

# HDPE Chelate Membranes Prepared by Preirradiation Grafting for Adsorption of Heavy Metal Ions

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**ABSTRACT:** A new chelate membrane was prepared by grafting of glycidyl methacrylate (GMA) onto high-density polyethylene membranes and subsequent amination of poly-GMA graft chains. The effects of grafting conditions such as radiation dose and temperature on grafting yield were studied. Effects of various parameters such as grafting yield, pH, and adsorption time on the metal uptake were investigated. The results show that the maximum metal uptake followed as given in the order Cr (III) > Fe (III) > Cu (II) > Cd (II). The metal uptake increased with

grafting yield, adsorption time, pH of the medium, and initial concentration. The chelated metal ions are easily desorbed with 0.1 mol/L hydrochloric acid at room temperature. The results obtained from the chelate membrane showed a promising application in extraction of heavy metal ions from industrial effluents. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 1252–1256, 2008

**Key words:** radiation; graft copolymer; metal-polymer complexes

## INTRODUCTION

The effective treatment of heavy metals from industrial effluent has been one of the major issues due to their toxicities. Among all conventional treatment methods, heavy metals can be removed by chemical precipitation,<sup>1</sup> ion exchange resins,<sup>2</sup> and adsorption.<sup>3</sup> Recently, chelate membranes have been applied for the adsorption of specific metal ions from industrial wastes. Chelate membranes,<sup>4</sup> having an affinity ligand, which contain atoms able to form donor–acceptor bonds with transitional-metal ions, such as Cu (II), Fe (III), Cr (III), Cd (II), are well known.

It is also well known that graft polymerization are widely used to modify chemical and physical properties of polymers.<sup>5</sup> Graft polymerization is achieved by some methods such as ionization radiation,<sup>6</sup> UV,<sup>7</sup> plasma,<sup>8</sup> or chemical initiators,<sup>9</sup> but among them radiation-induced grafting can be one of the most effective techniques because of its uniform creation of radical sites on the polymer matrix, penetrate effectively into the polymer and its moderate reaction condition. The most recent research in radiation-induced graft copolymerization involves two main methods: simultaneous irra-

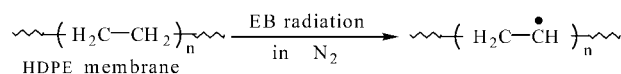
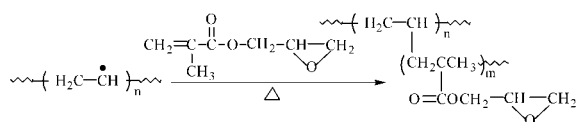
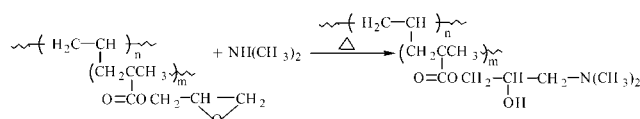
diation and preirradiation. In practice, the preirradiation method has been given much attention because the homopolymer formation is little, and the grafting can be carried out at anytime away from radiation sources.

Many studies have been reported in the preparation of chelate membranes using radiation-induced grafting technique with the aim focus on improving the adsorption affinity to heavy metals by optimization of the grafting conditions and selection of an appropriate monomer. There are mainly two ways to prepare chelate membranes using radiation-induced grafting technique. The first way is various vinyl monomers such as acyclic acid, acylamide, N-vinyl-2-pyrrolidone with suitable functional groups grafting onto the polymer membranes. The second way is some monomers which have easily modified groups grafting onto polymer membranes, and then various functional groups are introduced onto membrane by further reaction. Glycidyl methacrylate (GMA) is one of the monomers which have easily modified groups. After GMA is grafted onto polymer, the epoxy groups of poly-GMA are changeable to alcohols,<sup>10</sup> amines,<sup>11</sup> and sulfonic acid,<sup>12</sup> etc.

Therefore, in this study, chelate membranes were prepared by radiation grafting of GMA monomer onto high density polyethylene (HDPE) membranes followed by amination with dimethylamine solution. The adsorption ability of the chelate membrane toward Cr (II), Fe (III), Cu (II), and Cd (II) was investigated.

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**Preirradiation****Grafting****Amination**

**Scheme 1** Preparation of grafting membrane and modified with amino group.

**EXPERIMENTAL****Materials and instrument**

HDPE membrane with 15- $\mu\text{m}$  thickness was supplied by Shanghai Da yu Scientific, and GMA was provided by Beijing Tong yi chemical. Other chemicals, such as solvent, inorganic salts, and acid were for analysis grade and used as received. Accelerator (GJ-2, Shanghai Xianfeng Electric Machinery Plant) was used to irradiate HDPE membranes. A Fourier transform infrared spectrophotometer from Nicolite IR200 was used to analyze the chemical properties of grafted membrane. The concentration of metal ions were measured by ICP (Plasma-400, Thermo Elemental, USA). The pH value of the solution were determined with pH meter (PHB-4, Shanghai Leici Instrument Scientific).

**Grafting procedure**

Scheme 1 shows the preparation procedure of radiation-induced grafting of GMA onto HDPE membrane and amination of grafted membrane. The pre-irradiation grafting method was used. HDPE (5 cm  $\times$  8 cm) membranes were washed with acetone and dried in a vacuum oven at 50°C to constant weight. The HDPE membranes were sealed in PE bags after the atmosphere in bags was replaced by purified nitrogen. The sealed HDPE membranes were irradiated by electron beams from accelerator with 1.8 MeV and 5 mA. The irradiated membranes were put together with nonwoven polypropylene and rolled into a cylinder using glass sticks as axes, then were immersed in GMA solution diluted with methanol, and the mixture was placed in a glass ampoule. The mixture was deaerated by bubbling nitrogen for 10 min and the ampoule was sealed. The grafting reaction was carried out in a constant temperature bath.

After reaction the grafted membrane was removed and washed thoroughly with N, N-dimethylformamide for several times and immersed in a 1 : 1 (v:v) methanol and tetrahydrofuran mixture for 8 h to eliminate the unreacted monomer and the homopolymer which accumulated on the surface of membranes. The membranes were dried in a vacuum oven at 40°C to constant weight. The grafting yield (G) was calculated using the equation

$$G = \frac{W_g - W_0}{W_0} \times 100\%$$

$W_g$  and  $W_0$  are the weights of grafted HDPE and the original HDPE membrane, respectively.

**The introduction of amino groups onto HDPE-g-GMA membrane**

The HDPE-g-GMA membrane was immersed in 33% dimethylamine solution at 40°C. After 6–10 h the amination of epoxy groups in HDPE-g-GMA membrane were finished, the membrane was removed and washed with deionized water to eliminate excess reagents, and then dried in an oven at 40°C to constant weight. The conversion yield (%) of aminated membranes above were calculated as follows:

Conversion yield (%)

$$= 100[(W_a - W_g)/45]/[(W_g - W_0)/142]$$

where  $W_a$  is the weight of aminated membrane, 45 and 145 correspond to the molecular weights of dimethylamine and GMA.

**Metal uptake measurement**

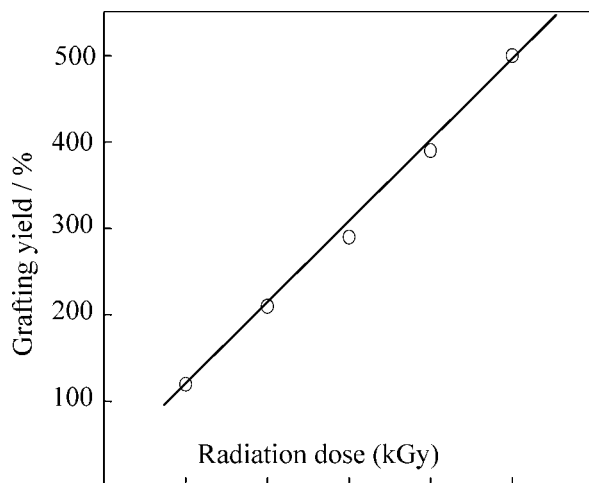
The HDPE-g-GMA membrane was immersed in the metal feed solution adjusted to the desired pH. The mixture was stirred throughout the experiment at 25°C, and then removed from the solution. The concentration of the feed solution was measured by ICP. The metal uptake (Q) was calculated as follows:

$$Q = \frac{(C_1 - C_2) \cdot V}{W}$$

where Q is the metal uptake (mmol/g), W is the weight of the HDPE-g-GMA membrane. V is the volume of solution (L), and  $C_1$  and  $C_2$  are the concentrations (mmol/L) of metal ion before and after adsorption, respectively.

**RESULTS AND DISCUSSION****Grafting copolymerization**

From Figure 1 we can see that the grafting yield increases with the irradiation dose. It can be



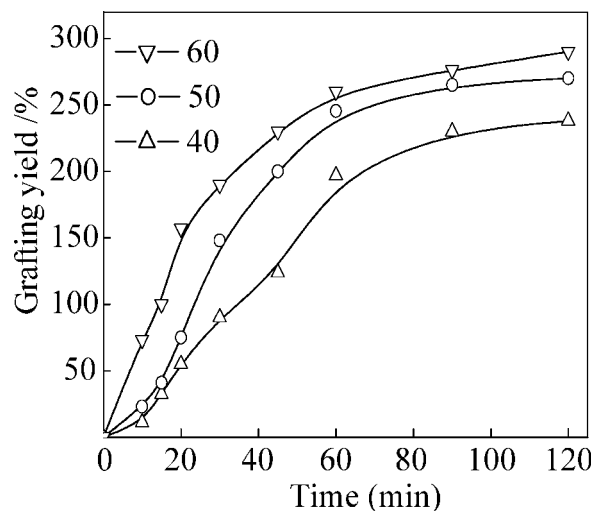
**Figure 1** Effect of irradiation dose on the grafting yield. Grafting conditions: GMA concentration in methanol, 20% (v/v); grafting temperature, 50°C; reaction time, 2 h.

assumed that the increase in the irradiation dose resulted in increasing concentration of free radicals formed in the HDPE substrate. Meanwhile, a higher absorbed dose can result in the membrane decomposition, affecting their mechanical properties.

Figure 2 shows the total grafting yield versus grafting times under different temperatures with 150 kGy preirradiation dose. In the initial reaction stage, the grafting rate increases with increase of reaction temperature. It may be explained by the fact that during this period the substrate radical concentration is very high, so the grafting reaction is controlled by the rate of monomer diffusion. The higher temperature allows more monomers to react with matrix radicals, which results in higher grafting rates and higher grafting yields under same reaction conditions. When the reaction continues for 1 h, grafting yield remains amostly constant under different temperatures. This can be attributed to the decay of the trapped radicals or termination of growing chain radical before monomers diffuse into the radical in the HDPE membrane. In a word, the preirradiation graft reaction is controlled by two factors: (1) the decaying rate of the substrate radicals and (2) the monomer diffusion rate. The increase of reaction temperature can speed up diffusion rate of monomer, but at the same time also accelerate the decay rate of the substrate radicals.

#### Characterization of the grafted membrane

The FT-IR spectrum of original HDPE (a) and HDPE-g-GMA (b) and grafted membranes treated by  $\text{NH}(\text{CH}_3)_2$  (c) are shown in Figure 3. Comparing the spectra (a) with (b), some new absorption bands appear in spectrum (b), one at  $1732\text{ cm}^{-1}$  that corresponds to the  $\text{C}=\text{O}$  group, and another at  $902\text{ cm}^{-1}$  that is due to the absorption of epoxy group

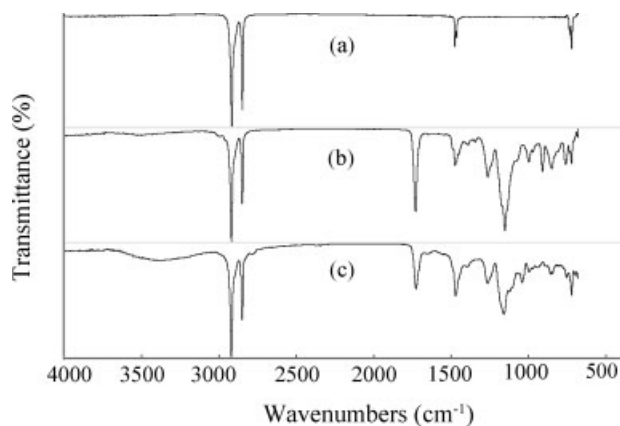


**Figure 2** Variation of grafting yield with time at various reaction temperature. Grafting conditions: preirradiation dose, 150 kGy; GMA concentration in methanol, 20% (v/v).

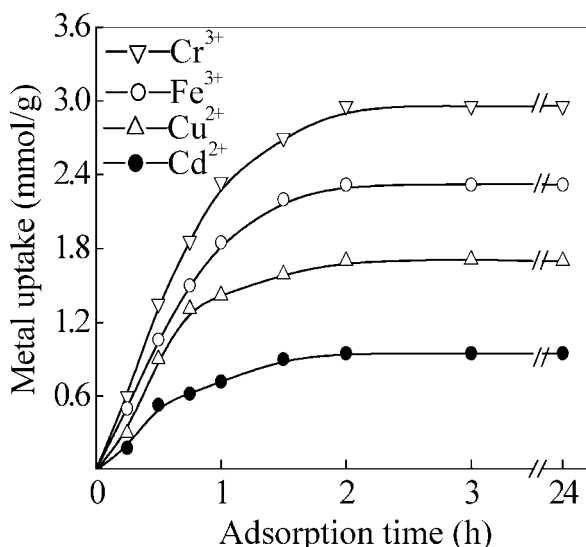
( $\text{C}-\text{O}-\text{C}$ ). The spectrum for  $\text{NH}(\text{CH}_3)_2$  treated membranes shows that the absorption peak at  $902\text{ cm}^{-1}$  disappears and a broad absorption band appears around  $3370\text{ cm}^{-1}$  and another peak around  $1037\text{ cm}^{-1}$ , which are assigned to stretching vibration of  $-\text{OH}$  and  $\text{C}-\text{N}$  groups. These results clearly indicate that GMA was grafted onto HDPE successfully and after amination epoxy group  $\text{C}-\text{O}-\text{C}$  had already become tertiary amines group  $-\text{CH}_2-\text{N}(\text{CH}_3)_2$ .

#### Effect of time on adsorption

The effect of adsorption time on the metal uptake is shown in Figure 4. As seen, metal uptake for the different metals, Cu (II), Fe (III), Cr (III), and Cd (II) increases with the adsorption time during the first 2 h and then level off toward the equilibrium. The



**Figure 3** FT-IR spectra of ungrafted HDPE (a), HDPE-g-GMA (b), and grafted membranes after amination (c).

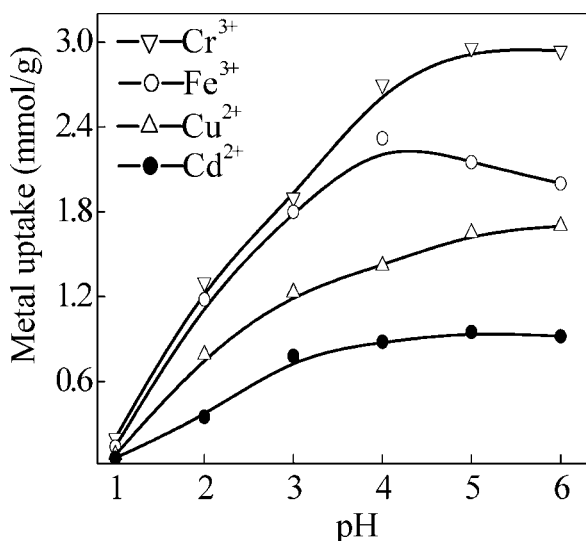


**Figure 4** Effect of adsorption time on metal uptake. Initial feed concentration: 0.015 mol/L; temperature: 25°C; pH: 5.0; grafting yield: 180%.

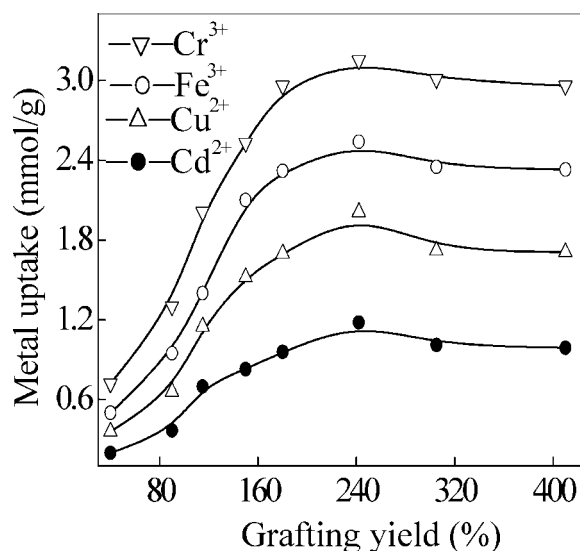
order of maximum adsorption capacity of chelate membrane was Cr (III)>Fe (III)>Cu (II)>Cd (II). This agree well with the reverse order of their atomic radii. In general, the lower is atomic radii, the higher is the metal uptake.

**Effect of pH on adsorption**

Adsorption capacity of chelate membranes for Cu (I), Fe (III), Cr (III), and Cd (II) was measured under different pH of feed solution that ranged from 1 to 6, and the results are given in Figure 5. It can be seen that the metal uptake increases obviously with the increasing pH and the maximum adsorption



**Figure 5** Effect of pH on metal uptake. Initial feed concentration: 0.015 mol/L; adsorption time: 2 h; temperature: 25°C; grafting yield: 180%.



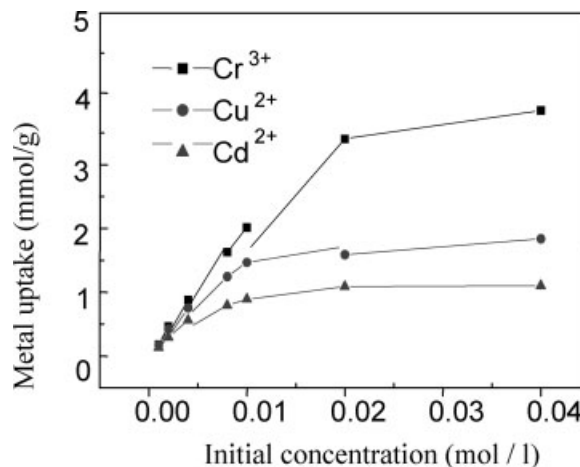
**Figure 6** Effect of grafting yield on metal uptake. Initial feed concentration: Cr<sup>3+</sup>, Fe<sup>3+</sup>, Cu<sup>2+</sup>, and Cd<sup>2+</sup>, 0.015 mol/L; adsorption time: 2 h, temperature: 25°C; pH: 5.0.

capacity was reached at pH 5.0. However, Fe (III) uptake reaches a maximum at pH 4.0. At higher pH Fe (III) would exists in solution in different forms, and some of Fe (III) change into hydroxide.

The results indicated that each metal ion has its optimum pH to form the chelated complex. Higher concentration of H<sup>+</sup> in feed solution can prevent the formation of chelated complex between membranes and metal ions. It can be seen from Figure 5 all metal ions are adsorbed poorly at pH 1.0.

**Effect of grafting yield on adsorption**

Grafting yield is another factor that affects the adsorption of metal ions by functional group of the



**Figure 7** Effect of initial concentration on metal uptake. Initial feed concentration: 0.015 mol/L; temperature: 25°C; pH: 5.0; grafting yield: 180%.

**TABLE I**  
**Effect of Regeneration Times on Metal Uptake**

Regeneration times	Maximal metal uptake (mmol/g)			
	Cr <sup>3+</sup>	Fe <sup>3+</sup>	Cu <sup>2+</sup>	Cd <sup>2+</sup>
1	2.87	2.24	1.65	0.92
2	2.75	2.13	1.59	0.9
3	2.68	2.09	1.54	0.87

modified membranes. Figure 6 shows the effect of grafting yield on the metal uptake. It can be seen that metal uptake increases with membranes grafting yield, then level off after 240% grafting yield. This increase in metal uptake can be attributed to the existence of functional groups such as epoxy which is grafted onto HDPE membrane. The leveling off of metal uptake may be attribute to the saturation of active sites on the membranes which can chelate metal ion. The similar results were observed by other researcher studies.<sup>13,14</sup>

#### Effect of initial concentration on adsorption

Figure 7 shows relationship between initial concentration of metal ions and metal uptake. It indicates that the metal uptake increased with increasing initial ion concentration, then reached a plateau volume at higher concentration. This is attribute to the chelating site of functional membrane become almost saturated when the metal ion concentration reached at 0.02 mol/L.

#### Reusability of chelate membranes

The adsorbed metal ions are easily desorbed with 0.1 mol/L hydrochloric acid at room temperature for 2 h. To evaluate the reusability of the chelating membranes, the adsorption–desorption cycle was repeated three times. As shown in Table I, the adsorption capacity of chelate membranes show a slight decrease after three times adsorption–desorp-

tion cycle. Less than 10% adsorption capacity loses after three times cycle.

## CONCLUSIONS

The chelating membrane with tertiary amines group was synthesized by grafting of GMA onto HDPE membrane using preirradiation and subsequently modified by reacting with dimethylamine. The grafting yield increases with increasing of irradiation dose. At high grafting temperature the grafting rate is fast. The adsorption of chelate membrane toward Cu (II), Fe (III), Cr (III), and Cd (II) were investigated. The adsorption capacity increase with grafting yield and reached a plateau value around 240% grafting yield. The order of maximum metal uptake was Cr (III) > Fe (III) > Cu (II) > Cd (II). The metal uptake firstly increased with adsorption time or initial concentration then leveled off. Each metal ion has its own optimum pH to form a chelated complex. The adsorbed metal ions are easily desorbed with 0.1 mol/L hydrochloric acid at room temperature.

## References

1. Charerntanyarak, L. *Water Sci Technol* 1999, 39, 135.
2. Eom, T. H.; Lee, C. H.; Kim, J. H.; Lei, C. H. *Desalination* 2005, 180, 163.
3. Moon, C. J.; Lee, J. H. *Process Biochem* 2005, 40, 1279.
4. Alami, S.; Larbot, A.; Persin, M. *J Membr Sci* 1994, 91, 87.
5. Betz, N.; Begue, J.; Goncalves, M. *Nucl Instrum Meth Phys Res Sect B* 2003, 208, 434.
6. Nho, Y. C.; Garnett, J. L.; Dworjany, P. A. *J Polym Sci* 1992, 30, 1219.
7. Choi, Y. J.; Kang, M. S.; Kim, S. H. *J Membr Sci* 2003, 223, 201.
8. Wavhal, D. S.; Fisher, E. R. *J Membr Sci* 2002, 209, 255.
9. Kang, D. W.; Choi, H. R.; Kweon, D. K. *J Appl Polym Sci* 1999, 73, 469.
10. Saito, K.; Kaga, T. H.; Yamagishi, S. *J Membr Sci* 1989, 43, 131.
11. Choi, S. H.; Nho, Y. C.; Kim, G. T. *J Appl Polym Sci* 1999, 72, 659.
12. Choi, S. H.; Nho, Y. C. *J Appl Polym Sci* 1999, 71, 2227.
13. Lin, W.; Hsieh, Y. L. *J Polym Sci Part A: Polym Chem* 1997, 35, 631.
14. Lu, Y.; Zhang, Z.; Zeng, H. *J Appl Polym Sci* 1994, 53, 405.