Polymer Bulletin 61, 311–318 (2008)
DOI 10.1007/s00289-008-0958-y

Polymer Bulletin

A new type of poly(glycidyl methacrylate) microbeads with surface grafted iminodiacetic acid: Synthesis and characterization

Tuncer Çaykara (✉), Ferhat Çakar and Serkan Demirci

Department of Chemistry, Faculty of Art and Science, Gazi University, 06500 Besevler, Ankara, Turkey

E-mail: caykara@gazi.edu.tr

Received: 1 January 2008 / Revised version: 21 May 2008 / Accepted: 10 June 2008

Summary

In this study, firstly, uniform poly(glycidyl methacrylate) (PGMA) microbeads with an average diameter of 230 μm were synthesized by suspension polymerization of GMA monomer and ethylene glycol dimethacylate (EGDMA) crosslinker in the presence of benzoyl peroxide (BPO) initiator . Secondly, the PGMA microbeads obtained were modified with iminodiacetic acid (IDA) to afford a new type of microbeads carrying two pendant carboxylic acid groups on the surface. The IDA modification was followed by Attenuated Total Reflectance Fourier Transformed Infrared (ATR-FTIR) measurements. The surface morphology and thermal behavior of the PGMA and their modificated form were also characterized by scanning electron microscopy (SEM) and thermogravimetric analysis (TGA) techniques further confirming modification.

Keywords: Poly(glycidyl methacrylate); suspension; microbeads; modification

Introduction

Polymer-metal complexes (consisting of a metal ion and its coordinating ligands) are currently attracting considerable attention of a variety of applications [1,2], such as developments in nuclear chemistry, hydrometallurgy, organic synthesis, polymer drug grafts, preconcentration and recovery of trace metal ions [3]. Moreover, they are also used as mechanochemical systems and as models of bioorganic and bioinorganic systems [4].

Among the multidentate ligands, ethylenediaminetetraacetic acid (EDTA) forms strong 1:1 stable complexes with various metal ions in a single step. However, it is difficult to introduce EDTA into polymer chains. With regard to the chemical structure, two aminopolycarboxylates of EDTA can share six pairs of electrons with a single metal ion. Furthermore, iminodiacetic acid (IDA) possesses one aminopolycarboxylate and provides reactive secondary amine hydrogen to react with alternate functional groups.

Hence, IDA can be more easily introduced to the side chain of a polymer. Therefore, this study presents an attempt to prepare a novel chelating polymeric microbeads via an epoxy group reaction of poly(glycidyl metacrylate) (PGMA) with IDA. This reaction has two primary advantages. Firstly, GMA is a commercial material, which is cheaper than any other vinyl monomers that possess an epoxy ring in the side chain. Secondly, it produces many novel cheating polymeric microbeads via an epoxy group reaction of PGMA with IDA, 3,3`-iminodipropionitrile (IDPN) and iminodiacetonitrile (IDAN)-type chelating agents [5-8].

To our knowledge, although a great deal of research has been conducted on various functional groups containing adsorbents, PGMA microbeads with surface grafted dicarboxylic acid groups have not been reported in the literature.

The objective of this study is to report the results on the synthesis of PGMA microbeads by suspension polymerization technique and their modification with IDA. In ATR-FTIR spectroscopy studies, the modification was ascertained from the change in the characteristic peak areas. Thermal analysis and surface morphology studies were also performed to determine changes in the thermal behavior and on surface appearance of the PGMA microbeads and their modificated forms.

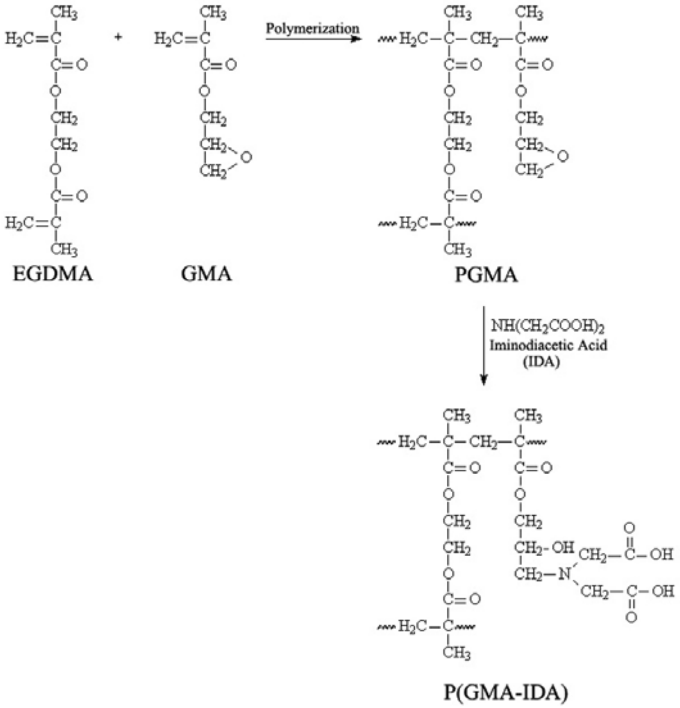
Experimental

Materials

Glycidyl methacrylate (GMA, Aldrich Chem. Co., Milwaukee, USA) and ethylene glycol dimethacylate (EGDMA, Aldrich Chem. Co.) were purified by passing through active alumina. Benzoyl peroxide (BPO, Merck, Darmstadt, Germany) and poly(*N*-vinyl-2-pyrrolidone) (PVP, M_w = 55 0000 g/mol, Aldrich Chem. Co.) and tricalcium phosphate (TCP, Merck) were utilized as the initiator and stabilizers, respectively. Iminodiacetic acid (IDA, Aldrich Chem. Co.) was used as received. Distilled water was used in all experiments.

Synthesis of PGMA microbeads

A typical procedure for the preparation of PGMA microbeads is exemplified below 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 0.25 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 microbeads were filtered and resuspended within 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.



Scheme 1. Synthesis of pol(glycidyl methacrylate) microbeads carrying iminodiacetic acid groups

Modification of PGMA microbeads

The PGMA microbeads obtained were immersed in 0.425 M iminodiacetic acid in methanol-water (1:1, v:v) solvent mixture. The reaction was performed at 80°C. During the modification reaction of epoxy group with IDA, samples were taken from the reaction vessel at certain time intervals and binding of iminodiacetic acid groups onto the epoxy group of PGMA was followed by determining the changes in -OH band areas of polymer from respective ATR-FTIR spectra. After grafting of iminodicarboxylic acid groups, the remaining unreacted epoxide groups were hydrolyzed with dilute hydrochloric acid solution for 2 h at 80°C. Subsequently, IDA modified PGMA microbeads were washed with methanol and then dried at 50°C in vacuum oven.

Characterization of PGMA microbeads and its modified form

In order to analyze the surface composition of the PGMA microbeads and their modified forms, detailed Attenuated Total Reflectance Fourier Transformed Infrared (ATR-FTIR) measurements were made. ATR-FTIR spectra were taken by using a Nicolet 6700 FT-IR Spectrometer equipped with a smart orbit assessor. Surface morphologies of the PGMA microbeads and their modified forms were determined by a scanning electron microscope (SEM) (JEOL, JSM-6360 LV, Tokyo, Japan). PGMA microbeads were coated with a thin layer of gold in vacuum and photographed in the electron microscope 50x and 1500x 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°C to 600°C at a scan rate of 10°C/min. Dynamic mass loss curves and their derivatives were obtained.

Results and discussion

A large number of chelating polymers or monomers incorporating a variety of ligands (e.g. amidoxime, phoshoric acid, amine, dithiocarbamate, oxime) have been prepared, and their adsorption characteristics investigated [7,8-12]. All studies have been focused on the adsorption capacities and efficiencies of metal ions. Therefore, it is difficult to compare our microbeads prepared by surfaced grafted method with others described in literature because of differences in their chemical structure and preparation method. However, the developments of chelating polymers contribute greatly to industrial wastewater treatments and biotechnological applications.

In this study, novel PGMA microbeads with surface grafted dicarboxylic acid groups were prepared at two steps. As mentioned in the experimental section, firstly, PGMA microbeads were synthesized by suspension polymerization technique. Then, IDA containing two carboxylic acid groups was attached onto PGMA microbeads by opening of the epoxy ring.

To compare the difference in the physical appearance of functionalized and original samples to see if there are any observable physical changes on the PGMA microbeads which might have occurred during the grafting process with IDA, surface morphology of these microbeads was investigated by using SEM technique. SEM photographs of the PGMA, IDA modified PGMA microbeads were given in Figure 1 and Figure 2 From these SEM photographs, an average diameter of the PGMA microbeads was determined as 230 μm and their diameter did not change via modification processes (Figure 1).

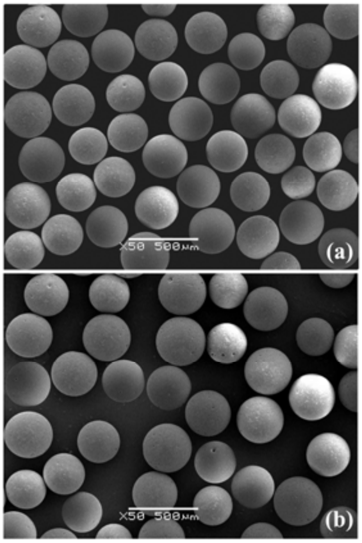


Figure 1. SEM photographs (magnification50) of (a) PGMA, (b) P(GMA-IDA)

On the other hand, as seen in Figure 2(a) and Figure 2(b), PGMA and their modified forms showed reasonably smooth and featureless surfaces. These results indicated that the modification processes do not lead to the morphological changes on the surface of these microbeads.

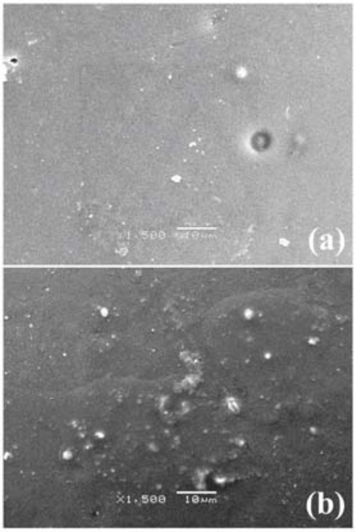


Figure 2. SEM photographs (magnification1500) of (a) PGMA, (b) P(GMA-IDA)

For the spectroscopic characterization of PGMA and the IDA grafted PGMA beads, a baseline ATR-FTIR spectrum of PGMA was recorded. In the IR spectrum of PGMA is given in Figure 3(a), the strong band observed at 1736 cm^{-1} is due to the C=O

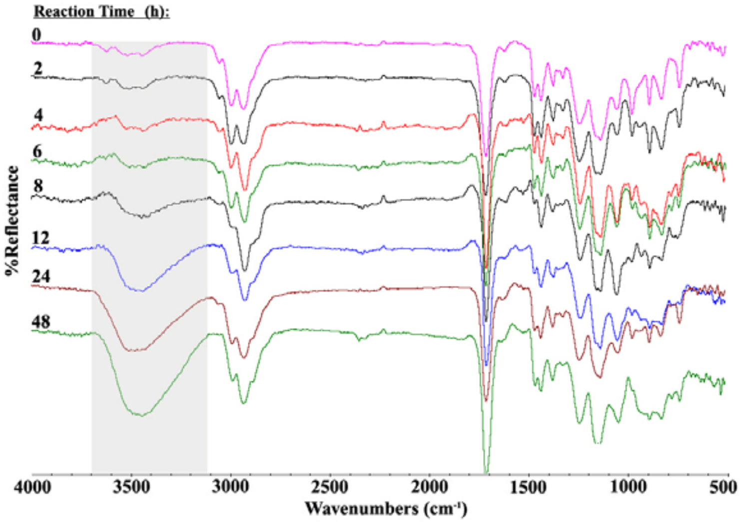


Figure 3. ATR-FTIR spectra of PGMA microbeads modified with iminodiacetic acid at different reaction times

stretching vibration whereas the band at 973 cm^{-1} is due to the symmetrical stretching of the epoxy ring.

In ATR-FTIR spectra of IDA modified PGMA, the board hydroxyl band, which formed during the ring opening of epoxy group of PGMA can be clearly seen at 3400 cm^{-1}. To follow the extent of reaction replacement of epoxide groups by IDA groups, area of the characteristic hydroxyl band at 3400 cm^{-1} was used (Figure 4). As can be seen from Figure 4, the -OH band area of the polymer increased proportionally with the reaction time. 48 hour after the beginning of reaction, the -OH band area at 3400 cm^{-1} almost changed and at the same, the band at 973 cm^{-1} corresponding to the symmetrical stretching of the epoxy ring disappeared, indicating that the reaction is complete in 48 h.

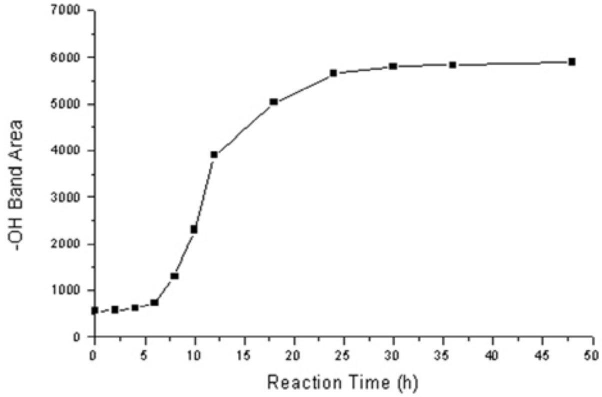


Figure 4. The change in the -OH band area of PGMA with reaction time

In addition to SEM and ATR-FTIR techniques used to characterize the IDA modified PGMA microbeads, 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 PGMA and IDA modified PGMA beads at a heating rate 10°C/min under nitrogen atmosphere are shown in Figure 5 and Figure 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 ~273°C and reaches to maximum at 301°C (Fig. 5). The TG curve of PGMA indicates one reaction stage which is reflected as single peak in the DTG curve. Initial degradation temperature of PGMA showed that the degradation was due to random chain scission [14]. On the other hand, the IDA modified PGMA nicrobeads degrade in two steps. This is evidenced by the appearance of single peak with a small shoulder in DTG thermogram. Stepwise degradation of IDA modified PGMA indicate that the functional group introduced on the trunk polymer had different thermal stability giving rise to the appearance of separate derivative peaks. DTG curves clearly show the sequence of chemical modifications introduced into PGMA.

The IDA modification however seem to render the base polymer more stable to thermal degradation. The modified PGMA microbeads can be used safely up to processing temperatures of 298°C. This is of practical importance since the micro-beads to be used for heavy metal ions adsorption need to be treated at relatively high temperatures for recovery purposes.

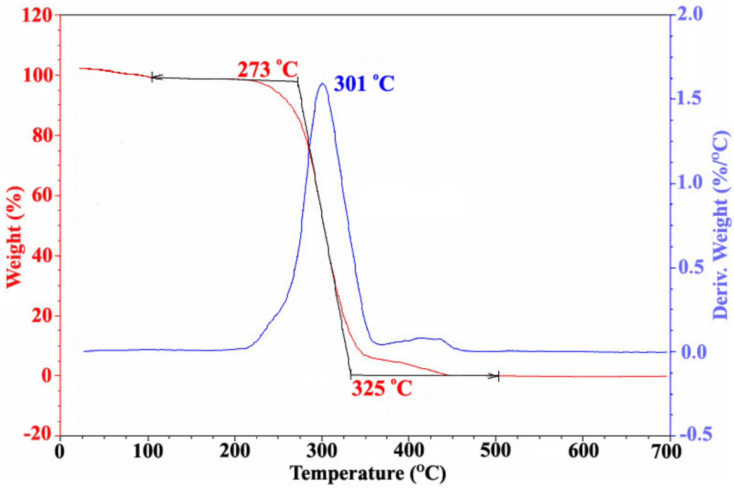


Figure 5. TGA thermograms of PGMA

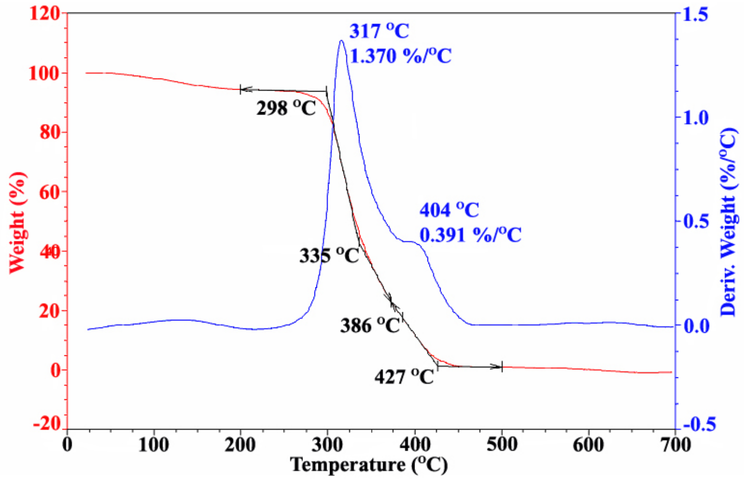


Figure 6. TGA thermograms of P(GMA-IDA)

Conclusions

In this study, novel PGMA microbeads with surface functionalized dicarboxylic acid were prepared by suspension polymerization of GMA monomer and EGDMA crosslinker in the presence of BPO initiator and by subsequent functionalization of epoxy groups of PGMA with IDA. The incorporation of the carboxylic acid groups was confirmed by ATR-FTIR spectra. The characteristics of the PGMA microbeads and their modificated forms were studied TGA and SEM analysis. It was found that the microbeads possessed both good morphological properties and chemical stability suitable for practical use. The unique advantage of the modified PGMA microbeads is that they contain dicarboxylic acid groups on the surface. Further studies related to use of these microbeads 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.

References

1. Choi S, Nho YC, (1999) J Appl Polym Sci 71:999
2. Menoud P, Cavin L, Renken A, (1998) Chem Eng Process 37:89
3. Reedijk J, Ciardelli F, Tsuchida E, Wöhrle D, (1996) Polymer-metal complexes Springer, Berlin Heidelberg 131
4. Chen J, Yiacoumi S, (1997) Sep Sci Technol 32:51
5. Chen CY, Chen SY, (2004) J Appl Polym Sci 94:2123
6. Kavakli PA, Seko N, Tamada M, Güven O, (2004) J Inter Abs Soc 10:309
7. Çaykara T, Alan ŞŞ, Inam R, (2007) J Appl Polym Sci 104:4168
8. Kavaklı PA, Uzun C, Güven O, (2004) React and Funtional Polym 61:245
9. Tsuneda S, Saito K, Furusaki S, Sugo T, Okamoto J, (1991) J Membr Sci, 158:221
10. Denizli A, Say R, Testereci HN, Arica MY, (1999) Sep Sci Technol, 34:2369
11. Denizli A, Say R, Arica MY, (2000) JMS Pure Appl Chem, A37:343
12. Denizli A, Buyuktuncel E, Tuncel A, Bektas S, Genc O, (2000) Environ Technol 21:609
13. Zulfigar S, Zulfigar M, Nawazi M, McNeill C, Gorman JG, (1990) Polym Degrad Stab 30:195