Plasma-Graft Filling Polymerization: Preparation of a New Type of Pervaporation Membrane for Organic Liquid Mixtures

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ABSTRACT: A new membrane for organic liquid separation, called the filling-polymerized membrane, is proposed. To develop an organic liquid permselective membrane, suppressing membrane swelling as well as enhancing the solubility difference is important. The membrane is composed of two kinds of polymer materials. One is a porous substrate film, which is inert to organic liquids, and the other is a polymer, soluble only in specific solvents, filling the substrate pores. The solubility difference of the filling polymer causes permselectivity while the substrate matrix restrains the swelling of the filling polymer. In the present study, the filling-polymerized membrane was prepared by the plasma-graft polymerization technique. A porous high-density polyethylene film and poly(methyl acrylate) were used as the substrate and grafted polymer, respectively; this grafted polymer is soluble in aromatic hydrocarbons, such as benzene, but insoluble in aliphatic hydrocarbons, such as cyclohexane. Morphological analysis of the grafted membrane by TEM and FT-IR analysis showed that the grafted polymer filled the pores of the substrate. The membrane swelling experiments in a benzene/cyclohexane mixture verified that the matrix of the substrate restrained the swelling of the grafted polymer. Pervaporation separation of the benzene/cyclohexane mixture through the membranes obtained was carried out. The separation took place through the grafted polymer, which filled the pores of the substrate film, and the membranes showed high permselectivity for benzene, as expected. Suppressing membrane swelling raised the selectivity in accordance with the concept of the filling-polymerized membrane.

Introduction

Much attention has been paid to pervaporation for separating organic liquid mixtures instead of distillation. In pervaporation, a membrane is placed between the liquid and the vapor, and the difference in the chemical potential between the two phases drives permeation. This process can separate azeotropic mixtures and mixtures close to the boiling point.

In the separation of an organic liquid mixture, the membrane material must have a solubility difference in the components of the feed mixture. However, excessive enhancement of the solubility for one component may lead to a decrease in the selectivity owing to membrane swelling. Accordingly, in order to develop an organic liquid permselective membrane, suppressing membrane swelling is important, as is enhancing the solubility difference.

Membranes made of polymeric alloys of poly(phosphonate)s or poly(phosphate)s and cellulose acetate are selectively permeable to benzene from benzene/cyclohexane mixtures.[1,2] Poly(phosphonate) and poly(phosphate), which have high affinities for only benzene, initiated selectivity through their solubility difference, and cellulose acetate, which has no affinity for either of the two components, suppressed membrane swelling.

In addition, through radiation-induced grafting,[3,4] preirradiation grafting, radiation-induced cross-linking, plasma polymerization,[5] and concentrated emulsion polymerization techniques,[6] preparation of pervaporation membranes for organic liquid separation have been reported.

In the present study, a new concept of a pervaporation membrane for organic liquid separation is proposed.

Pores in a porous substrate film are filled with another polymer. The porous substrate must be inert to organic liquids, and the filling polymer must be soluble only in a specific component in the feed mixture. Due to the solubility difference with the feed mixture, the filling polymer exhibits permselectivity, while the substrate matrix restrains the swelling of the filling polymer. The concept of the filling-polymerized membrane is schematically illustrated in Figure 1.

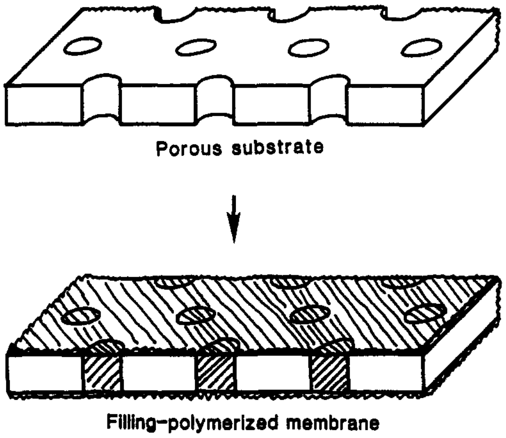

Figure 1. Concept of filling-polymerized membrane.

In the present study, the plasma-graft polymerization technique was employed to prepare the filling-polymerized membrane. Plasma is well-known to treat only the surface, and graft chains are formed on the surface of pores in a film or on the film surface itself. The solubility of substrate matrix itself shows no change due to use of this technique, unlike in radiation-induced graft polymerization. In addition, this technique in which the filling polymer is combined with the porous substrate by chemical bonds can prevent leakage at the interface between the pore wall and the filling polymer.

The plasma-graft polymerization technique has been applied to prepare a pervaporation membrane by Hirotsu et al.[7-9] The membrane consists of porous polypropylene film as the substrate and a hydrophilic grafted layer such as poly(acrylic acid), poly(methacrylic acid), poly(acrylamide), or poly(2-hydroxyethyl methacrylate). These membranes exhibited water permselectivity for water/ethanol mixtures. They reported that the hydrophilic grafted layers were mainly formed on the surface of the substrates.[10]

We thought that changing the materials and the reaction conditions might cause the grafted layer to be formed in

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Table I
Properties of Porous HDPE Films

	pore size, μm	thickness, μm	porosity, %	breaking load, kg
HDPE1	0.02	10	52	1.1 × 1.0
HDPE2	0.05	17	44	0.5 × 0.5

the pores of the substrate instead of on the substrate surface. We call this technique plasma-graft filling polymerization.

The objective of this study is the verification of the following three points.

(1) A filling-polymerized membrane can be prepared through the plasma-graft polymerization technique.

(2) This kind of structure can suppress membrane swelling.

(3) The suppressing of membrane swelling is effective in increasing pervaporation selectivity.

Experimental Section

Materials. As the porous substrate, two kinds of porous high-density polyethylene (HDPE) films supplied by Tonen Chemical Co. Ltd. were used. High-density polyethylene is widely known to form polymer radicals by plasma treatment and to be inert to organic liquids at normal temperature. These characteristics are shown in Table I. The breaking load indicates the maximum load to strain a square film (1 × 1 cm) in the horizontal and vertical directions to the point of breakage. HDPE1 has a higher breaking load than HDPE2 and is thus mechanically stronger.

As the graft monomer, methyl acrylate (MA) was used. The polymer of MA is soluble in aromatic hydrocarbons, such as benzene, but insoluble in aliphatic hydrocarbons, such as cyclohexane.[11]

Methyl acrylate was purified by distillation under vacuum and was dissolved in water, methanol, or toluene in 3, 5, and 5 vol %, respectively. The MA solutions were then degassed by repeated freezing and thawing under a vacuum of 1–2 Pa.

Plasma-Graft Filling Polymerization. The apparatus used is illustrated in Figure 2. A square film of HDPE was inserted in a glass tube, and the system was filled with argon gas. After the system was evacuated to 10 Pa, the film was treated for 60 s by radio-frequency plasma operating at 13.56 MHz and delivering at 10 W. Then this film was contacted with the graft monomer solution in the liquid phase, and graft polymerization was carried out in a shaking constant-temperature bath (30 °C) for a predetermined length of time.

The grafted films were washed in water and then rinsed overnight in toluene to remove the nonreacted monomer and homopolymer and dried in an oven at 40–50 °C. The amount of grafting was measured as the weight of the grafted polymer per square centimeter of substrate film.

Transmission Electron Microscopy. The morphological details of the plasma-graft filling-polymerized membrane were observed by transmission electron microscopy. The membrane was sliced, and the ultrathin sample was stained with tetraoxidized ruthenium to distinguish poly(MA) from the pores of the substrate.

FT-IR. The composition of the whole membrane and its surface was analyzed by FT-IR/TR and ATR. In ATR analysis, the ZnSe crystal was used as an internal reflection element, and the angle of incidence was 45°.

Swelling. The degree of membrane swelling was measured by the following procedure. The grafted membrane was immersed in a benzene/cyclohexane mixture (50/50 wt %) and shaken in a constant-temperature bath at 50 °C. After more than 20 h, the membrane was removed from the mixture and the membrane area was immediately measured. The swelling ratio, S_1, is defined in the following equation. A_1 and A_2 are the areas of dry and swollen membrane, respectively.

$$S_1 = \frac{A_2 - A_1}{A_1} \tag{1}$$

Pervaporation. Pervaporations of benzene/cyclohexane mixtures (50/50 wt %) through the membranes prepared were carried out. The experimental apparatus is schematically illustrated in Figure 3. The effective membrane area was 19.6 cm^2. The feed solution was kept at 50 °C. The downstream compartment was evacuated to 40–170 Pa. The permeate was collected in vacuum trap condensers cooled by liquid nitrogen. The feed and permeate concentrations were determined by gas chromatography.

The separation performance is measured in terms of permeation rate Q and separation factor α, which is defined as

$$\alpha = \frac{Y(1 - X)}{X(1 - Y)} \tag{2}$$

where Y and X denote the weight fraction of benzene in the permeate and feed, respectively.

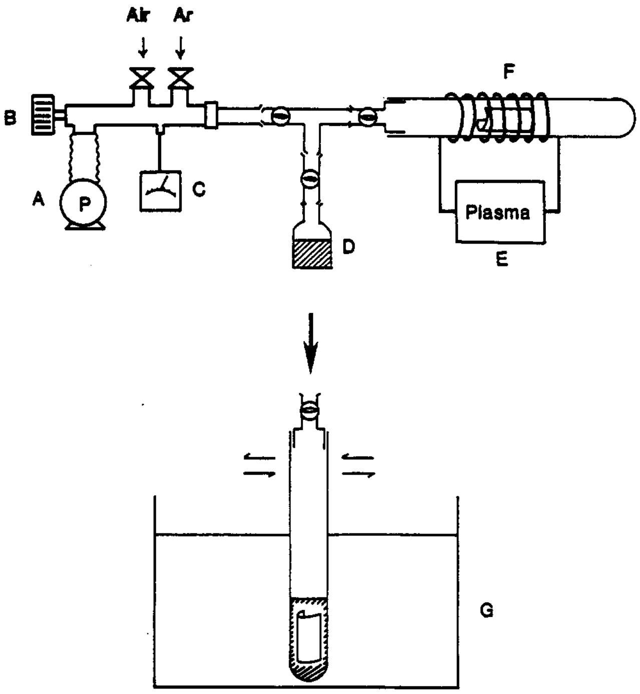

Figure 2. Apparatus of plasma-graft polymerization: (A) vacuum pump, (B) vacuum valve, (C) vacuum gauge, (D) monomer reservoir, (E) RF power generator, (F) substrate film, (G) constant-temperature bath.

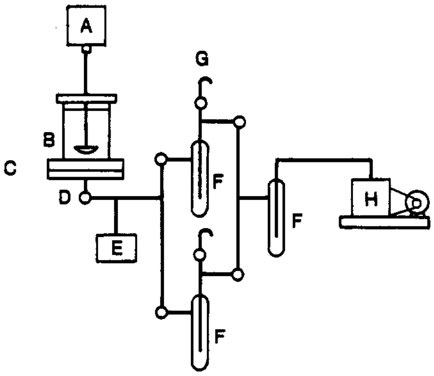

Figure 3. Pervaporation apparatus: (A) motor, (B) feed mixture (constant temperature), (C) membrane, (D) stop cock, (E) vacuum gauge, (F) cold trap, (G) leak to atmosphere, (H) vacuum pump.

Results and Discussion

Membrane Preparation. The relationship between the amount of grafting and the grafting time using HDPE2 is shown in Figure 4. The monomer solvent used greatly affects the polymerization rate. Water showed a much higher polymerization rate than other solvents. This solvent effect has been indicated in plasma-initiated polymerization.[12] When water was used as the monomer solvent, the weight of the grafted polymer after 30 min

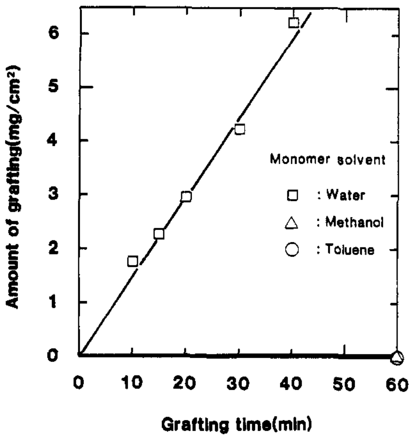

Figure 4. Relationship between the grafting time and the amount of grafting using a HDPE2 substrate.

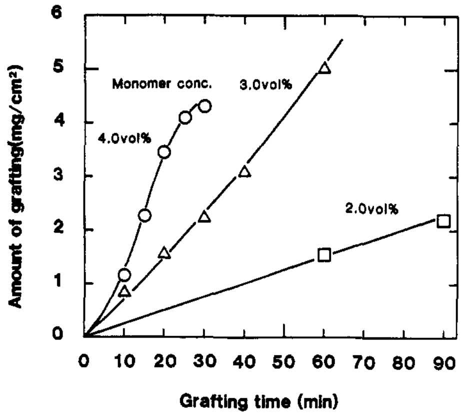

Figure 5. Relationship between the grafting time and the amount of grafting using a HDPE1 substrate.

was 5 times as great as the weight of the HDPE2 film, which is 0.95 mg/cm^2.

The grafted membranes were transparent in spite of the lack of transparency of the porous substrate film. The refractive indexes of HDPE and poly(MA) are 1.55 and 1.48, respectively, i.e., quite similar. These facts suggest that the grafted polymer filled the pores of the porous substrate and the membrane obtained became transparent.

Grafting rates are shown in Figure 5 when HDPE1 and water were used. The rate increased with an increase in the monomer concentration. The weight of the grafted polymer after a grafting time of 30 min with a monomer concentration of 3 vol % was 5 times as great as the weight of the substrate film, which was 0.45 mg/cm^2. Under a 3 vol % monomer concentration, the polymerization rate was close to that obtained by using HDPE2. All grafted membranes obtained by using water were transparent.

Morphological Analysis. (1) Transmission Electron Microscopy. TEM cross-section microphotographs of HDPE1 and grafted membranes are shown in Figure 6. The amounts of grafting vary between 0.6–4.3 mg/cm^2. The pores of the substrate film and the gaps between the crystal regions of polyethylene were stained, while poly(MA) and crystals were not stained.

The substrate film has black parts, indicating pores. The 0.63 mg/cm^2 grafted membrane has fewer black parts and more white parts than the substrate. These white parts indicate poly(MA). This suggests that graft polymerization took place in the substrate pores, and the pores were filled with grafted polymer from the early stage of the polymerization. This also suggests that the monomer diffusion rate is much faster than the polymerization rate, and graft polymerization can take place in the pores of the substrate film.

The grafted membranes have a white layer in the middle. The magnified photograph of this white layer indicates that this layer is crystals of polyethylene. The pores in this layer were not filled with grafted polymer, and swelling of the grafted polymer due to grafting and rinsing in toluene compressed the middle of the substrate and crushed the pores.

The membrane thickness increased with an increase in the amount of grafting, and the grafted membrane of which grafting exceeded 2 mg/cm^2 shows that its surface was torn by the grafted layer. The membrane with 4.3 mg/cm^2 grafting shows an extremely thick poly(MA) layer formed on the substrate surface.

Using the density of pure poly(MA), we defined the porosity of the membrane as the amount of openings among the grafted chains

$$\epsilon = 100\left\{1 - \frac{W_0/\rho_0 + W_1/\rho_1}{L}\right\} \qquad (3)$$

where L is membrane thickness (cm); W_0 and W_1 are the weights of the substrate and grafted polymer per unit area (g/cm^2), respectively; ρ_0 and ρ_1 are the densities of HDPE and poly(MA) (g/cm^3). The thickness was measured by TEM and a micrometer.

Using HDPE1, the dependence of the thickness and porosity of the grafted membranes on the amount of grafting is shown in Figure 7. The total pore volume among the grafted chains decreases with an increasing amount of grafting, as illustrated in Figure 7, because of the growth of the grafted chains in the pores. Above 2 mg/cm^2, porosity becomes almost zero, and the grafted layer density is equal to the density of pure poly(MA).

Figure 8 shows the results of the grafted membranes with HDPE2. In the region in which the amount of grafting exceeds 2.5 mg/cm^2, the pores in the substrate are completely filled with the grafted polymer.

(2) FT-IR Analysis. FT-IR/TR spectra of 0.51, 1.49, and 2.75 mg/cm^2 grafted membranes prepared from HDPE1 are shown in Figure 9. The peaks at 720 and 830 cm^{-1} are characteristic peaks of polyethylene and poly(MA), respectively. The peak ratio of these two peaks is proportionl to the weight ratio of HDPE and poly(MA) calculated from the amount of grafting. FT-IR/ATR spectra of these three membranes are shown in Figure 10. These spectra also have the characteristic peaks. The wavenumbers of these two peaks are near, and then both of the penetration depths of the peaks are nearly the same and the values are approximately 2.5 μm. Therefore, when the relationship between the weight ratio and the peak ratio from the TR spectra is used, the surface composition can be estimated from the ATR peak ratio and the result is shown in Figure 11. The dotted line indicates a weight fraction of poly(MA) in an entire grafted membrane, calculated from the amount of grafting.

The membrane grafting of 0.51 mg/cm^2 shows that the surface and whole composition are nearly the same. This indicates that the pores were filled with grafted polymer from the early stage of the polymerization. This result is in agreement with that from TEM microphotographs.

The poly(MA) content at the surface increased more than that of the whole membrane with an increase in the amount of grafting. In the region where the amount of grafting exceeded 2.75 mg/cm^2, the membrane surface consisted of only poly(MA). This confirms that the white layer at the surface, which was observed in the TEM microphotograph (Figure 6e), is a grafted layer growing on the substrate film surface.

TEM and FT-IR analysis indicate the following mechanisms of grafting: (1) The pores are filled with grafted

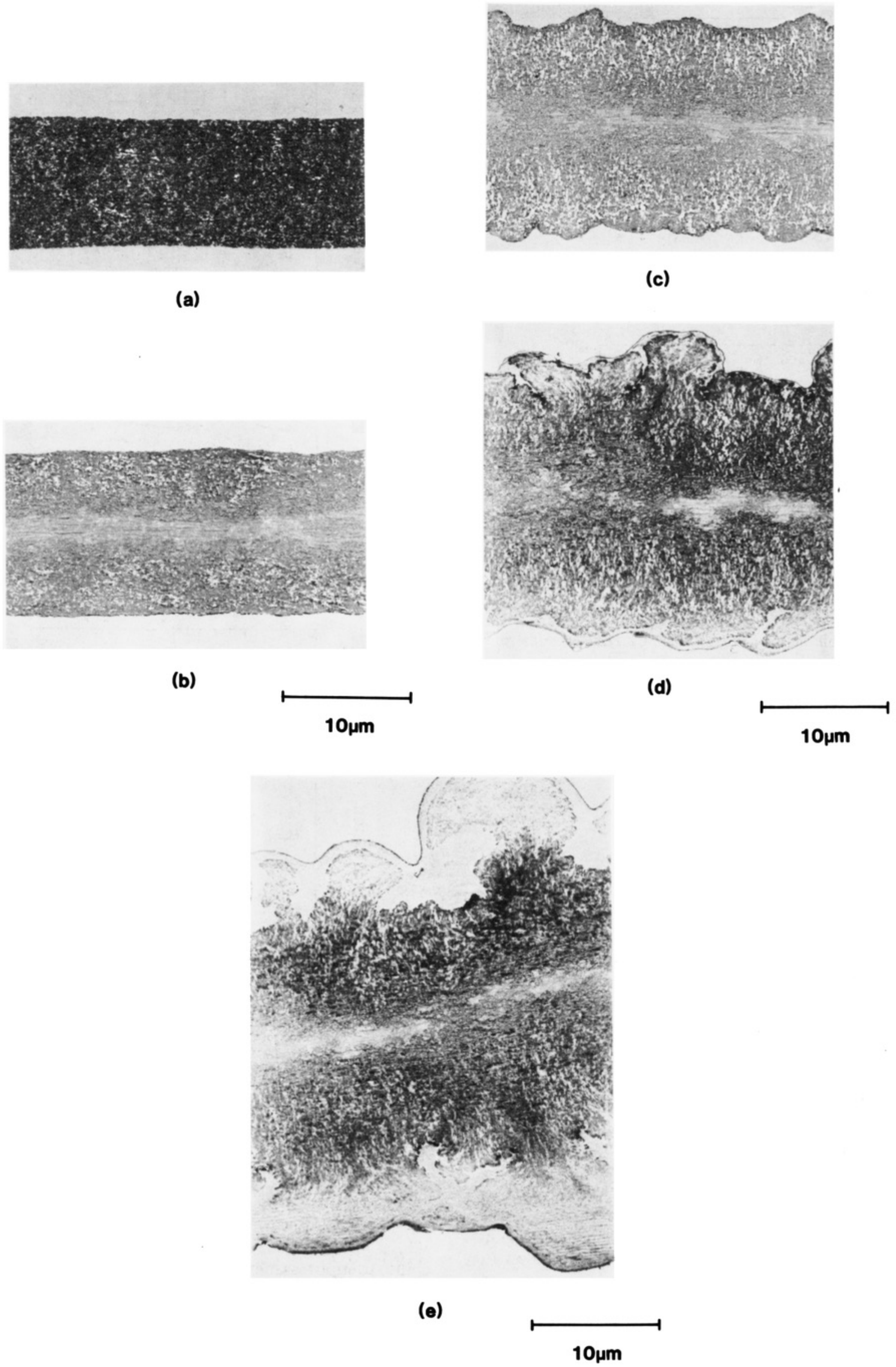

Figure 6. Transmission electron microphotographs of membrane cross sections using a HDPE1 substrate: (a) substrate film, (b) grafting amount of 0.6 mg/cm^2, (c) 1.4 mg/cm^2, (d) 2.3 mg/cm^2, (e) 4.3 mg/cm^2.

polymer from the early stage of the polymerization. (2) The decrease of membrane porosity makes it increasingly difficult to continue graft chain growth in the pores. (3) As a result, graft chains begin to grow preferentially on

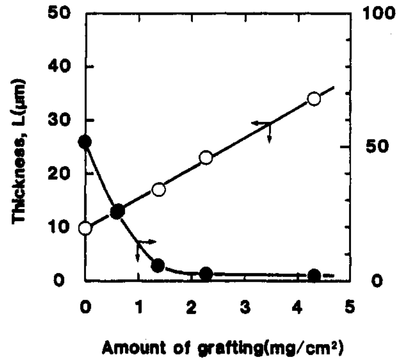

Figure 7. Relationships between the amount of grafting and the membrane thickness or porosity using a HDPE1 substrate.

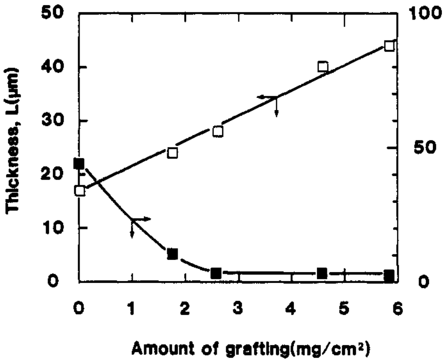

Figure 8. Relationships between the amount of grafting and the membrane thickness or porosity using a HDPE2 substrate.

the substrate film surface.

(3) Extension Ratio. The areas of the substrate film and grafted membrane were measured, and the extension ratio, S_0, due to graft polymerization was calculated with the equation

$$S_0 = \frac{A_1 - A_0}{A_0} \tag{4}$$

where A_0 and A_1 are the areas of substrate film and grafted membrane, respectively.

The extension ratio is shown in Figure 12 as a function of the amount of grafting. For the amount of grafting above 1.5 mg/cm², the substrate film matrix was stretched by the grafting and the membrane area spread. This suggests that, with a large amount of grafting, graft polymerization mainly occurred on the substrate surface but that the polymerization did not stop in the pores of the membrane. The diffusion of the monomer in the membrane was fast, even though the grafted polymer filled the pores.

The dependence of the extension ratio of these two substrates on the amount of grafting showed almost the same tendency. In addition, HDPE2 has a smaller porosity than HDPE1, and when HDPE1 and -2 are used as substrates, the porosity becomes almost zero at grafting amounts above 2 and 2.5 mg/cm², respectively. These results suggest that the grafted layer was formed in a region deeper below the substrate surface in HDPE2 than in HDPE1. The reason for this may be the large pore size of HDPE2 than HDPE1.

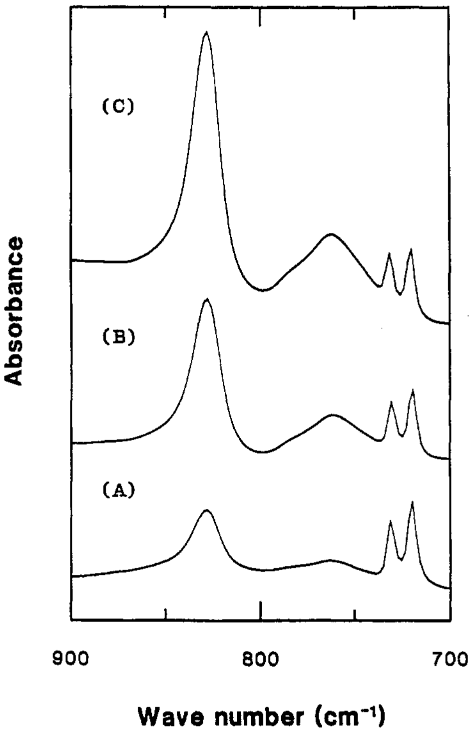

Figure 9. FT-IR/TR spectra of grafted membranes using a HDPE1 substrate: (A) grafting amount of 0.51 mg/cm², (B) 1.49 mg/cm², (C) 2.75 mg/cm².

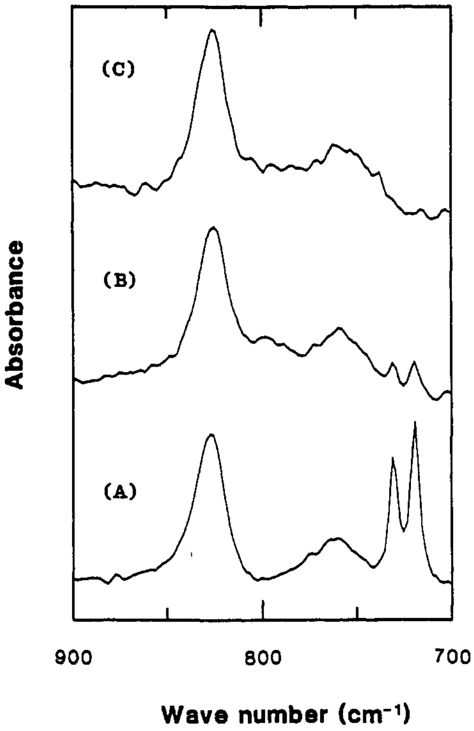

Figure 10. FT-IR/ATR spectra of grafted membranes using a HDPE1 substrate: (A) grafting amount of 0.51 mg/cm², (B) 1.49 mg/cm², (C) 2.75 mg/cm².

Membrane Swelling. The relationship between the amount of grafting and the swelling ratio in a benzene/cyclohexane mixture is shown in Figure 13. The swelling ratio of both substrate films showed no change above the amounts of grafting of 2 or 2.5 mg/cm². This constant value of the completely filled membrane using HDPE1 was about 0.1, while that of the membrane using HDPE2 was about 0.3. This suggests that HDPE1 has a higher ability to suppress membrane swelling than HDPE2. These results correspond with the breaking load of the substrate films. Therefore, the matrix of the substrate film can restrain membrane swelling.

Separation by Pervaporation. Separations of the benzene/cyclohexane mixture by pervaporation through these grafted membranes were carried out. Relationships between the amount of grafting and the permeation rate Q or separation factor α of the membranes with HDPE1 and HDPE2 are shown in Figure 14.

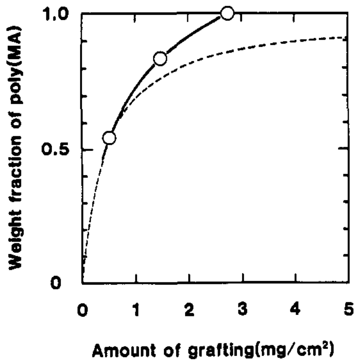

Figure 11. Relationship between the amount of grafting and the weight fraction of poly(MA) on the surface of the membrane using a HDPE1 substrate. The dotted line shows the weight fraction of poly(MA) in the whole membrane.

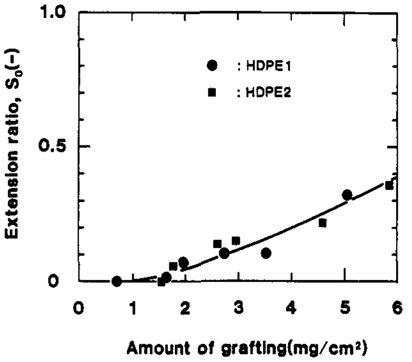

Figure 12. Relationship between the amount of grafting and the extension ratio, S_0.

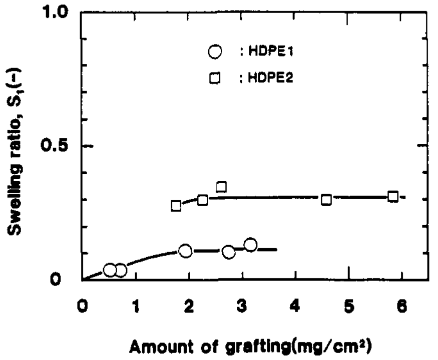

Figure 13. Relationship between the amount of grafting and the swelling ratio, S_1 (benzene/cyclohexane 50/50 wt %; temp 50 °C).

Every grafted membrane shows benzene permselectivity in accordance with grafted-polymer solubility.

With regard to the HDPE1 membrane, the permeation rate decreased and the separation factor increased with an increase in the amount of grafting at the values below 2 mg/cm^2 because graft chains grew in the pores and filled them, as illustrated in Figure 7. Above 2 mg/cm^2, although grafted polymer grew on the membrane surface, both the permeation rate and separation factor were constant, independent of the amount of the grafting. Therefore, the grafted layer on the surface does not have permeation resistance, and separation occurs through the grafted polymer filling the pores.

On the HDPE2 membrane, above 2.5 mg/cm^2, the pores of the substrates were filled with graft chains, and the permeation rate and separation factor were constant in the same way.

The membrane with HDPE1, which has a higher ability to suppress membrane swelling than HDPE2, showed a higher separation factor and lower permeation rate than the membrane with HDPE2. This is caused by the suppression of membrane swelling, which, in turn, causes high selectivity in accordance with the concept proposed in this study.

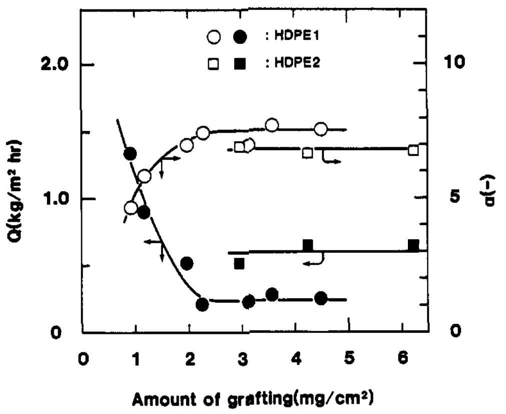

Figure 14. Relationships between the amount of grafting and the permeation rate, Q, or separation factor, α, in pervaporation of benzene/cyclohexane mixture through grafted membranes (feed temp. 50 °C, benzene concentration in feed 50 wt %).

Conclusions

We have proposed a new pervaporation membrane for organic liquid mixture separation called filling-polymerized membrane. We prepare the filling-polymerized membrane using the plasma-graft polymerization technique and draw the following conclusions.

(1) When a porous high-density polyethylene substrate and poly(methyl acrylate) as the grafted polymer were used, the plasma-graft polymerized membrane was prepared. Morphological analysis by TEM and FT-IR confirmed that the substrate pores were filled with the grafted polymer.

(2) Swelling experiments verified that the matrix of the substrate restrained membrane swelling.

(3) In pervaporation of a benzene/cyclohexane mixture, high benzene permselectivity was obtained in accordance with the solubility of the grafted polymer, and the suppressing effect of membrane swelling increased selectivity.

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Registry No. HDPE1 (graft copolymer), 135506-24-0; benzene, 71-43-2; cyclohexane, 110-82-7.