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Preparation and characterization of poly(isobutyl methacrylate) microbeads with grafted amidoxime groups

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Abstract

Poly(isobutyl methacrylate) (PiBMA) microspheres with a 800- to 1500- μm diameter range synthesized by suspension polymerization technique were used as the trunk polymer in the preparation of a highly efficient new adsorbent. Glycidyl methacrylate (GMA) was grafted onto the trunk polymer by pre-irradiation grafting technique. Grafting conditions were optimized, and GMA grafted PiBMA beads were modified with iminodiacetonitrile (IDAN) in ethanol at 80 °C. The nitrile groups were then amidoximated by using 6% (m/v) hydroxylamine hydrochloride in methanol solution. The IDAN modification and the conversion of the nitrile groups to amidoxime were followed by FT-IR spectroscopy. The surface morphology and thermal behavior of the PiBMA and its modified forms were also characterized by scanning electron microscopy (SEM) and thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) techniques further confirming modification and amidoximation.

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Keywords: Microspheres; Poly(isobutyl methacrylate); Radiation grafting; Amidoximation

1. Introduction

Uranium is a potential environmental pollutant, especially in mining industry wastewater, and the migration of uranium in nature is important in this context. In view of the anticipated exhaustion of terrestrial uranium reserve in the near future, research has been directed toward the recovery of uranium from nonconventional sources, such as coal and natural waters (0.1–10 mg U/m³), and especially from seawater (2.8–3.3 mg U/m³). The recovery of uranium from contaminated water of flooded mines (0.1–15 mg U/m³) may help to prevent a very important environmental problem (Akkaş Kavaklı and Güven, 2004). To recover uranium from different media, numerous resin with various chelating groups are used (Akkaş Kavaklı and Güven, 2004; Saito et al., 1990; Lei et al., 1994; Kabay and Egawa, 1993; Özyürek et al., 2003).

The most preferred of these adsorbents are those containing amidoxime groups, which show high selectivity towards uranyl ion. Sekiguchi et al. (1994) and Kobota and Shigehisa (1995) have prepared amidoxime group containing resin and showed the recovery of uranyl ion from seawater with high adsorption yield. Recently, Akkaş Kavaklı et al. (2004), Akkaş Kavaklı and Güven (2000) and Saraydın et al. (1995) have prepared a new type of fibrous adsorbent with adjacent amidoxime groups by radiation-induced graft polymerization to recover uranyl and other transition metal ions from seawater, and aqueous media at very low concentration levels more efficiently. The unique advantage of these polymers is that they contain double amidoxime groups per repeating unit, and additional diethylene spacer unit between neighboring amidoxime groups in each monomeric unit (Akkaş Kavaklı et al., 2004). In addition to using fibrous adsorbents, the polymeric beads with surface grafted chains carrying two pendant amidoxime groups in each monomeric unit may be also used as adsorbent for the purpose of separation of uranyl ions either for purification or enrichment. To the

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best of our knowledge, although a great deal of research has been conducted on the amidoxime group carrying adsorbents, poly(isobutyl methacrylate) (PiBMA) beads with grafted chains carrying two amidoxime groups per repeating unit have not been reported in the literature. The unique advantage of the modified PiBMA 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. In addition, these novel PiBMA beads carrying double amidoxime groups per repeating unit may be more accessible for the adsorption of uranyl ions in aqueous solutions at very low concentration levels (ppb) than conventional adsorbents having only one amidoxime group per repeating unit.

The objective of this study is to report the results on the grafting of glycidyl methacrylate (GMA) onto PiBMA beads by using the pre-irradiation grafting method, modification with iminodiacetonitrile (IDAN) and conversion of two adjacent pendant nitrile groups into amidoximes. PiBMA was chosen as the material for synthesizing the core of microspheres because of both porous properties and swollen in GMA-methanol mixture which make available a greater surface area on the bead for grafting. In FT-IR spectroscopy studies, the extent of the modification and 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 PiBMA and its modified forms. Further studies related to use of these beads for heavy metal ion adsorption from different media (e.g. sea water or aqueous solutions). The results pertaining to affinity of this novel adsorbent against heavy metal ions in batch and continuous adsorption process will be the subject of another publication.

2. Experimental

2.1. Materials

The isobutyl methacrylate (iBMA) and GMA monomers used in this study were supplied from Aldrich Company, were purified by passing through active alumina. The ethylene glycol dimethacrylate (EGDMA) crosslinking agent (Merck Darmstadt, Germany) was purified by the same method. Benzoyl peroxide (BPO) initiator supplied from BDH (Poole, England), was purified by recrystallization twice from methanol before use. Poly(*N*-vinyl-2-pyrrolidone) (PVP) and tricalcium phosphate (TCP) obtained from BDH and Merck, respectively, were selected as suspension stabilizers and used without further purification. Hexane and dioxane were purchased from BDH and used without any purification. IDAN and hydroxylamine hydrochloride ($\text{NH}_2\text{OH} \cdot \text{HCl}$) were obtained from Aldrich Company and used as received. Distilled water was used in all experiments.

2.2. Synthesis of PiBMA beads

To obtain porous PiBMA spheres with an average diameter of 800–1500 nm, the following procedure was applied. The monomer/water ratio selected as 1/5 by volume and dispersion medium was prepared by dissolving predetermined amounts of PVP and TCP in distilled water. The initiator concentration was selected as 1 g BPO/100 g iBMA. The crosslinking agent and porogen (hexane/dioxane = 1/4 weight ratio) were added to monomer phase. Monomer phase was then transferred into dispersion medium placed in a mechanically stirred (400 rpm) round-bottom cylindrical reactor which was thermostatically controlled to 61 °C. All experiments were carried out in nitrogen atmosphere at 70 °C. The experimental conditions described above were set after some preliminary trials of different conditions to achieve an average sphere size of 800–1500 nm. After completion of the polymerization, the spheres were cleaned by several washing steps with hydrochloric acid, alcohol water and then dried in a vacuum oven.

2.3. Preparation of PiBMA beads carrying two amidoxime groups per repeating unit

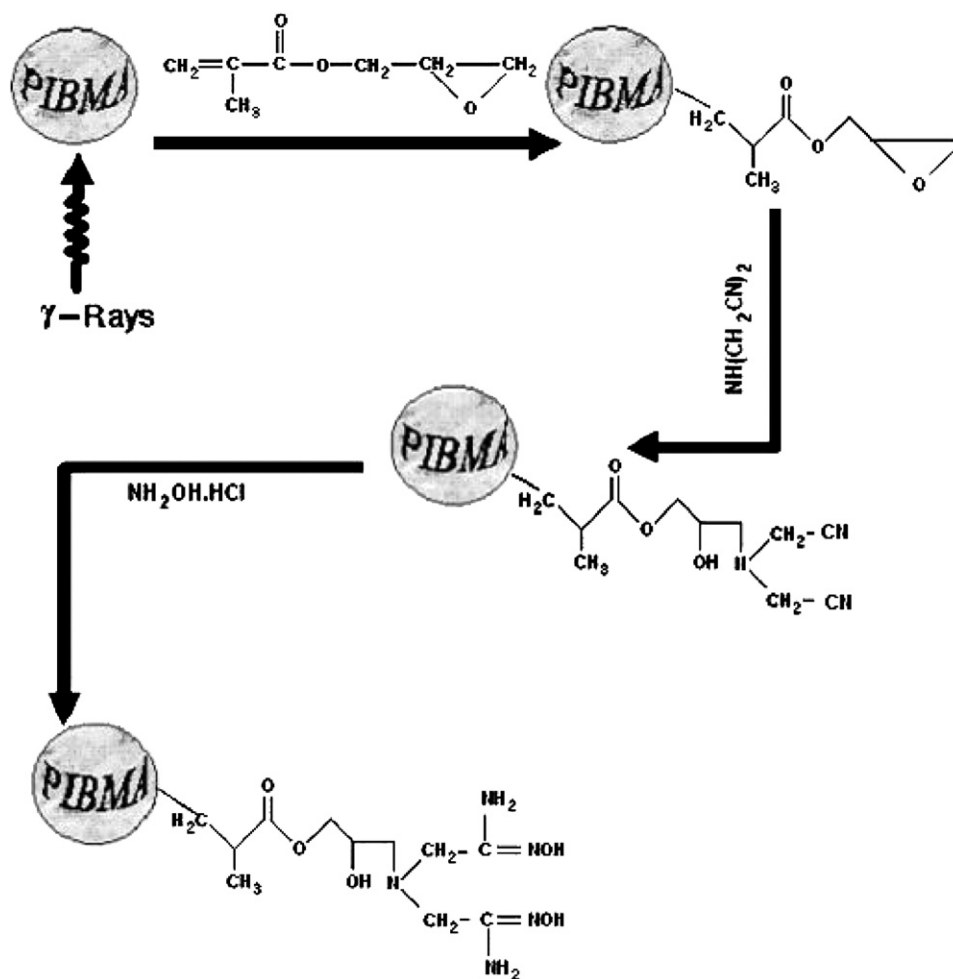
In order to prepare the PiBMA beads with surface grafted chains carrying two pendant amidoxime groups per monomeric unit the following three steps were applied; (1) grafting of an epoxy-group containing monomer (GMA) by pre-irradiation grafting technique, (2) modification of epoxy groups with IDAN, and (3) amidoximation reaction of nitrile groups on the grafted chains.

Firstly, the irradiation of PiBMA beads (1.0 g) under nitrogen atmosphere in a pyrex tube and sealed were carried out at a dose rate of 2.61 kGy/h in a PX- γ -30 Isslodovateji irradiator. After irradiation, the GMA solution in methanol (10% in volume, 10 mL) was injected into the sealed pyrex tube and waited for 24 h at 40 °C. The resulting grafted PiBMA was separated from the unreacted monomers and homopolymer by washing with methanol several times and dried under vacuum and weighed. The degree of grafting (DG) was calculated from the mass gain using the following equation:

$$\text{DG} = \frac{m_1 - m_0}{m_0} \times 100, \quad (1)$$

where m_0 and m_1 are the masses of the trunk PiBMA and GMA grafted PiBMA in dry state, respectively.

Secondly, the GMA grafted PiBMA beads were immersed in 0.425 M IDAN in ethanol solution (10 mL). 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 GMA was followed by determining the changes in $\text{C}\equiv\text{N}$ bonds of polymer from respective FT-IR spectra. After grafting reaction of IDAN groups, the remaining unreacted epoxide



Scheme 1.

groups were hydrolyzed with dilute HCl solution (10 mL, 0.1 M) for 2 h at 80 °C. Subsequently, IDAN modified PiBMA beads were washed with methanol and then dried at 50 °C in vacuum oven.

Finally, the IDAN modified PiBMA beads obtained were reacted with the methanol solution of hydroxylamine (1:1 in $\text{NH}_2\text{OH} \cdot \text{HCl}-\text{NaOH}$) at 80 °C. Similarly, as mentioned above, the conversion to amidoxime structure was also followed by determining the changes in $\text{C}\equiv\text{N}$ bonds of polymer from respective FT-IR spectra. After amidoximation reaction was completed, the amidoximated PiBMA beads taken from reaction vessel were washed with distilled water and then dried at 50 °C in a vacuum oven.

2.4. Characterization of PiBMA beads and its modified forms

In order to characterize PiBMA 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 PiBMA beads (about 0.1 g) was thoroughly mixed with KBr (0.1 g, IR Grade, Merck,

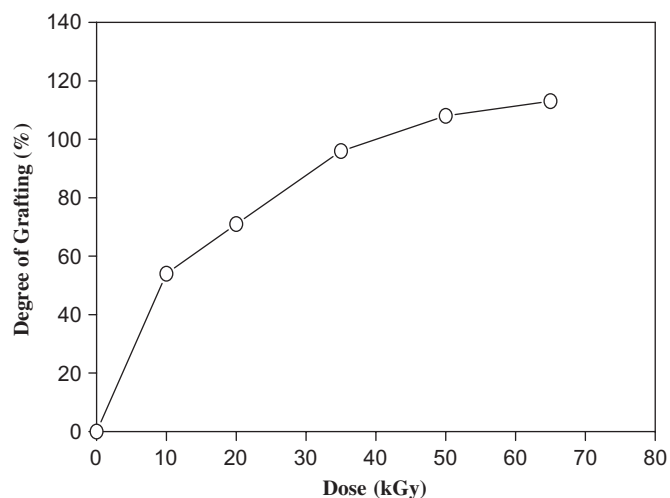


Fig. 1. Effect of irradiation dose on the degree of grafting of GMA onto trunk PiBMA beads.

Germany), and pressed into a pellet form and the spectrum was then recorded. Surface morphology of the unmodified and modified PiBMA beads were determined by a scanning

electron microscope (SEM) (JEOL, JSM-6360 LV, Tokyo, Japan). PiBMA beads were coated with a thin layer of gold in vacuum and photographed in the electron microscope $30\times$ 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. The glass transition temperatures of pure PiBMA and its modified forms were determined by use of a TA instrument DSC 2010 thermal analyzer system.

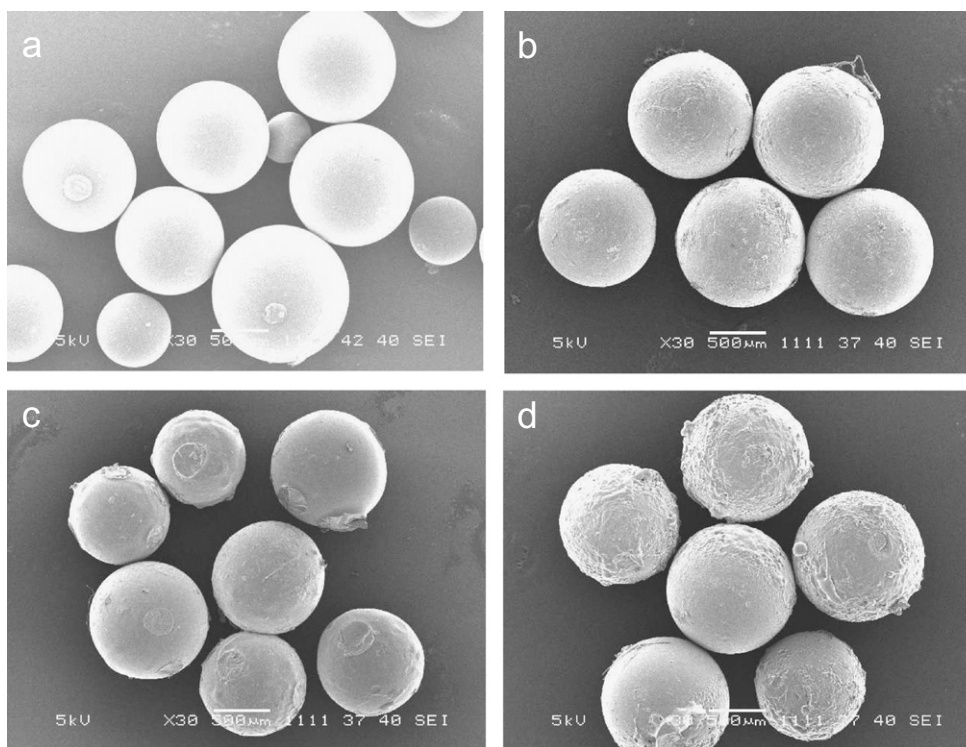


Fig. 2. The SEM photographs of (a) trunk PiBMA, (b) GMA grafted, (c) IDAN modified, and (d) amidoximated PiBMA beads (magnification:30 \times).

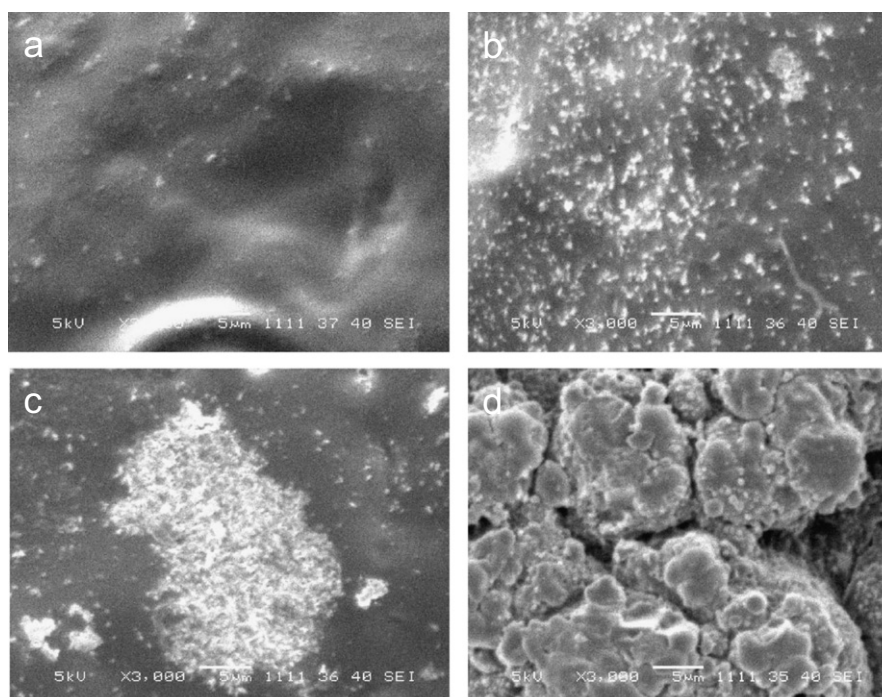


Fig. 3. SEM photographs of (a) trunk PiBMA, (b) GMA grafted, (c) IDAN modified, and (d) amidoximated PiBMA beads (magnification:3000 \times).

DSC was calibrated with metallic indium (99.9% purity). All samples were tested in crimped aluminum pans at a heating rate of 10 °C/min under dry N₂ gas (25 mL/min) over a temperature range from 20 to 170 °C. The glass transition temperatures were determined as the average at least three separate measurements as the midpoints of reverse “S”-shaped thermograms. The experimental errors in the individual measurements were estimated to be less than 0.5 °C.

3. Results and discussion

PiBMA beads with surface grafted chains carrying two amidoxime groups per repeating unit were prepared at three steps. As mentioned in the experimental section, firstly, GMA monomer was grafted onto PiBMA beads by pre-irradiation grafting technique. Secondly, IDAN containing two nitrile groups was attached onto GMA units 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.

The effect of total dose on the degree of GMA grafting on PiBMA beads was presented in Fig. 1. The optimum GMA grafting time (contact with monomer solution) and grafting conditions were previously determined to be 24 h and 10 wt% GMA in methanol at 40 °C, respectively. However, it is well known that the type of monomer, solvent, radiation dose rate, and total dose/time directly affect the degree of grafting. Fig. 1 exhibits an increase in percent grafting with the increase in dose of irradiation up to 50 kGy; beyond this there is tendency to level off. During the grafting reaction, the availability of GMA monomer is higher in the initial stages and hence, the monomer can diffuse very easily to the grafting sites and grafts readily onto PiBMA beads. The increasing content of grafted PGMA may act as a barrier against the diffusion of monomer into the trunk polymer matrix, and resulting with a decrease in the grafting inside of PiBMA microspheres. For all characterization and modification processes, 30 kGy pre-irradiated PiBMA beads were used.

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 PiBMA beads which 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 PiBMA, IDAN modified and amidoximated PiBMA beads were given in Figs. 2 and 3. As seen in Fig. 3(a), PiBMA beads had a reasonably smooth surface. It should be noted that surface morphologies of the GMA grafted, the IDAN modified and the amidoximated PiBMA beads were different than that of the unmodified PiBMA beads (Figs. 3(b)–(d)). That is, the smooth appearance of PiBMA bead surface observed in Fig. 3(a) disappeared with the modification process. These

changes in the surface appearance of the PiBMA beads are the physical evidences for the modification and amidoximation process. On the other hand, modification processes lead to increase in diameter of the PiBMA beads by at least 14, indicating that there is not only grafting on the surface but also inside of these beads.

For the spectroscopic characterization of the GMA grafted PiBMA and the IDAN modified structure, a baseline FT-IR spectrum of the GMA grafted PiBMA was recorded. In the FT-IR spectrum of the trunk polymer PiBMA given in Fig. 4(a), the strong band observed at 1736 cm⁻¹ is due to the C=O stretching vibration, whereas the bands at 950 and 810 cm⁻¹ in Fig. 4(b) spectrum are bending and an antisymmetric band of the epoxy ring belongs to the GMA units on the PiBMA beads. In FT-IR spectra of IDAN modified PiBMA, the sharp

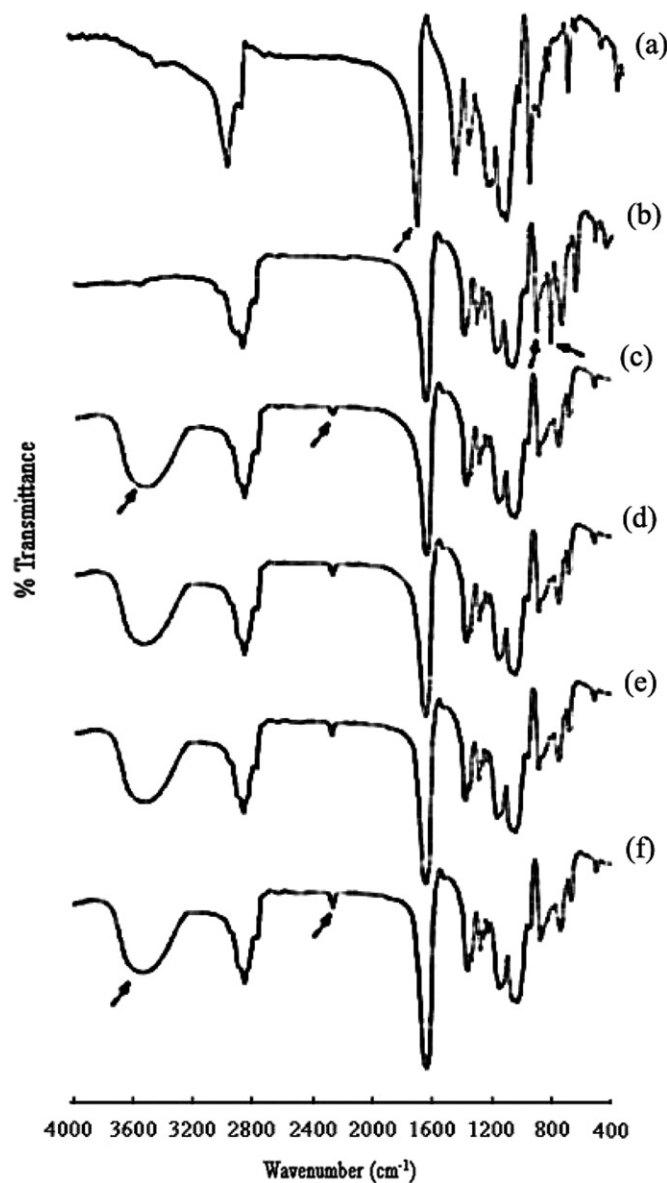


Fig. 4. FT-IR spectra of the IDAN modified PiBMA at different reaction times. (a) Trunk PiBMA, (b) 0 h, (c) 24 h, (d) 48 h, (e) 72 h, and (f) 96 h.

absorbance band at 2249 cm^{-1} is very characteristic of $\text{C}\equiv\text{N}$ and also the broad band at 3400 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 the GMA 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 band intensity of bending and an antisymmetric band of the epoxy ring at 950 and 810 cm^{-1} decrease as the intensity of the $\text{C}\equiv\text{N}$ band at 2249 cm^{-1} increases (Figs. 4(c)–(f)). After 96 h, these bands at 950 and 810 cm^{-1} corresponding to the bending and an antisymmetric band of the epoxy ring did not change, indicating that the reaction is almost complete in 96 h.

The course of the conversion of the IDAN modified PiBMA into amidoximated PiBMA was also followed by recording FT-IR spectra of different samples after 0.5, 1.0, 2, 3, and 4 h from the initiation of the reaction (as given in Figs. 5(b)–(f)). As can be seen from Fig. 5, intensities of the $\text{C}\equiv\text{N}$ band at 2249 cm^{-1} of the IDAN modified PGMA

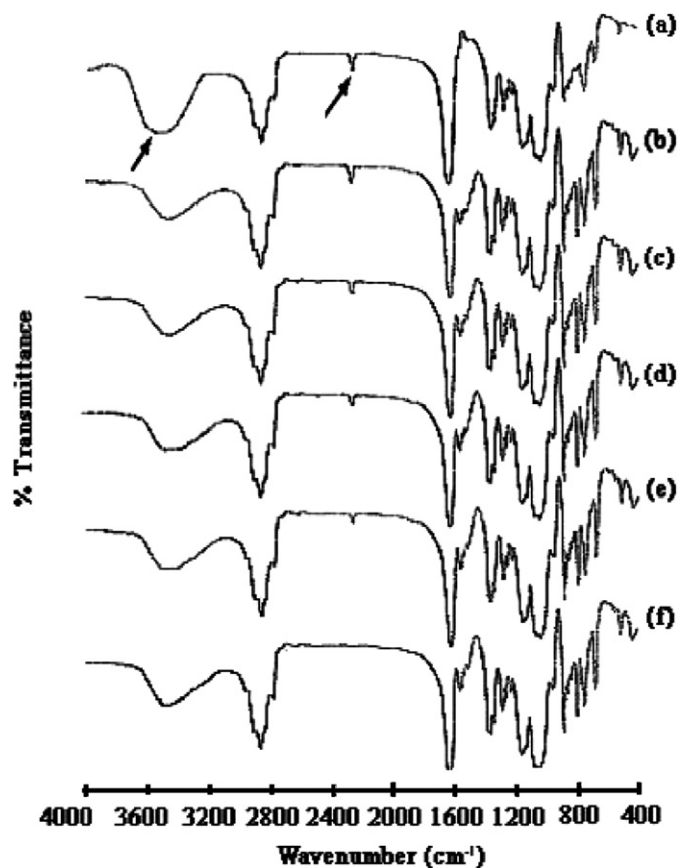


Fig. 5. FT-IR spectra of the amidoximated PiBMA at different reaction times. (a) 0 h, (b) 0.5 h, (c) 1.0 h, (d) 2.0 h, (e) 3.0 h, and (f) 4.0 h.

decreased proportionally 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 completed.

In addition to SEM and FT-IR techniques used to characterize the IDAN modified and amidoximated PiBMA beads, thermogravimetric analysis 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 PiBMA, GMA

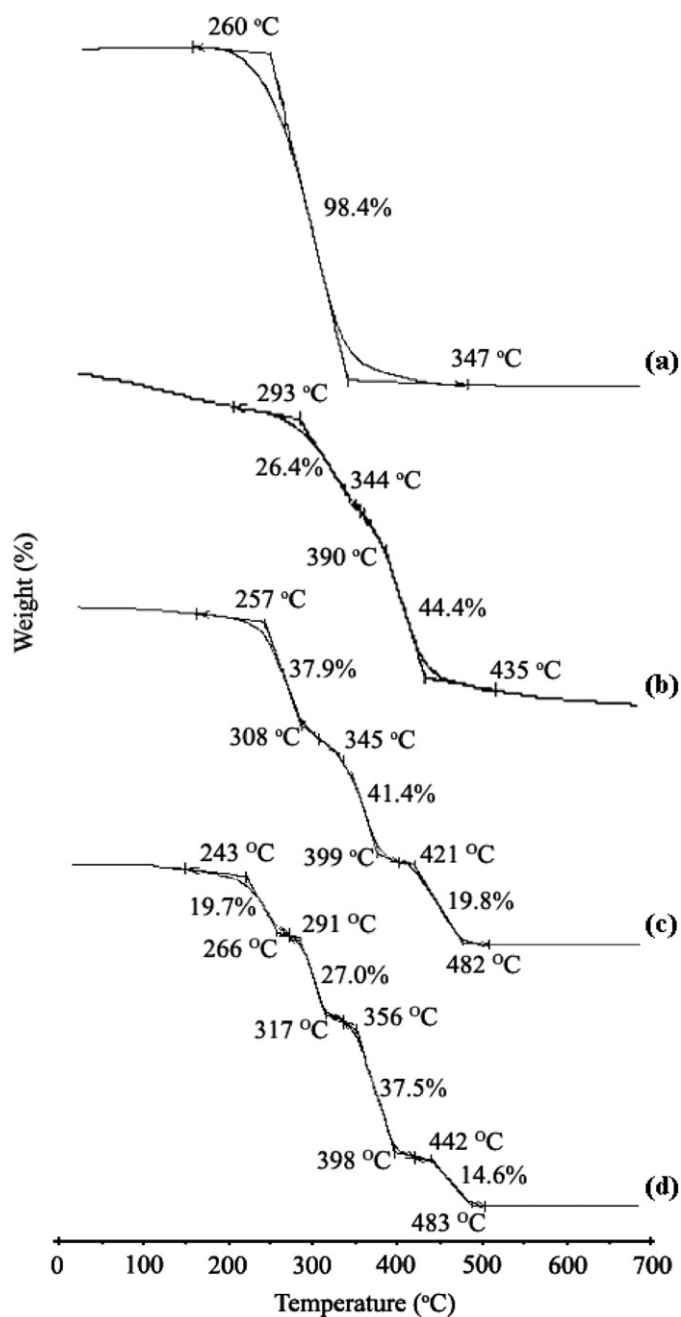


Fig. 6. TGA thermograms of (a) trunk PiBMA, (b) GMA grafted, (c) IDAN modified, and (d) amidoximated PiBMA beads.

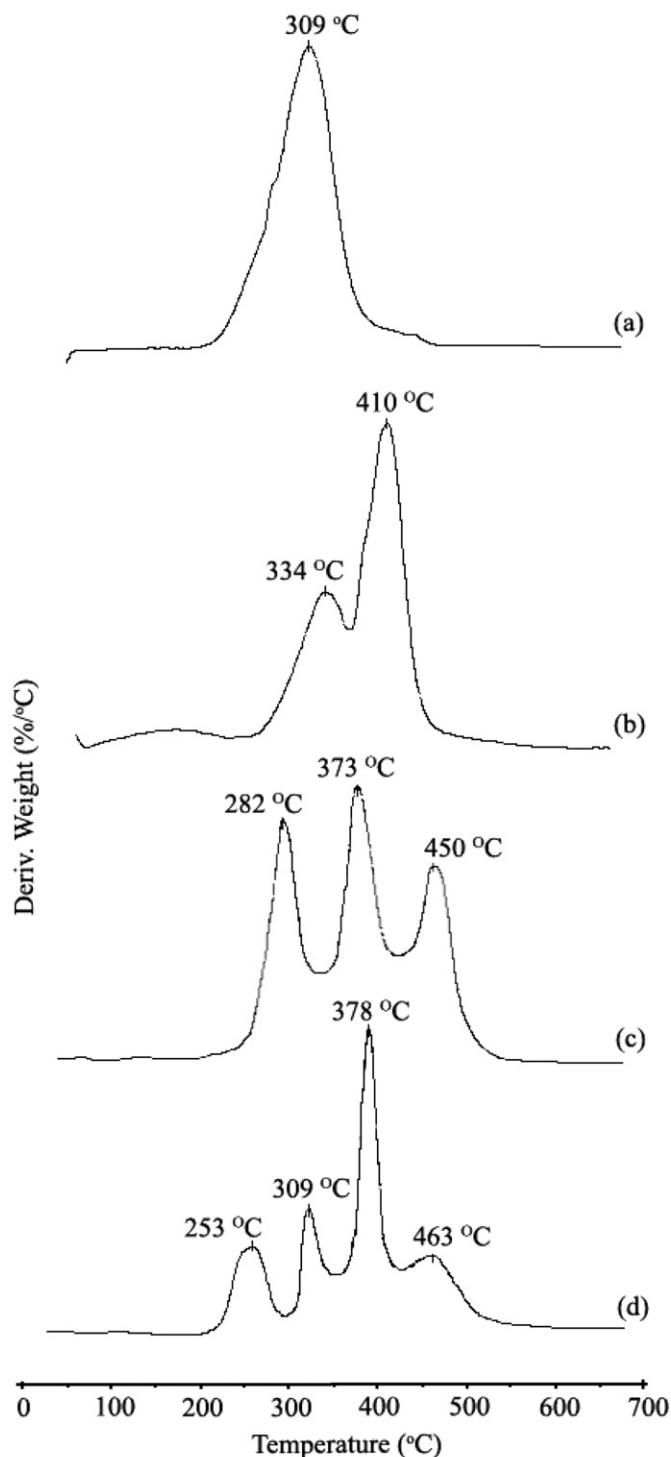


Fig. 7. DTGA thermograms of (a) trunk PiBMA, (b) GMA grafted, (c) IDAN modified, and (d) amidoximated PiBMA beads.

grafted, IDAN modified and amidoximated PiBMA beads at a heating rate $10^{\circ}\text{C}/\text{min}$ under nitrogen atmosphere are shown in Figs. 6 and 7. 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 PiBMA begins at $\sim 260^{\circ}\text{C}$ and reaches to maximum at 309°C . The TG curve of PiBMA indicates one reaction stage (Fig. 6(a)) which is reflected as single peak in the DTG curve (Fig. 7(a)). Initial degradation temperature of PiBMA showed that the degradation was due to random chain scission (Habi and Djadoun, 1999). On the other hand, the GMA grafted, IDAN modified and amidoximated PiBMA degrade in two, three and four steps, respectively. This is evidenced by the appearance of distinct peaks in DTG thermograms. Grafting of PiBMA with GMA seems to impart thermal stability to the base material since both the onset of degradation and maximum degradation temperatures were shifted to higher temperatures, Fig. 7(b). Stepwise degradation of GMA grafted, IDAN modified and amidoximated PiBMA indicate that every functional group introduced on the trunk polymer had different thermal stability giving rise to the appearance of distinct, separate derivative peaks. DTG curves clearly show the sequence of chemical modifications introduced into PiBMA. IDAN modification and amidoximation, however, seem to render the base polymer more susceptible to thermal degradation. On the other hand, in addition to SEM data, stepwise degradation of GMA grafted, IDAN modified and amidoximated PiBMA seems to indicate that grafting of GMA took place also in the bulk of PiBMA particles, strongly modifying its chemical composition. However, the grafted and modified PiBMA beads 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.

DSC was also used as a thermal analysis method for characterization of the PiBMA, GMA grafted, IDAN modified and amidoximated samples. The glass transition temperature (T_g) of unmodified PiBMA was found to be 67°C , whereas those of GMA grafted, IDAN modified and amidoximated PiBMA were 75 , 76 and 77°C , respectively. This difference is obviously due to the presence of modification and amidoximation processes.

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