Synthesis of Ion Exchange Membranes by E-beam Radiation-induced
Graft Polymerization and Their Adsorption of γ-Globulins

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Abstract: To obtain the optimum synthetic conditions for preparing functionalized glycidyl methacrylate-grafted polypropylene (PP-g-GMA) membranes, which selectively adsorb γ-globulins, PP-g-GMA was synthesized by E-beam mutual radiation-induced graft polymerization and subsequent functionalization with diethylamine and sodium sulfate. The amination conversion of the hollow PP-g-GMA membrane increased during the first 12 h of the reaction and then it reached equilibrium; the highest ion exchange capacity (2.6 meq/g) was obtained at a degree of grafting of 223%. The sulfonation conversion of the hollow PP-g-GMA membrane ranged from 18 to 40% after reacting for 6 h; the highest ion exchange capacity (1.7 meq/g) was obtained at a degree of grafting of 205%. From atomic force microscopy (AFM) and scanning electron microscopy (SEM) analyses, the surfaces of the original PP membrane and PP-g-GMA membrane had somewhat-rough topographies, while those of the anion exchange membrane were much smoother because of the pore filling that occurred as the diethylamino groups were introduced onto the PP membrane. In an investigation of the γ-globulin adsorption performance of the hollow PP ion exchange membranes as a function of pH, the maximum γ-globulin uptakes on the cation and anion exchange membranes were obtained at pH 6 and 8, respectively.

Keywords: ion exchange membrane, hollow PP membrane, E-beam radiation-induced polymerization, γ-globulins, pH

Introduction

Graft polymerization can be initiated by various methods, such as high-energy (γ-ray, e-beam), plasma, UV, excimer, or Ar+ laser irradiation, chemical initiation, and the oxidation of polymers [1-7]. Among these methods, radiation-induced graft polymerization is well-known as a method for the modification of the physical properties of polymeric materials, and it is of particular interest for achieving specifically desired properties, such as excellent mechanical properties [8,9]. This process is one of the most convenient and most effective methods for industrial use because of the ease with which active sites can be created on many kinds of polymers, the effective penetration onto the polymer, and the moderate reaction conditions. The radiation-induced graft polymerization techniques are classified based on three factors: (a) irradiation source, (b) irradiation opportunity [10-12], and (c) nature of the monomer phase, such as vapor or liquid phase [13-15].

In recent years, rapid developments of membranes for applications in biotechnology have led to a demand for efficient methods for the high-quality purification of large amounts of materials [16-18]. Membranes are used conventionally for size-based separations. The advantage of membranes over conventional preparative fibrous ion exchangers is the elimination of pores with long diffusive path lengths. Ion exchange group-containing membranes are used more extensively in the separation or purification

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of proteins than in the medical industry. Functional group-containing membranes are divided into three classes based on the chemical interactions between the functional groups and the protein: ion exchange membranes (IEM), affinity membranes, and hydrophobic interaction membranes [19-22]. The ionization properties of the proteins based on the specific value of pH can be used for the IEMs because proteins have their own isoelectric points (pI) [23].

Therefore, in this work, anion exchange (AEM) and cation exchange membranes (CEM) were synthesized by the mutual radiation-induced graft copolymerization of glycidyl methacrylate (GMA) onto a hollow PP membrane followed by subsequent functionalization with diethylamine and sodium sulfite, respectively, to introduce functional groups into the membrane.

We confirmed that the graft reaction time affected the degree of grafting and functionalization conditions. Also, to determine the optimum adsorption conditions, we investigated the γ-globulin adsorption properties as a function of the pH using the synthesized PP membranes.

**Experimental**

**Materials**
The hollow PP membranes, which we used as trunk polymers in E-beam radiation-induced graft polymerization, had a mean pore diameter of 0.2 μm and 70% porosity; they were obtained in the form of Accurel® hollow PP membranes purchased from Membrana Co., Germany. GMA (Junsei Chemical Co., Japan) was used after the removal of hydroquinone. Diethylamine and sodium sulfite, which were used as functionalization reagents, were purchased from Aldrich Chemical Co., USA, and γ-globulin, used for the adsorption experiments, was obtained from the Sigma Chemical Co., USA. All other solvents were obtained from Duksan Chemical Co., Korea. All reagents and chemicals used in these studies were of analytical grade.

**Grafting Copolymerization of GMA**
The PP-g-GMA hollow membranes were prepared by E-beam mutual radiation-induced graft copolymerization of GMA onto the PP hollow membrane as shown in Figure 1. The PP hollow membrane containing GMA was irradiated under a nitrogen atmosphere using 15–25 Mrads of a 2-MeV E-beam (ELV-4, EB Tech Co., Daejeon, Korea).

The PP hollow membrane was cleaned with acetone and, subsequently, with distilled water and then dried in a 60°C dry oven. The dried hollow PP membranes (0.5 g) were placed with GMA/methanol (80/20 vol%) into a reactor having an inner diameter of 4 mm, and the air in the reactor was then substituted by nitrogen for 2 h and allowed to swell over the course of 12 h. The grafting reaction was carried out at a total dose of 25 Mrad.

After the grafting reaction, the homopolymer and unreacted monomer were completely removed by dissolving them in benzene, until no subsequent weight decrease occurred, and then we dried the copolymers at 60°C in vacuum and calculated the degree of grafting according to equation (1) [24].

\[
\text{Degree of grafting (\%) = } \frac{W_g - W_o}{W_o} \times 100 \tag{1}
\]

where \(W_g\) is the weight of the PP-g-GMA membrane and \(W_o\) is the weight of the original PP membrane used as the trunk polymer.

**Functionalization Reaction (1)**

To introduce the anion exchange functional group, which has a selective adsorption property for γ-globulins, the PP-g-GMA membrane was immersed in a diethylamine water (50:50, v/v) solution and then functionalized at 50°C for 24 h [25]. After the functionalization reaction, the membrane was washed with acetone and distilled water and then dried in an oven at 60°C. The incorporation of diethylamino groups was determined by elemental analysis (EA 1110, CE Instruments, Milan, Italy).

**Functionalization Reaction (2)**

The PP-g-GMA membrane was prepared by sulfonation for the purpose of synthesizing the CEM. For the sulfonation of the PP-g-GMA membrane, a reactor (250 mL), which was filled with sodium sulfite/isopropyl alcohol/water (10/15/75 wt%), was equipped with an
adapter attached to the nitrogen line, a mechanical stirrer, and a condenser, and the PP-g-GMA membrane (0.5 g) was degassed and sealed. The sulfonation was carried out at 80°C for 15 h. After the functionalization reaction, the CEMs were washed with acetone and distilled water and then dried in an oven at 60°C. The incorporation of introduced sulfonic acid groups was determined by elemental analysis.

**Analysis of IEMs**

Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra were obtained on an ATR-FTIR spectrometer (AIM-8800, Shimadzu, Kyoto, Japan) over the region 4000 ~ 400 cm\(^{-1}\), with a resolution of 4 cm\(^{-1}\), to confirm the structures of the PP membranes synthesized through the grafting reaction and subsequent functionalizations. The contents of C, H, and N in the PP and PP-g-GMA membranes and the number of functional groups introduced onto the PP-g-GMA membrane were analyzed by means of an elemental analyzer. The morphology changes of the membrane upon grafting and functionalization were confirmed by AFM (SPM-9500 J2, Shimadzu Co., Kyoto Co., Japan). The AFM images were obtained, using the dynamic mode and at a scan rate of 1 Hz, throughout the grafting and functionalization reactions.

**Adsorption Properties of γ-globulins**

The γ-globulin adsorption properties of the functionalized PP membranes were measured in a batch adsorption system that was regulated at pH 4 (in acetate buffer solution), pH 6 (in phosphate buffer solution), pH 8 (in Tris-HCl buffer solution), and pH 10 (in NaOH buffer solution) [26]. The initial concentration of the γ-globulins was 0.2 mg/mL. Each adsorption experiment was conducted for 250 min at room temperature. The effluent was sampled continuously at the scheduled times, and the amount of γ-globulin adsorbed was determined spectrophotometrically at 280 nm by means of UV adsorption spectroscopy (UV-3101, Shimadzu Co., Kyoto, Japan).

**Results and Discussion**

The degrees of grafting as a function of reaction time of the hollow PP-g-GMA membrane are summarized in Table 1. The degree of grafting ranged from 168 to 310% according to the reaction time at 25 Mrad.

<table>
<thead>
<tr>
<th>Reaction time (min)</th>
<th>3</th>
<th>5</th>
<th>10</th>
<th>20</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Degree of grafting (%)</td>
<td>168</td>
<td>203</td>
<td>223</td>
<td>274</td>
<td>310</td>
</tr>
<tr>
<td>Mean pore diameter (μm)</td>
<td>0.20</td>
<td>0.16</td>
<td>0.11</td>
<td>0.10</td>
<td>0.08</td>
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![Figure 2. ATR-FTIR spectra of (a) the PP hollow membrane, (b) the GMA-grafted PP hollow membrane, (c) AEM, and (d) CEM.](image)

Figure 2. ATR-FTIR spectra of (a) the PP hollow membrane, (b) the GMA-grafted PP hollow membrane, (c) AEM, and (d) CEM. and 910 cm\(^{-1}\), respectively. This spectrum confirms that the grafting copolymer was synthesized. The spectrum shown in Figure 2c is the ATR-FTIR spectrum that confirms that amination occurred. The characteristic intensity of the epoxy band at 910 cm\(^{-1}\) decreased remarkably and new broad absorption bands at 3400 cm\(^{-1}\), due to hydroxyl (-OH) and secondary amino (-NH) groups, can be observed in Figure 2c. Figure 2d presents the ATR-FTIR spectrum that confirms that sulfonation occurred. The characteristic intensity of the epoxy band at 910 cm\(^{-1}\) decreased remarkably and new broad absorption bands at 3400 cm\(^{-1}\), due to hydroxyl groups, appear in Figure 2d. In addition, the characteristic bands of sulfonic acid groups (-SO3H), which were introduced into the hollow PP CEM by sulfonation, appear from 1200 to 1300 cm\(^{-1}\) and at 1020 cm\(^{-1}\).

Figure 3 shows the amination conversion of the hollow PP AEM according to the reaction time. The amination conversion decreased as the degree of grafting increased. This observation can be explained as follows: In the initial graft reaction, by the mutual radiation method, the formation of radicals is so fast to enable them to penetrate into the pores and the grafting proceeds, while the amination reaction takes place only on the surface because of pore blocking by the fast grafting reaction. The amination conversion increased until a reaction time of 12 h.
Figure 3. Amination conversion for several degrees of grafting (reaction temp: 50°C; total dose: 25 Mrad; 80% GMA/20% methanol).

Figure 4. Conversion and anion exchange capacity of the AEM depending on the degree of grafting (reaction time: 15 h; reaction temperature: 50°C).

Figure 5. Sulfonation conversion for several degrees of grafting (reaction temp: 40°C; total dose: 25 Mrad; 80% GMA/20% methanol).

Figure 6. Conversion and cation exchange capacity of the CEM depending on the degree of grafting (reaction time: 5 h; reaction temperature: 40°C).

and then it reached equilibrium. The amination conversion of the hollow PP AEM ranged from 38 to 79% at a reaction time of 12 h.

Figure 4 shows the variation in the amination conversion and ion exchange capacity of the hollow PP AEM prepared after a reaction time of 15 h and at a reaction temperature of 50°C. The amination conversion decreased upon increasing the degree of grafting. The highest ion exchange capacity (2.61 meq/g) was obtained at a degree of grafting of 223%. The existence of the maximum results from the increased compactness of the surface in the membrane as the degree of grafting increased. This speculation is supported by the observation that the number of amino groups introduced to the surface increased despite the decrease of the amination conversion.

Figure 5 shows the sulfonation conversion of the hollow PP CEM as a function of the reaction time. The sulfonation conversion increased rapidly during the first 6 h of the reaction, regardless of the degree of grafting, and then it reached equilibrium. The sulfonation conversion of the hollow PP CEM ranged from 18 to 40% after a reaction time of 6 h. The sulfonation conversion was lower than the amination conversion. The reason why the sulfonation conversion increases more rapidly than did the amination conversion at the initial reaction stage is believed to be because the ring opening reaction of the epoxy group in the graft chain takes place rapidly when sodium sulfite was used as the functionalization reagent.

Figure 6 shows the variation in the sulfonation conversion and ion exchange capacity of the hollow PP CEM after a reaction time of 9 h and at a reaction temperature of 80°C as a function of the degree of grafting. As shown in Figure 6, the sulfonation conversion displays a similar tendency to that of the amination conversion. The highest ion exchange capacity (1.64 meq/g) was obtained at a degree of grafting of 203%; cf. the maximum observed at a degree of grafting of 223% in Figure 4. We speculate that the swelling of the hollow PP membrane by the sulfonation solvent (isopropyl
alcohol/water) is sufficient for the sulfonation reaction to take place inside the pores. This hypothesis was confirmed by AFM.

Representative $10 \times 10 \mu m$ three-dimensional AFM images of the hollow PP membranes, namely the original PP membrane, the PP-$g$-GMA membrane, CEM, and AEM, are shown in Figure 7. The original PP membrane (Figure 7a) shows a nodular morphology [27]. The surfaces of the original PP (Figure 7a) and PP-$g$-GMA (Figure 7b) membranes have relatively rougher topographies, while that of the AEM (Figure 7c) is much smoother because of pore filling that is due to the introduction of the diethylamino groups. The PP-$g$-GMA membranes (Figure 7b) exhibit more growth of graft chains relative to the original PP membranes. The average roughness of the AEM (Figure 7d) decreased as a result of the introduction of the diethylamino groups, but no significant differences between the surface morphologies of the PP-$g$-GMA membrane (Figure 7b) and CEM (Figure 7d) are observed.

Figure 8 shows the adsorption properties of $\gamma$-globulins on two types of hollow PP membranes (AEM and CEM) as a function of pH. As shown in Figure 8, the maximum $\gamma$-globulins uptakes on the CEM and AEM were obtained at pH 6 and 8, respectively. However, the adsorption capability of the IEM was very low at other values of pH. These results indicate that the pH of the adsorptive solution has an important effect on the ion exchange of the $\gamma$-globulins. The pI of $\gamma$-globulin is about 6.90 [28, 29]. Therefore, $\gamma$-globulins have a positive net charge at pH 6.0. This result fits well with the results reported by Scopes and coworkers [30]. On the other hand, AEM showed high anion exchange characteristics in the basic region and CEM showed high cation exchange characteristics in the acidic region. The adsorption behavior of the $\gamma$-globulins on both AEM and CEM indicate that ionic interaction between the IEMs and the $\gamma$-globulins may be present. The adsorption capability of the CEM
toward γ-globulins was superior to that of AEM.

Conclusions

The AEM and CEM were synthesized by the mutual radiation-induced graft copolymerization of GMA onto PP hollow membranes, followed by the subsequent functionalization with diethylamine and sodium sulfite. The degree of grafting of the hollow PP membranes increased rapidly during the first 20 min. For the introduction of the amino functional group into the hollow PP-g-GMA membrane, we observed that the amination conversion of the AEM decreased upon increasing the degree of grafting up to a reaction time of 12 h and then it reached equilibrium. As the reaction time increased, the sulfonation conversion increased rapidly, during the first 6 h of the reaction, regardless of the degree of grafting, and then it reached equilibrium. In an investigation of the γ-globulins adsorption performance of the hollow PP IEMs according to the various values of pH, the maximum γ-globulin uptakes on the CEM and AEM were obtained at pH 6 and 8, respectively.

References