Adsorption of Co²⁺ by Stylene-*g*-Polyethylene Membrane Bearing Sulfonic Acid Groups Modified by Radiation-Induced Graft Copolymerization

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Received 20 March 1998; accepted 5 September 1998

ABSTRACT: Cation-exchange hollow fiber membrane was prepared by radiation-induced grafting polymerization of styrene onto polyethylene hollow fiber membrane and its sulfonation. Adsorption characteristics for the cation-exchange membranes are examined when the solution of Co^{2+} permeates across the cation-exchange fiber membrane. The maximum grafting peak was obtained from 70% styrene concentration at 50°C. The degree of grafting (%) was enhanced with additives such as H_2SO_4 and divinylbenzene. The content of $-\text{SO}_3\text{H}$ groups ranged from 2 to 5 mmol g⁻¹ with chlorosulfonic acid (ClSO₃H) in dichloroethane, from 0.5 to 6 mmol g⁻¹ with ClSO₃H in H_2SO_4 , respectively. The adsorption of Co^{2+} by the cation-exchange membranes increased with increasing $-\text{SO}_3\text{H}$ content. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 2227–2235, 1999

Key words: cation-exchange hollow fiber membrane; radiation-induced graft copolymerization; styrene; cobalt; adsorption characteristics

INTRODUCTION

The search for new and improved membrane properties, using almost every available polymeric material, $^{1-6}$ has been the subject of very considerable and extensive research because of its great practical importance.

Graft polymerization is a well-known method for modification of the chemical and physical properties of polymeric materials, and is of particular interest for achieving specifically desired properties, as well as excellent membrane quality, because various commercial polymers can be used as the grafting substrate. Graft polymerization can be achieved by ionizing radiation,⁷ UV,⁸ plasma treatment,⁹ or chemical initiators.¹⁰ Of these, the radiation process is one of the most promising techniques, because it is possible to get the uniform formation of active sites for initiating grafting throughout the matrix.¹¹

A hollow fiber membrane has an advantage in terms of the ratio of surface area to volume comparing with a flat sheet membrane because the former has the high ratio. A polymer with a functional group cannot always be molded into a porous hollow fiber membrane. Therefore, the chemical modification of existing hollow fibers is effective in adding new properties to collect proteins¹² and metallic ions.¹³

The role of additives is important in the radiation grafting process, because the addition of appropriate compounds can enhance grafting yields. In this study, the grafting of styrene onto polyethylene hollow fiber membrane (PEHM) was conducted by the preirradiation grafting technique. The effects of the reaction time, the reac-

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Journal of Applied Polymer Science, Vol. 71, 2227-2235 (1999)

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tion temperature, and additives [such as sulfuric acid (H_2SO_4) and divinylbenzene on grafting reaction] were studied.

In a previous article,¹⁴ the adsorption characteristics of lead and palladium ions were examined when two ions were permeated across six types of the chelating hollow fiber membranes containing trimethylamine, dimethylamine, ethylenediamine, hexamethyldiamine, diethylenetriamine, iminodiacetate, respectively.

In this study, cation-exchange hollow fiber membrane was prepared by radiation-induced grafting of styrene onto PEHM and its subsequent chemical modification. When the cobalt (Co^{2+}) solution is permeated across the cationexchange hollow fiber membrane with —SO₃H, the adsorption characteristics of cation-exchange membrane on Co^{2+} were examined.

EXPERIMENTAL

Materials

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

Grafting Procedures

PEHM irradiated by γ -ray from Co-60 under atmospheric pressure and ambient temperatures was added in a reaction ampoule with a cock. After evacuating the ampoule, the monomer solution was placed into the ampoule. Grafting copolymerizations were conducted at 30°C and 50°C.

After grafting reaction, the monomer and homopolymer were removed from the membrane by extraction with benzene, and styrene-grafted microfiltration membrane obtained was dried in vacuum at 60°C for 4 h.

To study 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 polyethylene hollow fiber, respectively.



Scheme 1 Preparation of cation-exchange hollow fiber membrane. PE, polyethylene; ST, styrene.

Preparation of Cation-Exchange Hollow Fiber Membrane

Scheme 1 shows the preparation procedure of radiation grafting of styrene onto PEHM and introduction of a functional group of sulfonic acids $(-SO_3H)$.

Styrene was grafted onto the preirradiated PEHM, and then reacted with chlorosulfonic acid (ClSO₃H) in ClCH₂CH₂Cl, and ClSO₃H in H₂SO₄ in a glass ampoule at various times and concentrations, respectively. After sulfonation, the cation-exchange hollow fiber are washed with the order of 99% H₂SO₄ > 50% H₂SO₄ > 20% H₂SO₄ > deionized water, and was dried under reduced pressure, and then weighted (W_s). The —SO₃H content (mmol g⁻¹) was calculated as follows:

-SO₃H Content (mmol g^{-1})

$$=rac{(W_s-W_g)}{W_s} imesrac{1000}{81}$$
 (2)

where W_s is the weight of the cation-exchange hollow fiber containing —SO₃H and factor 81 corresponds to the molecular weight of SO₃H.

Subsequently, —SO₃H group content was also measured by titration. —SO₃H form membrane was immersed in 5% NaCl aqueous solution at room temperature for 12 h, and then the hydrogen ion liberated from the membrane was titrated with 0.02M NaOH aqueous solution.

Breakthrough Curve

Scheme 2 shows the experimental apparatus for measuring pure flux and breakthrough curves. The inner and outer diameters and the length of hollow fiber membrane were measured in the wet state with a microscope, respectively. After the hollow fiber was dried under reduced pressure, the pore volume distribution was measured by the mercury intrusion method. Flux, u_i , was determined by

$$u_i = (\text{volumetric flow rate})/\pi D_i L$$
 (3)



Scheme 2 Experimental apparatus for determining flux and breakthrough curves. PE, polyethylene.

where D_i is the inner diameter and L is the length of the hollow fiber membrane (9.0 cm). The volumetric flow rate of pure water was measured from the dropping amount from the outside of the membrane. The pressure in the feed tank, shown in Scheme 2, was 1.0×10^5 Pa. A measuring cylinder was used to collect Co²⁺ during permeation of the solution across the membrane under a constant pressure of $1.0 imes 10^5$ Pa. The concentration of Co^{2+} ion obtained during permeation was determined by inductively coupled plasma atomic emission spectroscopy. The extent of adsorption was determined by a ratio of $C : C^{\circ}$, C° being the initial concentration of Co^{2+} before the permeation across sulfonated membrane, and C being the final concentration after permeation. The permeation volume (PV) was determined by:

$$PV = \pi D_i L u_i t \tag{4}$$

where t is the time of permeation.

RESULTS AND DISCUSSION

Grafting Copolymerization

The grafting of styrene onto PEHM was conducted by the preirradiation grafting technique. The effects of reaction time, reaction temperature, and additives (such as H_2SO_4 and divinylbenzene) on the grafting reaction were studied in this study.

The role of additives is important in the radiation grafting process, because the addition of appropriate compounds can enhance grafting yields. Thus, the radiation dose required to achieve a particular percentage graft can be lowered in the presence of additives. This is of value especially for backbone polymer, which is radiation sensive. This concept is also of economic significance in commercial processing, because lower radiation doses are required to produce a given product.

Figure 1 illustrates the effects of styrene concentration on the grafting of styrene onto 40 kGyirradiated PEHM in the presence and absence of H_2SO_4 using methanol (MeOH) as solvent. The degree of grafting (%) was increased with increased reaction temperature. The maximum degree of grafting was observed \sim 70% monomer concentration at 50°C, presumably due to a Trom-msdorff-type effect.¹⁵ On the other hand, the grafting reaction was insignificant at 30°C. Therefore, a relatively high temperature is required for a high grafting yield, which indicates that another important factor for grafting is the reaction temperature. The grafting yield increased significantly with the addition of H₂SO₄. The effect of H₂SO₄ concentration on the grafting yield is shown in Figure 2. As shown in Figure 2, the grafting yield increased rapidly with increased H_2SO_4 .

Mechanistically, the acid enhancement effect in grafting, based on Garnett's¹⁶ work, has been



Figure 1 Grafting of styrene onto 40 kGy-irradiated polyethylene hollow fiber for 14 h.



Figure 2 Grafting of styrene onto 40 kGy-irradiated polyethylene hollow fiber at 50°C for 14 h.

attributed to a partitioning phenomenon. Thus, in the present polyethylene system involving the grafting of styrene in MeOH, partitioning of monomer into the backbone polymer may be significantly improved by the inclusion of H_2SO_4 in the grafting solution. With nonpolar polyethylene, acid will remain predominantly partitioned onto the more polar bulk grafting monomer solution and thus becomes available for increasing the partitioning of styrene onto the backbone polymer and thus enhancing grafting. Generally, the extent of this improved monomer partitioning depends on the polarity of the monomer, the substrate, solvent, and the concentration of H_2SO_4 present in the grafting solution.

Divinylbenzene, having a similar chemical structure with styrene, was used for examining the effect of multifunctional monomer on the grafting yields (Fig. 3). The addition of divinylbenzene to the grafting solution enhanced the grafting yield. When divinylbenzene monomer was combined with H_2SO_4 , the synergistic effect in radiation grafting was observed, with the enhancement on grafting yield being accentuated at the Trommsdorff peak. The inclusion of divinylbenzene and H_2SO_4 increases the grafting yields for all solutions studied. The level of enhancement by divinylbenzene is generally not as significant as found with H₂SO₄. The enhancement of grafting yield by multifunctional monomer seems to accelerate grafting by chain branching.

Figure 4 shows the effects of reaction time on the grafting of styrene onto 40 kGy-irradiated PEHM at a temperature of 30°C and 50°C in the presence and absence of H_2SO_4 . The degree of grafting increased with increased reaction time at 50°C. On the other hand, the grafting reaction proceeded very slightly at 30°C, regardless of the inclusion of H_2SO_4 .

Figure 5 shows the relationship between pore diameter distribution and the grafting yield when PEHM was grafted with styrene. Styrene-grafted PEHM consisted mostly of the pore diameters ranging from 1 to $10^{-1} \mu$ m. While ungrafted, PEHM has the broad range of pore diameter, compared with grafted PEHM. The pore volume decreased with decreased grafting yield. The pore volume of 2.7 L kg⁻¹ for the ungrafted PEHM was reduced to 1.75 L kg⁻¹ for the 100% grafting yield, to ~ 0.8 L kg⁻¹ for 250% grafting yield. The pore volume was approximately linearly in inverse proportion to the degree of grafting up to 250%.

Figure 6 shows the pure water flux of ungrafted and grafted PEHM. Pure water flux was decreased with increased grafting yield. The increase in grafting yield caused decreased water permeability because the grafted polymer branches are formed on the micropore.

Figure 3 Grafting of styrene onto 40 kGy-irradiated polyethylene hollow fiber at 50°C for 14 h. DVB, divinylbenzene.

Figure 4 Grafting of styrene (70% v/v) onto 40 kGyirradiated polyethylene hollow fiber in MeOH.

Sulfonation of Styrene-Grafted PEHM

Styrene-grafted PEHM (150%) was dipped into a mixture of $ClSO_3H/ClCH_2CH_2Cl$ to make the cation-exchange membrane having the —SO₃H

Figure 5 Pore diameter distribution of polyethylene (PE) hollow fiber. St, styrene.

Figure 6 Pure water flux of polyethylene and styrene-grafted PE hollow fiber.

group, varying the parameters, such as $\rm ClSO_3H$ concentrations and swelling agents for polyethylene membrane.

Figure 7 shows the effects of swelling agents on the sulfonation reaction when 150% styrenegrafted PEHM was treated by 5% ClSO₃H in

Figure 7 Sulfonation of 150% styrene-grafted polyethylene with 5% $ClSO_3H$ in $ClCH_2CH_2Cl$ at room temperature for 30 min.

Figure 8 Sulfonation of 150% styrene-grafted polyethylene hollow fiber with $ClSO_3H$ in $ClCH_2CH_2Cl$.

ClCH₂CH₂Cl at room temperature for 30 min. In the case where the swelling solvents (such as ClCH₂CH₂Cl, CCl₄, and CHCl₃) were used, the content of —SO₃H (mmol g⁻¹) ranged from 3.2 to 3.8 mmol g⁻¹. The content of —SO₃H was only ~ 2.2 mmol g⁻¹ without swelling agent. It was almost impossible to get the high yield of sulfonation unless the internal part of the polymer is sulfonated by using swelling agents. The swelling effect followed in order of ClCH₂CH₂Cl > CCl₄ > CHCl₃.

Figure 8 shows the effects of $ClSO_3H$ concentration in $ClCH_2CH_2Cl$ on the sulfonation as a function of reaction time. The high concentration of $ClSO_3H$ in $ClCH_2CH_2Cl$ is effective for sulfonation at initial time (5 min); however, low concentration of $ClSO_3H$ in $ClCH_2CH_2Cl$ was effective after 10 min of sulfonation. Concerning the sulfonation of 150% styrene-grafted PEHM, the content of sulfonation increased with increased reaction time.

Figure 9 shows the effects of $ClSO_3H$ concentration in H_2SO_4 on the content of $-SO_3H$. The sulfonation of styrene-grafted PEHM increased with the increased $ClSO_3H$ concentration in H_2SO_4 . The content of $-SO_3H$ was linearly proportional to the reaction time.

Figure 10 shows the comparison of $-SO_3H$ content determined from weight gain and titration. It was shown that $-SO_3H$ content deter-

Figure 9 Sulfonation of 150% styrene-grafted polyethylene hollow fiber with $ClSO_3H$ in H_2SO_4 .

mined by the weight gain accurately coincided with that by titration.

Properties of Cation-Exchange Hollow Fiber and Breakthrough Curves

Figure 11 shows the breakthrough curves of Co²⁺ with inlet concentration of Co^{2+} of 50 ppm and 80 ppm. With 80 ppm Co^{2+} , C/C° remained 0 until the PV value reached 0.008. After this point, the C/C° rose gradually with increasing PV. A lower inlet concentration required higher PV until C/C° = 1. At C/C° = 1, the amount of Co^{2+} adsorbed by the cation-exchange fiber membrane with the -SO₃H 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 Co^{2+} by the same —SO₃H content was ~ 18 g kg⁻¹, regardless of the inlet concentration of Co^{2+} . These results indicate that the amount of adsorbed Co^{2+} adsorbed by the cation-exchange membrane is constant, regardless of the inlet concentration.

Figure 12 shows the breakthrough curves of Co^{2+} ion to the cation-exchange hollow fiber with —SO₃H of 3.56 mmol g⁻¹ and 4.16 mmol g⁻¹. In the case of modified membrane where —SO₃H density was 3.56 mmol g⁻¹, after PV reached 0.142 L, the C/Co rose gradually with increasing

Figure 10 Comparison of sulfonic acid by titration and weight gain.

PV. After PV reached 0.29 L for the cation-exchange hollow fiber with — SO_3H of 4.16 mmol g^{-1} , C/Co rose gradually with increasing PV. A higher sulfonic acid group density resulted in a higher PV required to reach C/Co = 1. The amount of Co²⁺ absorbed by sulfonated membranes of 3.56 and 4.16 mmol g^{-1} were ~ 18 and

Figure 11 Adsorption characteristics of Co^{2+} ion to polyethylene hollow fiber with 3.56 mmol —SO₃H g⁻¹.

Figure 12 Adsorption characteristics of Co^{2+} ion to polyethylene hollow fiber in the inlet concentration of 80 ppm $Co^{2+} L^{-1}$.

25 g kg⁻¹, respectively. If the amount of Co^{2+} adsorbed by sulfonated membranes of 3.56 mmol g⁻¹ is 18 g kg⁻¹, a membrane with 4.16 mmol g⁻¹ density should adsorb ~ 21 g kg⁻¹ of Co^{2+} by means of functionality of —SO₃H. However, a membrane with 4.16 mmol g⁻¹ density adsorbed 25 g kg⁻¹ of Co^{2+} . These results may explain that the membrane with high —SO₃H functionality involves the more physical adsorption than that with low —SO₃H functionality.

The Co^{2+} adsorbed by the cation exchange membrane was eluted by permeating across the hollow fiber membrane with 1.0M HCl aqueous solution. The content of Co^{2+} was calculated from the amount of Co^{2+} in the eluate. Figure 13 shows the desorption curves of Co^{2+} to the cation-exchange hollow fiber membrane with -SO₃H of 3.56 and 4.16 mmol g⁻¹. The cation-exchange hollow fiber membrane with -SO₃H density showed different elution curves. The amount of Co^{2+} adsorbed by the cation-exchange fiber membrane was calculated from the area of elimination curves. The amount of Co^{2+} desorbed by the membranes having $-SO_{3}H$ of 3.56 and 4.16 mmol g⁻¹ were ~ 18 and 25 g kg⁻¹, respectively, which are the same as the adsorbed amounts of Co^{2+} .

Figure 14 shows the breakthrough curves of readsorption for cation-exchange hollow fiber membrane that was washed with 1.0 mol HCl aqueous solution. It was shown that the adsorption curve had an identical shape with a readsorption curve. From the results, the cation-exchange hollow fiber membrane was found to have a good regeneration property.

CONCLUSIONS

Cation-exchange hollow fiber membrane was prepared by radiation-induced grafting of styrene onto the PEHM and its sulfonation. The adsorption characteristics for the cation-exchange membranes are examined when the solution of Co^{2+} permeates across the cation-exchange fiber membrane.

1. In the grafting reaction of styrene onto preirradiated polyethylene hollow fiber, the degree of grafting (%) exhibited the maximum in 70% styrene concentration. The degree of grafting was remarkably enhanced with inclusion of additives such as H_2SO_4 and divinylbenzene. When divinylbenzene was combined with H_2SO_4 , the synergistic effect in radiation grafting was observed, with the enhancement on grafting yield being accentuated at the Trommsdorff peak. The inclusion of divinylbenzene and H_2SO_4 increases the grafting yields for all solutions studied. The level of enhance-

Figure 13 Desorption characteristics of Co^{2+} ion to cation-exchange fiber.

Figure 14 Readsorption characteristics of Co^{2+} to the cation-exchange fiber that is HCl washing.

ment by divinylbenzene is generally not as significant as found with H_2SO_4 .

- 2. It was almost impossible to get the high yield of sulfonation without swelling agent. The swelling effect followed in order of $ClCH_2CH_2Cl > CCl_4 > CHCl_3$.
- 3. The adsorbed amounts of Co^{2+} by the same $-\text{SO}_3\text{H}$ content was definite, regardless of the inlet concentration of Co^{2+} . The cation-exchange fiber showed a good regeneration property.

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