Adsorption of Pb²⁺ and Pd²⁺ on Polyethylene Membrane with Amino Group Modified by Radiation-Induced Graft Copolymerization

SEONG-HO CHOI,¹ YOUNG CHANG NHO,¹ GEUG-TAE KIM²

¹ Korea Atomic Energy Research Institute, Taejon 305-600, Korea

² Department of Chemical Engineering, Hannam University, Taejon 306-791, Korea

Received 10 February 1998; accepted 3 July 1998

ABSTRACT: Six chelating hollow fiber membranes were prepared by radiation-induced grafting of glycidyl methacrylate onto a polyethylene hollow fiber membrane and its subsequent amination. The adsorption characteristics of Pb^{2+} and Pd^{2+} for the chelating hollow fiber membranes were presented when the solution of Pb^{2+} and Pd^{2+} permeates across the chelating membrane, respectively. The degree of grafting for glycidyl methacrylate increases with increasing monomer concentration, reaction temperature, and preirradiation dose. The adsorption of Pd^{2+} by chelating hollow fiber membranes modified with five kinds of amines was in the following order: diethylene triamine > hexamethyl diamine > ethylene diamine > dimethyl amine > trimethyl amine. The chelating hollow fiber membrane modified with iminodiacetic acid adsorbed Pb^{2+} ions much more than Pd^{2+} . © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 643–650, 1999

Key words: radiation-induced graft copolymerization; chelating hollow fiber membrane; glycidyl methacrylate; amination; iminodiacetic acid

INTRODUCTION

The effective treatment of heavy metals in the environment has been one of the major issues owing to their toxicities. The treatment of aqueous wastes, including soluble heavy metals, needs concentration of the metallic solution into a small volume, followed by recovery or secure disposal. Heavy metals can be removed by the adsorption on solid materials.¹ Activated carbon, metallic oxides, and ion-exchange resins^{2,3} have been used as nonspecific adsorbents. Recently, chelating resins⁴ have been applied for the selective adsorption of specific metallic ions from industrial

Correspondence to: Y. C. Nho.

wastes. Guler and colleagues⁵ reported that a new polymeric adsorbent bearing both hydrophilic groups caused swelling in the water and amidoxime groups for chelating with uranyl ions.⁵

The microfiltration membrane, having an affinity ligand and an ion-exchange group, is capable of separating a trace of specified ions during permeation across the membrane. Graft polymerization of vinyl monomers onto polymer substrates has attracted considerable interest because it imparts some desirable properties, such as chelation, ion exchange, biocompatibility, and protein adsorption. Graft polymerization is one of the methods for preparing functional materials with new properties. This technique has enabled the preparation of a polymeric material containing functional groups on its branch grafted onto a

Journal of Applied Polymer Science, Vol. 71, 643-650 (1999)

^{© 1999} John Wiley & Sons, Inc. CCC 0021-8995/99/040643-08



Scheme 1 Preparation of chelating hollow fiber membrane.

variety of substrate polymers, such as films,⁶ fibers, nonwoven fabric,^{7–9} and hollow fibers.^{10,11}

Graft polymerization is achieved by ionization radiation,¹² UV,¹³ plasma,¹⁴ or chemical initiators,¹⁵ but among them radiation-induced grafting can be one of the most effective techniques because of its uniform creation of radical sites in the polymer matrix. In general, two techniques for radiation grafting can be used: (1) the direct method,¹⁶ whereby a polymer substrate is immersed or dissolved in either an individual monomer or a solution of monomers, and then the whole mixture is irradiated; and (2) the preirradiation method,¹⁷ where a polymer substrate is activated by irradiation, regardless of the presence of oxygen, and sequentially allowed to react with the monomer.

In recent years, preirradiation techniques have been extensively reported on some crystalline polymers.^{17,18} Graft polymerization of glycidyl methacrylate (GMA) onto polymer substrates is advantageous because the epoxy group of GMA is modified easily to have functions such as ion exchange¹⁹ and adsorption of toxic gases,²⁰ with the original properties remaining intact. Tsuneda and colleagues²¹ introduced iminodiacetate chelating groups onto the polyethylene membrane for the purpose of the removal of cobalt ion from the aqueous solution using the radiation-induced grafting process. Konishi and colleagues²² reported a method for the introduction of the highdensity iminodiacetate group without lowering the liquid permeability of the porous membrane.

In this study, six chelating hollow fiber membranes were prepared by radiation-induced grafting of GMA onto a polyethylene (PE) hollow fiber membrane (PE-HM) and its subsequent amination. When the lead and palladium solution was permeated across the chelating hollow fiber membranes for six types of chelating hollow fiber membranes containing trimethyl amine (TMA), dimethyl amine (DMA), ethylene diamine (EDA), hexamethyl diamine (HMDA), diethylene triamine (DETA), and iminodiacetic acid (IDA), respectively, the adsorption characteristics of these chelating hollow fiber membranes on Pb^{2+} and Pd^{2+} were examined.

EXPERIMENTAL

Materials

A commercially available microfiltration hollow fiber membrane (Asahi Chemical Industry Co., Ltd.) was used as a trunk polymer for the grafting. The inner and outer diameters of the porous PE-HM were 1.95 and 3.01 mm, respectively. PE-HM has $0.34 \ \mu m$ pore diameter and 71% porosity. GMA (CH₂=CCH₃COOCH₂CHOCH₂) was used without further purification. Other chemicals were of reagent grade.

Grafting Procedures

PE-HM was irradiated by γ -rays from cobalt-60 under atmospheric pressure and ambient temperature, and then was added to a reaction ampoule with a cock. After evacuating the ampoule, the monomer solution was placed into the ampoule. Grafting copolymerization was conducted at temperatures of 30°C, 50°C, and 70°C.

After a grafting reaction, the monomer and homopolymer were removed with tetrahydrofuran (THF), and the GMA-grafted microfiltration membrane obtained by grafting copolymerization was dried in a vacuum at 60°C for 4 h.

In studies on the effects of various parameters on grafting copolymerization, the degree of grafting is defined as

Degree of grafting (%) =
$$\frac{(W_g - W_o)}{W_o} \times 100$$
 (1)

where W_g and W_o denote the weights of the grafted and ungrafted PE hollow fibers, respectively.

Preparation of Chelating Hollow Fiber

Scheme 1 shows the preparation procedure of ra-

diation grafting of GMA onto PE-HM and the introduction of functional groups, such as TMA, DMA, EDA, HMDA, DETA, and IDA. GMA was grafted onto the preirradiated PE-HM, and then subsequently reacted with various amines, such as EDA, TMA, DMA, DETA, HMDA, and IDA in a glass ampoule at various temperatures and times, respectively. A 30% aqueous amine solution was used in this study, except for IDA and EDA. The conversion yields (%) of the aminated hollow fiber membranes above were calculated as follows:

EDA × (%) = 100[(
$$W_s - W_g$$
)
/60]/[($W_g - W_o$)/142] (2)

$$TMA \times (\%) = 100[(W_s - W_g)/77] /[(W_g - W_o)/142]$$
(3)

$$DMA \times (\%) = 100[(W - W_g)/45] /[(W_g - W_o)/142]$$
(4)

DETA × (%) = 100[(
$$W_s - W_g$$
)/103]
/[($W_g - W_o$)/142] (5)

HMDA × (%) = 100[
$$(W_s - W_g)/116$$
]
/[$(W_g - W_o)/142$] (6)

$$IDA \times (\%) = 100[(W_s - W_g)/133] /[(W_g - W_o)/142]$$
(7)

where W_s is the weight of the aminated PE-HM 60, 45, 103, 116, and 133 in eqs. (2) through (7) correspond to the molecular weights of EDA, DMA, DETA, HMDA, and IDA, respectively. 77 in



Scheme 2 Experimental apparatus for determining flux and breakthrough curves.



Figure 1 Grafting of GMA onto irradiated PE hollow fiber at 50°C for 1 h.

eq. (3) is the molecular weight of the $[-N^+(CH_3)_3]$ -OH⁻ complex. 142 in eqs. (2) through (7) corresponds to the molecular weight of GMA.

Breakthrough Curve

Scheme 2 shows the experimental apparatus for measuring pure flux and breakthrough curves. The inner and outer diameters and the lengths of PE-HM were measured in the wet state with a microscope, respectively. After the hollow fiber was dried in a vacuum, the pore volume distribution was measured by a mercury intrusion method. The flux, u_i , was determined by

$$u_i = (\text{volumetric flow rate})/\pi D_i L$$
 (8)

where D_i is the inner diameter and L is the length of the hollow fiber membrane (10 cm). The volume flow rate of pure water was measured from the amount of dropping from the outside of the membrane. The pressure in the feed tank, shown in Scheme 2, was 1.0×10^5 Pa. The collection of Pb²⁺ and Pd²⁺ during permeation of the solution across the membrane was conducted in a measuring cylinder under a constant pressure of 1.0×10^5 Pa. The concentrations of Pb²⁺ and Pd²⁺ obtained during permeation were determined by inductively coupled plasma atomic emission spectroscopy. The extent of adsorption was determined by a ratio of C to C° , with C° being the



Figure 2 Grafting of GMA onto 40 kGy-irradiated PE hollow fiber in MeOH for 1 h.

initial concentration of Pb^{2+} and Pd^{2+} , respectively, before the permeation across the membrane, and *C* being their final concentrations after permeation. The permeation volume (PV) was determined by

$$PV = \pi D_i L u_i t \tag{9}$$

where t is the time of permeation.

RESULTS AND DISCUSSION

Grafting Copolymerization

The grafting of GMA onto PE-HM was conducted by the preirradiation grafting technique. Attention was paid to the effects of irradiation dose, reaction time, reaction temperature, and solvents on the extent of grafting. Figure 1 illustrates the effects of GMA concentration on the grafting of GMA onto PE-HM at 50°C in methanol (MeOH) for 1 h. The grafting yields increased by increasing both the GMA concentration and irradiation dose. As shown in Figure 1, similar curves for the degree of grafting versus GMA concentration (%) are obtained for three different irradiation doses, which indicates the same grafting mechanism at fixed experimental conditions of temperature, time, and GMA concentration. Over a GMA concentration ranging from 70 to 100%, the grating degree was more sensitive, compared with the same other range. Therefore, the select ion of a suitable monomer concentration is a valuable factor to get a desirable grafting yield.

Figure 2 shows the effect of reaction temperature on the grafting of GMA onto the irradiated PE-HM in MeOH at reaction temperatures of 30° C, 50° C, and 70° C for 1 h. The degree of grafting increased with increasing temperature and GMA concentration. A slight increase in GMA concentration greatly increased the degree of grating at 70° C, compared with 50° C and 30° C. The reason for this is due to radicals formed when the peroxide caused by oxygen during irradiation in air is decomposed at the temperature of 70° C. Therefore, a relatively higher temperature is required to obtain a high grating yield, indicating that another important factor for grafting is the reaction temperature.

Figure 3 shows variations in the degree of grafting with GMA concentrations onto preirradiated PE-HM for various solvents, such as MeOH, acetone, and THF. As for Figure 3, GMA was grafted on 40 kGy-irradiated PE-HM at a fixed temperature of 50°C for 1 h. Among the solvents, a slight deviation in the degree of grafting was observed, which is likely to be related to the solvent or nonsolvent for polyGMA. It was shown that a nonsolvent system, such as MeOH for polyGMA, was slightly beneficial to the grafting



Figure 3 Grafting of GMA onto 40 kGy-irradiated PE hollow fiber at 50°C for 1 h.



Figure 4 Pore diameter distribution of PE hollow fiber.

yield. Such an example was shown in the grafting of styrene onto a PE film in good solvent and nonsolvent for polystyrene. Nonsolvents, such as MeOH for polystyrene, which is formed during the grafting reaction of styrene, is beneficial to a



Figure 5 Dimensional change accompanied by grafting of GMA.



Figure 6 Amination of 80% GMA-grafted PE hollow fiber using 100% EDA as a function of reaction temperature.

high grafting yield. As seen in Figures 1–3, the highest grafting yield was obtained at a 100% GMA concentration for the irradiation doses, reaction temperatures, and solvents under consideration in this study.

Figure 4 shows the relationship between the pore volume distributions and the grafting yield. The pore volume on a region ranging from a 1 to $10^{-1} \mu m$ pore diameter was found to be large. The pore volume decreased with a decrease in the degree of grafting. The pore volume of 2.6 L kg⁻¹ for the ungrafted PE-HM was reduced to 1.75 L kg⁻¹ for the 50% grafting yield, and to ~ 1.5 L kg⁻¹ for the 80% and 100% grafting yield. The pore volume was approximately linearly proportional to the degree grafting of up to 80%, but nonproportional beyond the grafting value.

The dimensional change in the hollow fiber accompanied by the grafting was shown in Figure 5. It was observed that the size of the inner diameter and outer diameter increased with an increase in the grafting yield. This is because the increase in the degree of grafting caused the GMA-grafted hollow fiber to swell.

Amination of GMA-Grafted PE Hollow Fiber

TMA, DMA, EDA, HMDA, DETA, and IDA were introduced onto 80% and 100% GMA-grafted



Figure 7 Effect of reaction time and temperature on 80% GMA-grafted PE hollow fiber with 50% EDA aqueous solution.

PE-HM to make chelating membranes having various amino groups by varying conditions, such as temperature, time, solvent, and concentration. Figure 6 shows the effect of reaction time on the extent of amination conversion. 80% GMAgrafted PE-HM was used for amination with



Figure 8 Effect of EDA concentration on 80% GMAgrafted PE hollow fiber at 50°C.



Figure 9 Amination of 80% GMA-grafted PE hollow fiber using 0.425M IDA solution at 80°C. DMSO, dimethylsulfoxide; EtOH, ethanol.

100% EDA concentration. In all cases at 30°C, 50°C, and 70°C, the conversion (%) increased with increasing reaction time. In particular, the sharp increase in conversion occurred over a 0- to 5-min span. Figure 7 shows the effect of EDA concentration on the amination extent. The addition reaction of EDA to an 80% GMA-grafted PE-HM was linearly proportional to the EDA concentration.

TMA, DMA, EDA, DETA, and HMDA were introduced onto an 80% GMA-grafted PE-HM to make a chelating membrane having various amino groups at 50°C (Fig. 8). The reaction of TMA and DMA increased rapidly up to 5 min, and then decreased slowly, whereas EDA, DETA, and HMDA, having lower reaction rates than TMA and DMA, increased slowly up to 30 min.

Figure 9 shows the effects of reaction time and solvents on the amination of 80% GMA-grafted PE-HM using 0.425*M* IDA at 80°C. The amination reaction increased with the reaction time for mixed solvents, such as dimethylsulfoxide/water, MeOH/water, ethanol/water, dioxane/water, dimethylformamide/water, acetone/water, and THF/ water, but amination did not occur in the presence



Figure 10 Dimensional change accompanied by conversion of EDA.

of water. Among the mixed solvents, dimethylformide/water was the most effective for introducing IDA to GMA-grafted PE-HM. As long as the mixed solvent can dissolve IDA for any kind of mixed sol-



Figure 11 Breakthrough curves of Pb^{2+} ion by the PE hollow fiber membrane (dg = 100%) modified with EDA.



Figure 12 Breakthrough curves of Pd^{2+} ion by the PE hollow fiber membrane (dg = 100%) modified with various amino groups.

vents, the small ratio of water versus organic solvent led to the large conversion yield of IDA.

Properties of Chelating Hollow Fiber and Breakthrough Curves

Figure 10 shows the dimensional change of hollow fiber accompanied by introducing EDA onto GMA-grafted PE-HM. It was observed that the sizes of the inner and outer diameters increased with an increase in the conversion yield of EDA. The increase in diameter of the hollow fiber membrane can be attributable to the increase in hydrophilicity by the introduction of EDA onto GMA-grafted PE-HM.

Characteristics of the chelating hollow fiber membrane were discussed for the Pb^{2+} and Pd^{2+} ions. The solution (200 mg L⁻¹) was forced to permeate across the chelating hollow fiber membrane containing EDA and IDA, respectively.

Figure 11 shows the breakthrough curves of Pb^{2+} with respect to the chelating hollow fiber membranes with three different EDA conversions (25%, 55%, and 95%). Pb^{2+} [200 mg L⁻¹ (200 ppm)] was used for the inlet concentration. In a 95% EDA yield, C/C° remained 0 until the PV value reached 0.08. After this point, the C/C° rose



Figure 13 Breakthrough curves of Pb^{2+} and Pd^{2+} ion by the PE hollow fiber membrane (dg = 100%), with a conversion yield of 15% IDA.

gradually with increased PV. A higher EDA conversion required higher PV until $C/C^{\circ} = 1$. At $C/C^{\circ} = 1$, the amount of Pb^{2+} adsorbed by the chelating fiber membrane with EDA functionality can be calculated from the area of $PV \times C$, which is the area of the upper portion above the breakthrough curves. The adsorbed amounts of Pb^{2+} were 17.8, 26.4, and 37.4 g kg⁻¹ PE-HM with EDA conversion yields of 25%, 55%, and 95%, respectively. These results indicated that the adsorption amount of Pb^{2+} across the chelating fiber modified with EDA increased with increasing EDA conversion.

Figure 12 shows the breakthrough curves of Pd^{2+} for the chelating fibers with TMA, DMA, EDA, DETA, and HMDA functionality. Pd²⁺ (200 mg L^{-1}) was used for inlet concentration. A DETA-modified hollow fiber membrane was found to be superior to TMA, DMA, EDA, and HMDAmodified hollow fiber membranes. In a 79% conversion yield for DETA, C/C° remained 0 until the PV value reached 0.44 L. After this point, the C/C° rose gradually with increased PV. The adsorbed amount of Pd^{2+} was estimated to be 129.7 g kg⁻¹ (DETAmodified hollow fiber membrane). PE-HM with DETA functionality had a higher PV to reach C/C° = 1, compared with other amino groups. The adsorption effect of Pd²⁺ flowed in the order of DETA > HMDA > EDA > DMA > TMA.

Figure 13 shows the breakthrough curves of Pb^{2+} and Pd^{2+} by a chelating fiber membrane modified with IDA. The inlet concentration of Pb^{2+} and Pd^{2+} were both 200 mg L⁻¹. *C/C*° remained 0 until the *PV* value reached the breakthrough point (0.06 L and 0.13 L) in Pd^{2+} and Pb^{2+} , respectively. The chelating hollow fiber containing IDA was found to have a higher adsorption capacity for Pb^{2+} than Pd^{2+} .

REFERENCES

- Yigitoglu, M.; Ersoz, M.; Coskun, R.; Sanli, O.; Unal, H. I. J Appl Polym Sci 1998, 68, 1935.
- Hebeish, A.; Waly, A.; Abdel-Mohdy, F. A.; Aly, A. S. J Appl Polym Sci 1997, 66, 1029.
- 3. Lehrfeld, J. J Appl Polym Sci 1997, 66, 491.
- Lezzi, A.; Cobianco, S.; Roggero, A. J Polym Sci Part A 1994, 22, 1877.
- Guler, H.; Sahiner N.; Aycik, G. A.; Guven, O. J Appl Polym Sci 1997, 66, 2475.
- Turmanova, S.; Dimitrova, A.; Kostov, G.; Nedkov, E. Macromol Chem Phys 1996, 197, 297.
- Sugo T.; Saito, K. Bull Seawater Sci Jpn 1989, 43, 3.
- Kim, M.; Saito, K.; Frusaki, S.; Saito, T.; Sugo, T.; Ishigaki, I. J Chromatogr 1991, 585, 45.
- 9. Tsuneda, S.; Shinano, H.; Saito, K.; Furusaki, S.; Sugo, T.; Makuuchi, K. Biotechnol Bioeng 1994, 10, 76.
- Omichi, H.; Katakai, A.; Sugo, T.; Okamoto, J. Separ Sci Tech 1986, 21, 563.
- 11. Yamagishi, H.; Saito, K.; Frusaki, S.; Sugo, T.; Ishigaki, I. Ind Eng Chem Res 1991, 30, 2234.
- Nho, Y. C.; Garnett, J. L.; Dworjanyn, P. A. J Polym Sci 1992, 30, 1219.
- Nho, Y. C.; Garnett, J. L.; Dworjanyn, P. A. J Polym Sci Polym Chem Ed 1991, 31, 1621.
- 14. Seguchi T.; Tamura, N. J Polym Sci Polym Chem Ed 1974, 12, 1671.
- 15. Wu, S. Polymer Interface and Adhesion; Marcel Dekker: New York, 1982.
- Shinano, H.; Tsuneda, S.; Saito, K.; Frusaki, S.; Sugo, T. Biotechnol Prog 1993, 9, 193.
- 17. Nho, Y. C.; Park, J. S.; Jin, J. H. H M S-Pure Appl Chem A34 1997, 831.
- Jansen B.; Ellinghorst, G. J Biol Mater Reser 1985, 19, 1085.
- Kim, M.; Saito, K.; Frusaki, S.; Sato, T.; Sugo, T.; Ishigaki, I. J Chromatogr 1996, 586, 27.
- Park, J. S.; Nho, Y. C. Polymer (Korea) 1997, 21, 325.
- 21. Tsuneda, S.; Saito, K.; Frusaki, S.; Sugo, T.; Okamoto, J. J Membr Sci 1991, 58, 221.
- 22. Konishi, S.; Saito, K.; Frusaki, S.; Sugo, T. Ind Eng Chem Res 1992, 31, 2722.