

# Preparation of amidoximated poly(glycidyl methacrylate) microbeads

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## Abstract

Poly(glycidyl methacrylate) (PGMA) microbeads were synthesized by a simple suspension polymerization of glycidyl methacrylate and ethylene glycol dimethacrylate. The epoxy groups of the microbeads were firstly modified with 3,3'-iminodipropionitrile (IDPN) and the resulting nitrile groups were then converted to amidoxime. From scanning electron microscopy studies, the average size of the PGMA microbeads was determined as 170  $\mu\text{m}$ , which was not changed by the modification processes. For the modification of epoxy groups with IDPN, the intensity of the  $\text{C}\equiv\text{N}$  absorption band at  $2249\text{ cm}^{-1}$  increased proportionally with reaction time; for the conversion of nitrile groups to amidoxime, it decreased. Attenuated total reflectance Fourier transform infrared spectroscopy measurements clearly showed the disappearance of the original nitrile groups and the formation of amidoxime groups through treatment with hydroxylamine under the reaction conditions specified. The microbeads possessed good thermal and morphological properties and chemical stability suitable for practical use. Therefore, the amidoximated PGMA microbeads could be used in batch and continuous processes for the adsorption of uranyl ions from seawater or aqueous media.

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**Keywords:** poly(glycidyl methacrylate); suspension; microbeads; amidoximation

## INTRODUCTION

In view of the anticipated exhaustion of terrestrial uranium reserves in the future, research has been directed towards the recovery of uranium from non-conventional sources, such as coal and natural waters ( $0.1\text{--}10\text{ mg U m}^{-3}$ ) and especially from seawater ( $2.8\text{--}3.3\text{ mg U m}^{-3}$ ). The recovery of uranium from contaminated water of flooded mines ( $0.1\text{--}1.5\text{ mg U m}^{-3}$ ) may help to prevent a very important environmental problem.<sup>1–3</sup> Many types of adsorbents have been developed and used for the recovery of uranyl ions from seawater or aqueous media.<sup>3–6</sup> Among them, adsorbents containing amidoxime groups have been shown to be the most selective towards uranyl ions.<sup>3,7–10</sup> The standard procedure for the preparation of amidoximated adsorbents is first to synthesize acrylonitrile-containing graft copolymers followed by conversion of the nitrile groups to amidoxime groups.<sup>11–13</sup> Sekiguchi *et al.*,<sup>14</sup> Kabay and Egawa<sup>15</sup> and Kavakli *et al.*<sup>16</sup> reported the preparation of adsorbents carrying amidoxime groups by radiation-induced graft copolymerization of individual acrylonitriles onto various kinds of trunk polymer followed by amidoximation with hydroxylamine.

In our previous work, amidoximated poly(glycidyl methacrylate) (PGMA) microbeads, which were the first methacrylate bidentate amidoxime microbeads in the amidoxime microbead family, were synthesized.<sup>17</sup> In another work, we prepared new poly(isobutyl methacrylate) microbeads with adjacent amidoxime groups by radiation-induced graft polymerization.<sup>18</sup> The unique advantage of these microbeads is that they contain double amidoxime groups to recover uranium ions from seawater and aqueous media at very low concentration levels more efficiently.

The aim of the work reported here was to prepare a new type of PGMA microbeads carrying two amidoxime groups and an additional diethylene spacer unit between neighbouring

amidoxime groups. To our knowledge, there have been only a few attempts<sup>19,20</sup> at the preparation of resins with diamidoxime units so far, all of which completely differ from our approach. Modification of the microbeads with 3,3'-iminodipropionitrile (IDPN) and conversion of the nitrile groups to amidoxime groups were followed using attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy. The surface morphology and thermal behaviour of the microbeads were also analysed using SEM, TGA and DSC techniques, further confirming the modification and amidoximation.

## EXPERIMENTAL

### Materials

Glycidyl methacrylate (GMA; Aldrich Chemical Co., Milwaukee, USA) and ethylene glycol dimethacrylate (EGDMA; Aldrich) were purified by passing through active alumina. Benzoyl peroxide (BPO; Merck, Darmstadt, Germany) was utilized as the initiator and poly(*N*-vinyl-2-pyrrolidone) (PVP;  $M_w = 55\,000\text{ g mol}^{-1}$ , Aldrich) and tricalcium phosphate (TCP; Merck) as stabilizers. IDPN (Aldrich) and hydroxylamine hydrochloride ( $\text{NH}_2\text{OH} \cdot \text{HCl}$ ; Aldrich) were used as received. Distilled water was used in all experiments.

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### Amidoximated PGMA microbeads

The microbeads were produced by a suspension polymerization of GMA and EGDMA in an aqueous medium, as described previously.<sup>17</sup> The dispersion medium was prepared by dissolving 1 g of PVP and 1 g of TCP in 50 mL of deionized water. An amount of 0.14 g of BPO was dissolved in the monomer phase comprised of 2 mL of GMA and 0.25 mL of 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. The reactor temperature was then raised and kept at 70 °C for 2 h. At the end of this period, the temperature was increased to 85 °C and the polymerization was completed after 2 h. A washing procedure was applied after the polymerization to remove the diluents and any unreacted monomer from the product. The microbeads were filtered and re-suspended in ethyl alcohol. The new dispersion was stirred for about 2 h at room temperature and the microbeads were isolated by decanting the liquid part. The microbeads were washed twice with ethyl alcohol and then three times with deionized water using the same procedure. The washed microbeads were dried in a vacuum oven at 50 °C for 24 h.

The preparation of the amidoximated microbeads consisted of two steps: (1) modification of epoxy groups with IDPN and (2) amidoximation reaction of nitrile groups. Firstly, the microbeads were immersed in a 0.425 mol L<sup>-1</sup> IDPN solution in ethanol. The reaction was performed at 80 °C. During the modification reaction of epoxy groups with IDPN, microbeads were taken from the reaction vessel at certain time intervals and the progress of the modification with IDPN was followed from the increase in the C≡N band intensity of ATR-FTIR spectra. After the modification reaction was completed, the modified microbeads were removed from the reaction vessel, washed with methanol and then dried at 50 °C in a vacuum oven.

Secondly, the IDPN-modified microbeads thus obtained were reacted with a methanol solution of hydroxylamine (1:1 in NH<sub>2</sub>OH · HCl–NaOH) at 80 °C. The conversion of nitrile groups to amidoxime groups was followed from the decrease in the C≡N band intensity of ATR-FTIR spectra. After the amidoximation reaction was completed, the microbeads were removed from reaction vessel, washed with distilled water and then dried at 50 °C in a vacuum oven.

### Characterization of microbeads

In order to analyse the surface structure of the microbeads and their modified forms, detailed ATR-FTIR spectroscopy measurements were made. ATR-FTIR spectra were obtained using a Nicolet 6700 FTIR spectrometer equipped with a smart orbit accessory.

Surface morphologies of the microbeads were investigated using SEM (JSM-6360 LV, JEOL, Tokyo, Japan). The microbeads were coated with a thin layer of gold in vacuum and imaged in the electron microscope with ×50 and ×1500 magnifications.

Thermal analysis was performed using a 2050 TGA (TA Instruments). All tests were conducted in a nitrogen purge (25 mL min<sup>-1</sup>) using sample weights of 5–10 mg over a temperature range of 20–600 °C at a scan rate of 10 °C min<sup>-1</sup>. Dynamic mass loss curves and their derivatives were obtained. DSC measurements were performed using a 2010 DSC (TA Instruments) with a heating rate of 10 °C min<sup>-1</sup> under nitrogen flow.

## RESULTS AND DISCUSSION

The preparation of the amidoximated microbeads essentially involves three steps: synthesis of PGMA microbeads; modification with IDPN; and conversion of nitrile groups to amidoxime groups (Scheme 1). The first step is the synthesis of PGMA microbeads by a suspension polymerization. The second step is the modification with IDPN containing two nitrile groups by opening of the epoxy ring of PGMA. The final step is the amidoximation of the nitrile groups using hydroxylamine hydrochloride in methanol solution.

To determine if there are any observable physical changes to the PGMA microbeads that might have occurred during the modification or amidoximation processes, their surface morphology was investigated using SEM. SEM images of PGMA, IDPN-modified and amidoximated microbeads are shown in Figs 1 and 2. From these images, the average diameter of the PGMA microbeads is determined as 170 μm and this does not change following the modification processes (Fig. 1). As seen in Fig. 2, PGMA and its modified forms show reasonably smooth and featureless surfaces. These results indicate that the modification processes do not lead to morphological changes on the microbead surfaces.

For the spectroscopic characterization of the PGMA microbeads and their modified forms, a baseline ATR-FTIR spectrum of PGMA was recorded. In the ATR-FTIR spectrum of PGMA (Fig. 3(a)), the strong band observed at 1736 cm<sup>-1</sup> is due to the C=O stretching vibration and the band at 973 cm<sup>-1</sup> is due to the symmetric stretching of the epoxy ring. In the ATR-FTIR spectrum of IDPN-modified PGMA (Fig. 3(b)), the sharp band at 2249 cm<sup>-1</sup> is very characteristic of the C≡N group. The broad band at 3500 cm<sup>-1</sup> is attributed to oxime OH, primary NH<sub>2</sub> stretch or OH resulting from epoxide ring (Fig. 3(c)). To follow the extent of the replacement reaction of epoxide groups by nitrile groups, the characteristic C≡N band at 2249 cm<sup>-1</sup> was used (Fig. 4). The appearance of the C≡N band with time can be monitored to check and control the completion of the reaction. As can be seen from Fig. 4, the intensity of the C≡N band at 2249 cm<sup>-1</sup> increases proportionally with reaction time. Moreover, the broad hydroxyl band formed during the ring-opening reaction of the epoxy group of PGMA can be clearly seen at 3400 cm<sup>-1</sup>. After 36 h, the intensity of the C≡N band at 2249 cm<sup>-1</sup> does not change with reaction time, indicating that the reaction is almost completed in 36 h.

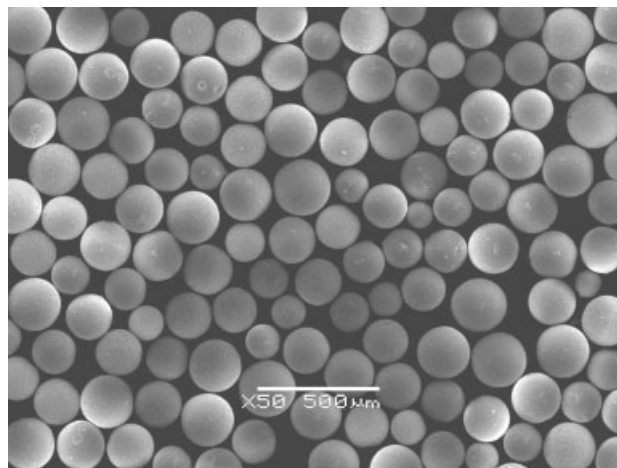
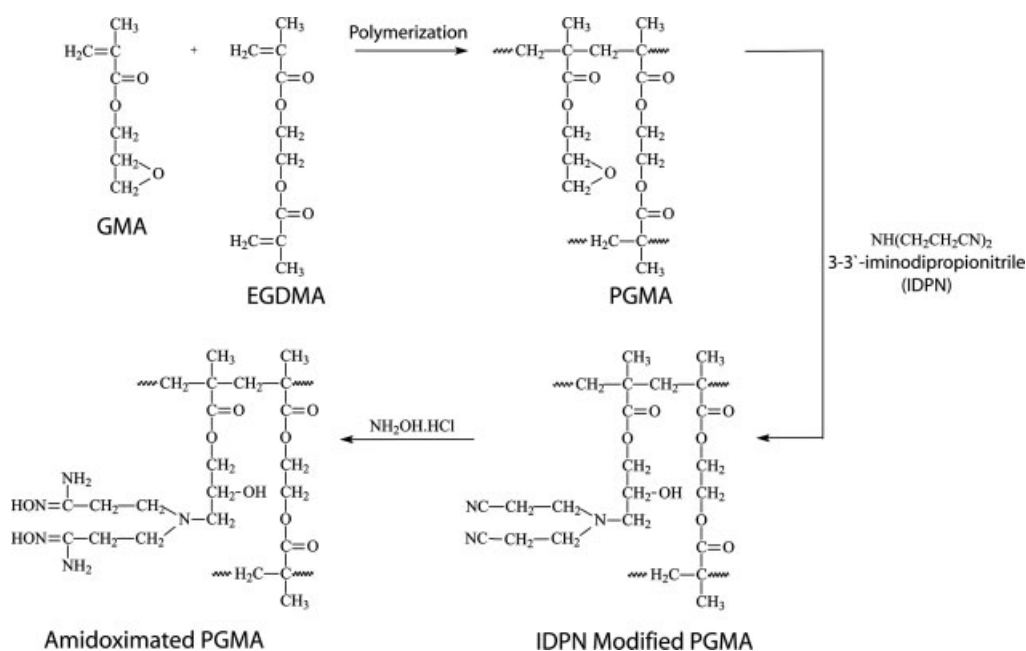
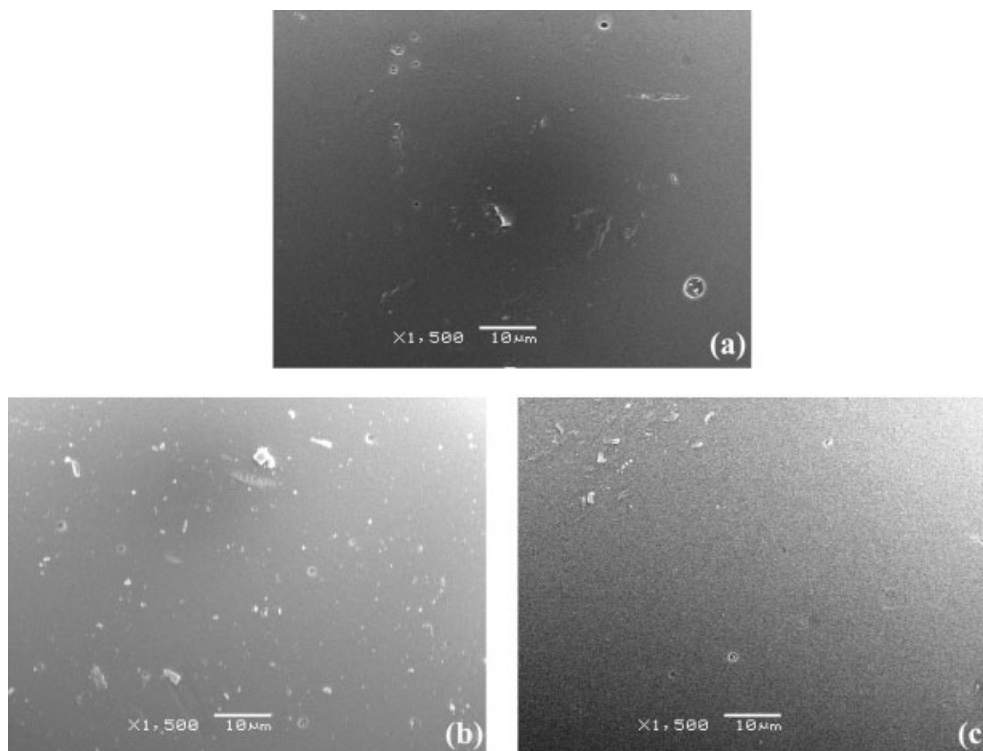


Figure 1. SEM image (×50 magnification) of PGMA.



**Scheme 1.** Preparation of amidoximated PGMA microbeads.

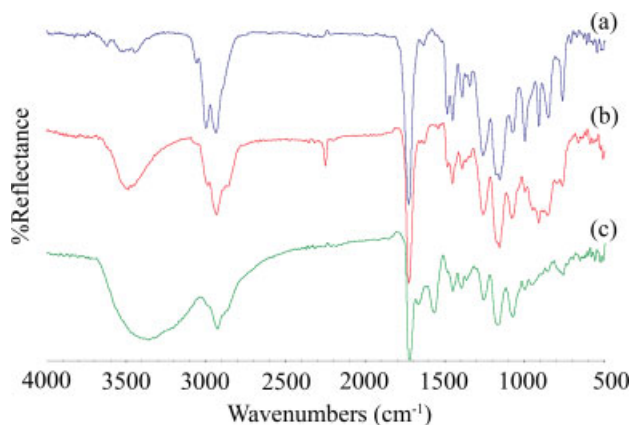


**Figure 2.** SEM images ( $\times 1500$  magnification) of (a) PGMA, (b) IDPN-modified PGMA and (c) amidoximated PGMA.

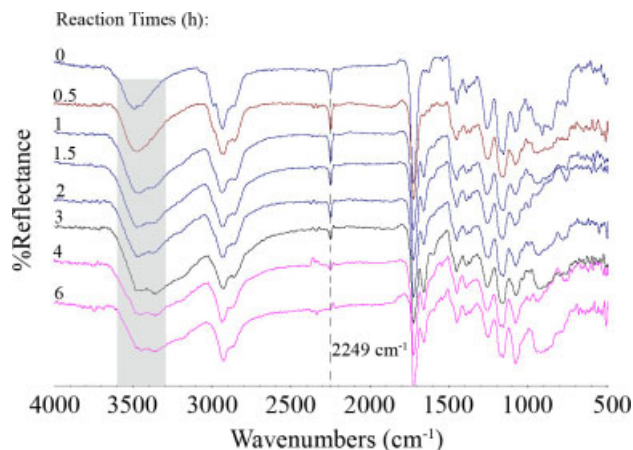
The course of the conversion of the IDPN-modified PGMA into amidoximated PGMA was also followed by recording ATR-FTIR spectra of samples after various times from the initiation of the reaction, as shown in Fig. 5. As can be seen, intensity of the  $\text{C}\equiv\text{N}$  band at  $2249\ \text{cm}^{-1}$  of the IDPN-modified PGMA microbeads decreases proportionally with reaction time. After 6 h of amidoximation time, the band at  $2249\ \text{cm}^{-1}$  is observed to disappear due to depletion of the nitrile groups, supporting the

idea that the conversion of nitrile groups to  $\text{H}_2\text{N}-\text{C}=\text{NOH}$  groups is almost completed. In addition, oximes also show a weak band at  $\text{ca } 1640\ \text{cm}^{-1}$ . These results clearly show the disappearance of the original nitrile groups and formation of  $\text{H}_2\text{N}-\text{C}=\text{NOH}$  groups through the treatment with hydroxylamine under the reaction conditions used.

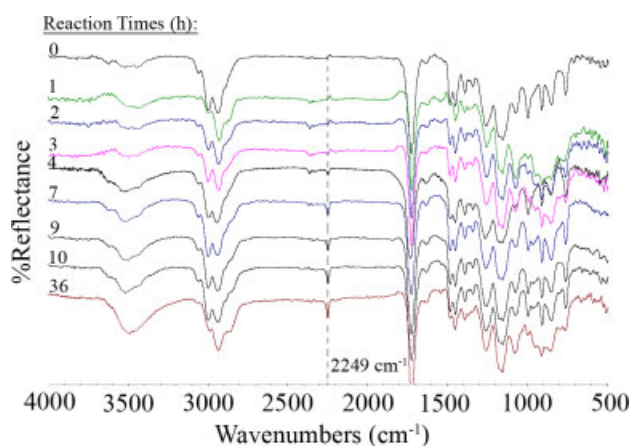
In order to understand the thermal behaviour of the amidoximated PGMA microbeads, TGA measurements were performed



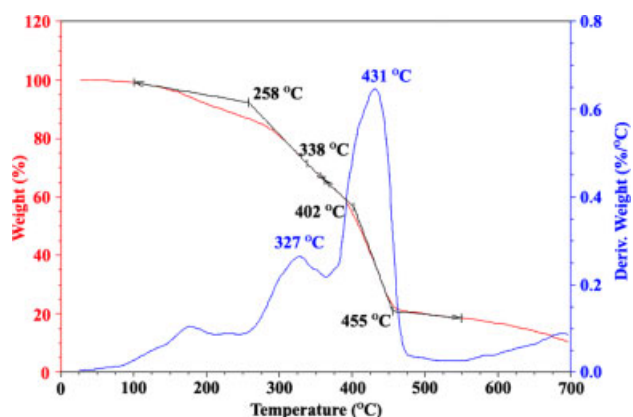
**Figure 3.** ATR-FTIR spectra of (a) PGMA, (b) IDPN-modified PGMA and (c) amidoximated PGMA.



**Figure 5.** ATR-FTIR spectra showing the progress of the amidoximation reaction at various reaction times as indicated.



**Figure 4.** ATR-FTIR spectra of PGMA microbeads modified with IDPN at various reaction times as indicated.



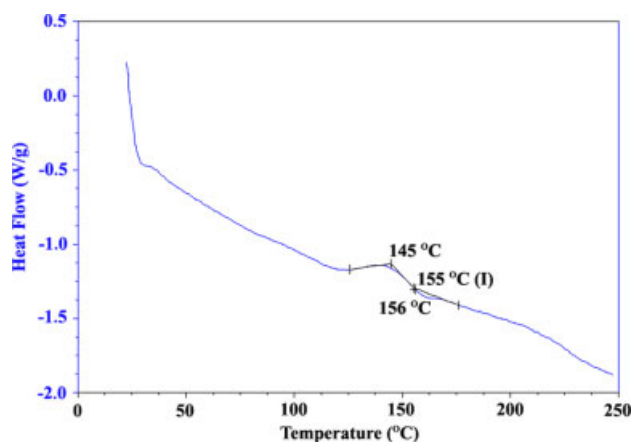
**Figure 6.** TGA thermograms of amidoximated PGMA.

in nitrogen atmosphere at a heating rate of  $10^{\circ}\text{C min}^{-1}$ . The dynamic TG and derivative (DTG) thermograms of the amidoximated PGMA are shown in Fig. 6. The TG curve indicates two reaction stages which are reflected as two peaks in the DTG curve. Stepwise degradation of amidoximated PGMA indicates that each functional group introduced on the polymer backbone has different thermal stability giving rise to the appearance of distinct, separate derivative peaks. The derivative curve clearly show the sequence of chemical modifications introduced into PGMA. The amidoximation, however, seem to render the base polymer more susceptible to thermal degradation.<sup>17</sup> This is of practical importance since microbeads to be used for uranyl ion adsorption need to be treated at relatively high temperatures for recovery purposes.

The glass transition temperature of the PGMA microbeads is determined as  $155^{\circ}\text{C}$  and it is not affected by the modification processes (Fig. 7). This behaviour also shows that the modification processes take place on the surface predominantly and not inside of the PGMA microbeads.

## CONCLUSIONS

PGMA microbeads containing double amidoxime groups and an additional diethylene spacer unit between neighbouring amidoxime groups were synthesized with the anticipation of an enhanced uranyl ion adsorption capacity. For this purpose,



**Figure 7.** DSC thermogram of PGMA.

the uniform PGMA microbeads synthesized by a suspension polymerization method were first modified with IDPN, and then reacted with hydroxylamine to produce amidoxime groups. The structure and morphology of the amidoximated microbeads were characterized using ATR-FTIR, SEM, TGA and DSC. To the best of our knowledge, these microbeads are the first methacrylate polymers carrying both bidentate amidoxime groups and an additional

diethylene spacer unit between neighbouring amidoxime groups of the amidoxime microbead family reported in the literature. Further studies are required relating to the use of these microbeads for uranyl ion adsorption from various media (e.g. seawater or aqueous solutions). The results pertaining to the affinity of this new adsorbent for uranyl ions in batch and continuous adsorption processes will be the subject of a separate publication.

## REFERENCES

- 1 Spence R, *Talanta* **15**:1307 (1968).
- 2 Wilson JD, Webster RK, Milner GWC, Barnett GA and Smales AA, *Anal Chim Acta* **23**:505 (1960).
- 3 Kavaklı PA and Güven O, *J Appl Polym Sci* **93**:1705 (2004).
- 4 Rivas BL, Pooley SA, Maturana HA and Villegas S, *Macromol Chem Phys* **202**:443 (2001).
- 5 Caykara T, Inam R and Ozyurek C, *J Polym Sci A: Polym Chem* **39**:277 (2001).
- 6 Saraydin D, Karadag E and Güven O, *Sep Sci Technol* **30**:3287 (1995).
- 7 Omichi H, Katakai A, Sugo T and Okamado J, *Sep Sci Technol* **21**:563 (1986).
- 8 Kabay N, Katakai A and Sugo T, *Radiat Phys Chem* **46**:833 (1995).
- 9 Choi SH and Nho YC, *Radiat Phys Chem* **57**:187 (2000).
- 10 Katragadda S, Chow A and Gesser HD, *Talanta* **45**:257 (1997).
- 11 Egawa H and Harada H, *Nippon Kagaku Kaishi* 958 (1979).
- 12 Egawa H, Harada H and Nonaka T, *Nippon Kagaku Kaishi* 1767 (1980).
- 13 Egawa H, Harada H and Nonaka T, *Nippon Kagaku Kaishi* 1773 (1980).
- 14 Sekiguchi K, Saito K, Konishi S, Furusaki S, Sugo T and Nobukawa H, *Ind Eng Chem Res* **33**:662 (1994).
- 15 Kabay N and Egawa H, *Sep Sci Technol* **28**:1985 (1993).
- 16 Kavaklı PA, Uzun C and Güven O, *React Funct Polym* **61**:245 (2004).
- 17 Caykara T and Alaslan SS, *J Appl Polym Sci* **106**:2126 (2007).
- 18 Caykara T, Alaslan SS, Gürü M, Bodugoz H and Güven O, *Radiat Phys Chem* **76**:1569 (2007).
- 19 Kise H and Sato H, *Macromol Chem* **186**:2449 (1985).
- 20 Park IH and Suh JM, *Angew Macromol Chem* **239**:121 (1996).