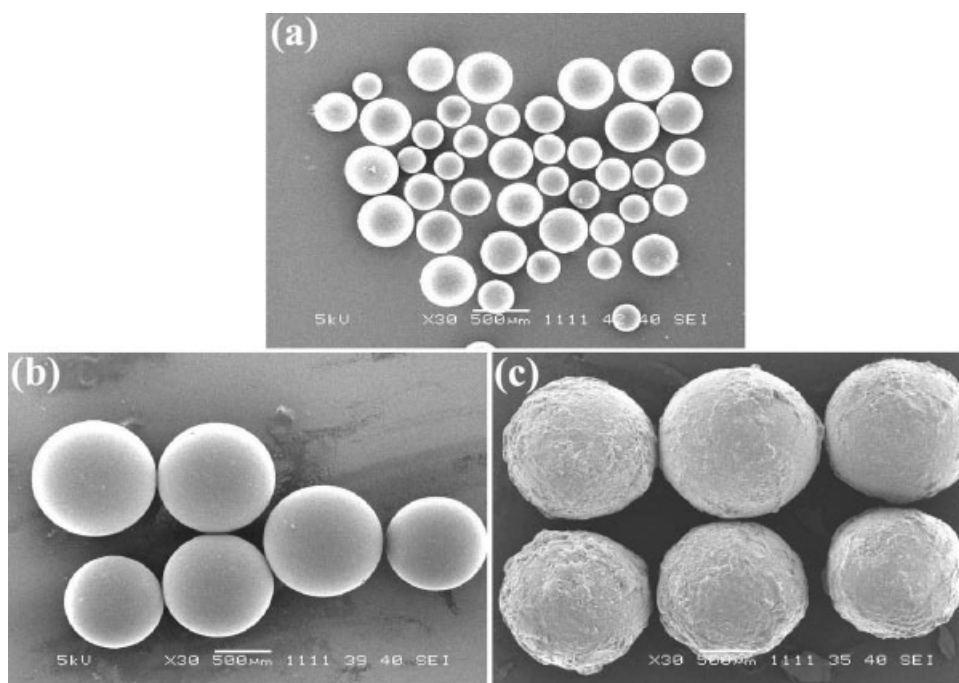


Figure 1 SEM photographs of (a) PGMA, (b) IDAN-modified (96 h), and (c) amidoximated PGMA beads (4.0 h) (magnification: $\times 30$).

were prepared at three steps. As mentioned in the experimental section, first, PGMA beads were synthesized by suspension polymerization technique. Second, IDAN-containing two nitrile groups was attached onto PGMA beads by opening of the epoxy ring. Finally, the pendant nitrile groups were converted to amidoxime groups by using hydroxylamine hydrochloride in methanol solution. Possible reaction mechanism was shown in Scheme 1.

To compare the difference in the physical appearance of functionalized, amidoximated, and original samples, and to see if there were any observable physical changes on the PGMA beads that might have occurred during the conversion process and subsequent treatment with IDAN or after amidoximation reaction, surface morphology of these samples was investigated by using SEM technique. SEM photographs of the PGMA, IDAN-modified, and amidoximated PGMA beads were given in Figures 1 and 2. As seen in Figure 2(a), PGMA beads had a reasonably smooth surface. It should be noted that surface morphologies of both the IDAN modified and the amidoximated PGMA beads were different than that of the unmodified PGMA beads [Fig. 2(b,c)]. That is, the smooth appearance of PGMA bead surface observed in Figure 2(a) disappeared with the modification process. These changes in the surface appearance of the treated PGMA beads are the physical evidences for the modification and amidoximation process. On the other hand, modification processes lead to increase in diameter of the PGMA

beads by at least 20, indicating that there is not only grafting on the surface but also inside of these beads.

For the spectroscopic characterization of PGMA and the IDAN-grafted PGMA beads, a baseline FT-IR spectrum of PGMA was recorded. In the IR spectrum of PGMA given in Figure 3(a), the strong band observed at 1736 cm^{-1} is due to the $\text{C}=\text{O}$ stretching vibration, whereas the band at 1265 cm^{-1} is due to the symmetrical stretching of the epoxy ring. In FT-IR spectra of IDAN, the sharp absorbance band at 2249 cm^{-1} is very characteristic of $\text{C}\equiv\text{N}$ and also the broad band at 3500 cm^{-1} is the $-\text{OH}$ group, which originates from ring opening of epoxy group. To follow the extent of reaction replacement of epoxide groups by IDAN groups, the characteristic $\text{C}\equiv\text{N}$ band at 2249 cm^{-1} was used. The appearance of the $\text{C}\equiv\text{N}$ band with time can be monitored to check and control the reaction completion. Moreover, the broad hydroxyl band, which formed during the ring opening of epoxy group of PGMA, can be clearly seen at 3400 cm^{-1} . After 24 h of the beginning of reaction, the sharp band at 2249 cm^{-1} was observed due to the formation of characteristic $\text{C}\equiv\text{N}$ bonds in polymer. During the course of the reaction conversion, the 1265 cm^{-1} band shows that the epoxy group content decreases [Fig. 3(b-e)]. After 96 h, this band at 1265 cm^{-1} corresponding to the symmetrical stretching of the epoxy ring did not change, indicating that the reaction is almost complete in 96 h.

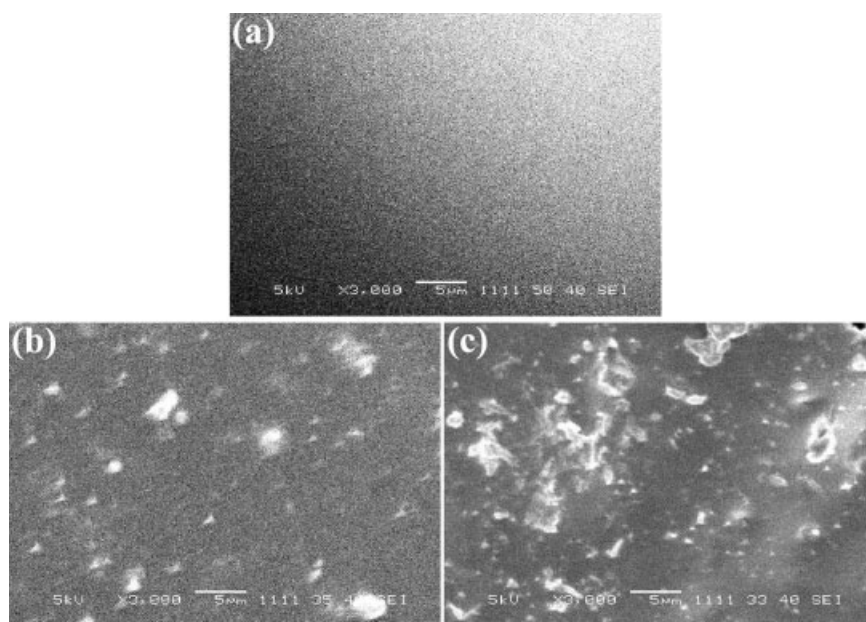


Figure 2 SEM photographs of (a) PGMA, (b) IDAN-modified (96 h), and (c) amidoximated PGMA beads (4.0 h) (magnification: $\times 3000$).

The course of the conversion of the IDAN-modified PGMA into amidoximated PGMA was also followed by recording FT-IR spectra of different samples after 0.5, 2, 3, and 4 h from the initiation of the reaction [as given in Fig. 4(a–f)]. During the modification process, the 2249 cm^{-1} band shows that the $\text{C}\equiv\text{N}$ group content decreases with the reaction time. After 4 h of amidoximation time, the band at 2249 cm^{-1} was observed to disappear due to depletion of the $\text{C}\equiv\text{N}$ groups [Fig. 4(f)], supporting the idea that the conversion of $\text{C}\equiv\text{N}$ groups to $\text{H}_2\text{N}-\text{C}=\text{NOH}$ groups were almost complete. In addition, oximes also show a weak band around 1640 cm^{-1} . These results clearly show the disappearance of original $\text{C}\equiv\text{N}$ groups and formation of $\text{H}_2\text{N}-\text{C}=\text{NOH}$ groups through the treatment with hydroxylamine under specified reaction conditions.

In addition to SEM and FT-IR techniques used to characterize the IDAN-modified and amidoximated PGMA beads, TGA method was also employed to understand the thermal behavior of these products of conversion. Typical weight loss (TG) and derivative of weight loss (DTG) curves of PGMA, IDAN-modified, and amidoximated PGMA beads at a heating rate $10^\circ\text{C}/\text{min}$ under nitrogen atmosphere are shown in Figures 5 and 6. From the TG curves, initial and final degradation temperatures were determined. From DTG curves, the maximum temperature of weight loss was also noted.

The mass loss of PGMA begins at $\sim 228^\circ\text{C}$ [Fig. 5(a)] and reaches to a maximum at 247°C [Fig. 6(a)]. The TG curve of PGMA indicates one reaction stage [Fig. 5(a)], which is reflected as a single peak in the DTG curve [Fig. 6(a)]. Initial degradation tempera-

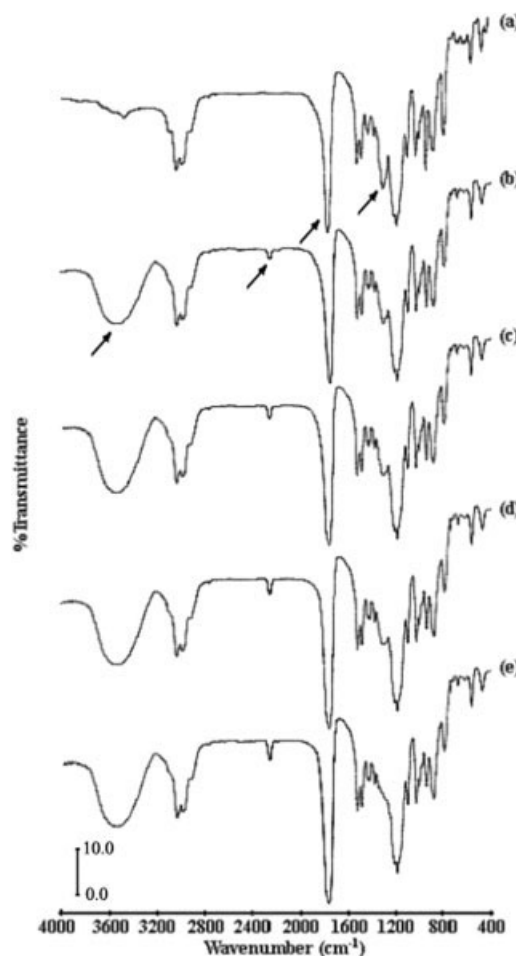


Figure 3 FT-IR spectra of the IDAN-modified PGMA at different reaction times. (a) Trunk PGMA, (b) 24 h, (c) 48 h, (d) 72 h, and (e) 96 h.

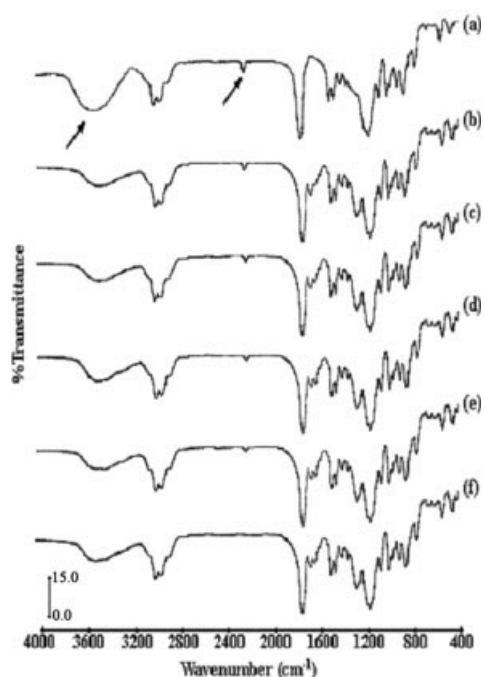


Figure 4 FT-IR spectra of the amidoximated PGMA at different reaction times. (a) 0 h, (b) 0.5 h, (c) 1.0 h, (d) 2.0 h, (e) 3.0 h, and (f) 4.0 h.

ture of PGMA showed that the degradation was due to random chain scission.²³ On the other hand, the IDAN-modified and amidoximated PGMA degrade

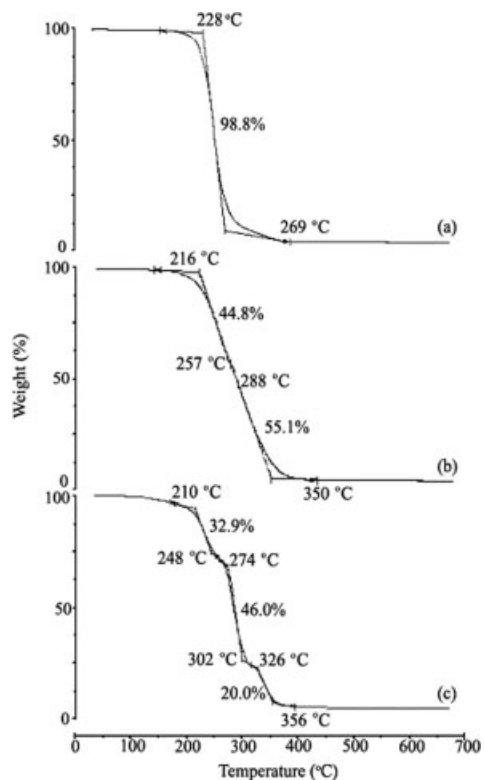


Figure 5 TGA thermograms of (a) PGMA, (b) IDAN-modified (96 h), and (c) amidoximated PGMA (4.0 h).

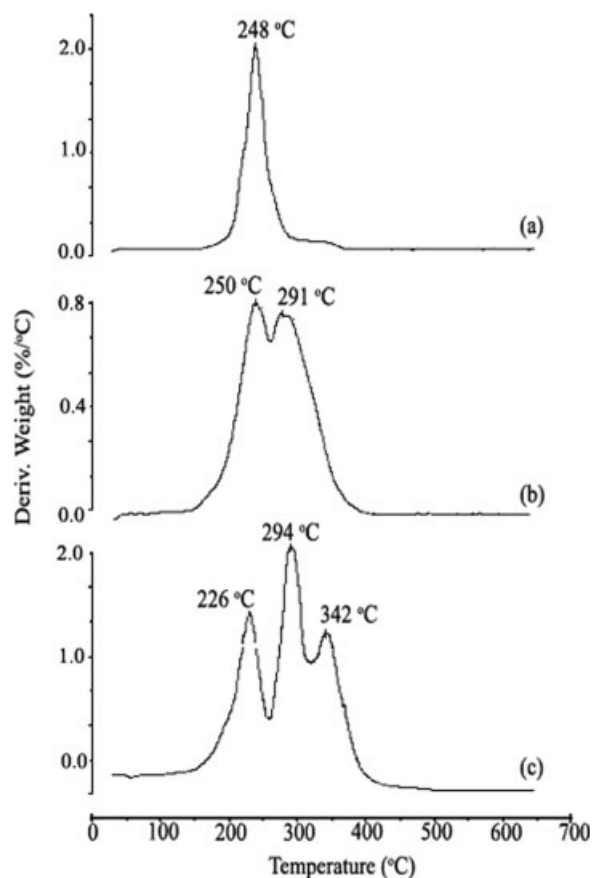


Figure 6 DTGA thermograms of (a) PGMA, (b) IDAN-modified (96 h), and (c) amidoximated PGMA (4.0 h).

in two and three steps, respectively. This is evidenced by the appearance of distinct peaks in DTG thermograms. Stepwise degradation of IDAN-modified and amidoximated PGMA indicates that every functional group introduced on the trunk polymer had different thermal stabilities, giving rise to the appearance of distinct, separate derivative peaks. DTG curves clearly show the sequence of chemical modifications introduced into PGMA. IDAN modification and amidoximation, however, seem to render the base polymer more susceptible to thermal degradation. The modified PGMA beads, however, can still be used safely up to processing temperatures of 200°C. This is of practical importance, since the beads to be used for uranyl and other heavy metal ions adsorption need to be treated at relatively high temperatures for recovery purposes.

CONCLUSIONS

In this study, a novel PGMA beads containing double amidoxime groups per repeating unit were synthesized with the anticipation of enhanced uranyl ion uptake capacity. The incorporation of the amidoxime groups was confirmed by FT-IR spectra. The characteristics of

the PGMA and its modified forms were studied by TGA and SEM analysis. It was found that the beads possessed good morphological properties, and thermal and chemical stability suitable for practical use. The unique advantage of the modified PGMA beads is that they contain double amidoxime groups per repeating unit, an additional dimethylene spacer unit between neighboring amidoxime groups in each monomeric unit on the surface. Further studies related to the use of these beads for uranyl ion adsorption from different media (e.g., sea water or aqueous solutions). The results pertaining to affinity of this novel adsorbent against uranyl ions in batch and continuous adsorption process will be the subject of another publication.

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