

Preparation and Properties of Radiation-Grafted Membranes for Eliminating Sodium Alkylbenzenesulfonate from Water

INTRODUCTION

Reverse osmosis characteristics of membranes prepared by grafting of hydrophilic polymers onto hydrophobic polymers have been examined by several workers.¹⁻⁴ Yasuda et al. studied the relationship between the salt rejection and water permeability of ionic membranes and explained it in terms of a transport depletion of salt flux relative to water flux due to different transport volumes available to the water molecules and the mobile ions that are repulsed by the fixed ion charge.^{1,2}

Pegoraro et al. studied the purification of water containing sodium alkylbenzenesulfonate (ABS) by reverse osmosis with membranes prepared by grafting.³ In their study the membranes were prepared by graft copolymerization of acrylic acid onto polypropylene in homogeneous phase and subsequent formation of thin films on glass surfaces.

We have studied the water permeability of polymer films modified by grafting and found that polyethylene and nylon-*g*-poly(vinylpyrrolidone) films exhibited excellent permeability.⁵ In the present study we have attempted to utilize polymer films graft-polymerized with a hydrophilic monomer, without further modification, for the elimination of ABS from water. Nylon was chosen as the backbone polymer for its excellent strength and inherent affinity to water, and sodium styrenesulfonate was chosen as the hydrophilic monomer, for a large extent of rejection was expected in the reverse osmosis using the grafted film because of the repulsive effect between the ions of grafted poly(styrenesulfonate) and the solute ions.

EXPERIMENTAL

Materials

Three kinds of polycaprolactam (nylon 6) films, A, B, and C, were employed as starting materials of the membranes. A and B are unstretched films and are 16.5 and 25 μ thick, respectively. C is a biaxially stretched (ten times in area) film 14 μ thick. These nylon films were washed with ethyl ether and dried *in vacuo* before use. Sodium styrenesulfonate (Wako Pure Chemical Co.) was purified by repeated recrystallizations from water.

Graft Copolymerization

A sheet of nylon film (ca. 7 \times 11.5 cm, 0.16–0.22 g) was placed in a glass tube, and a water-ethanol (1:1) solution of sodium styrenesulfonate was added to the glass tube until the nylon film was completely soaked in it. The entire content was evacuated and sealed after freezing and thawing the solution. Graft copolymerization was carried out by irradiation with gamma rays from ⁶⁰Co at 22°C, 2.2 \times 10⁴ R/hr. After the irradiation, the grafted film was washed repeatedly with water-ethanol and finally with ethanol, and then dried *in vacuo*. The degree of grafting was calculated from the weight increase of the grafted film.

Reverse Osmosis

The membranes were immersed in distilled water prior to the reverse osmosis operation. The apparatus (Kuri Chemical Engineering Co. RO-300) consists of a cell (volume 300 ml) and an internal magnetic stirrer. The membranes were supported at the bottom of the cell by a sinterized stainless steel plate through which the permeate flowed down and was weighed. The operating pressure was maintained by nitrogen gas at 20 atm. The concentration of ABS in the permeate was measured by a colorimetric method based on the complex formation between the sulfonate and methylene blue.⁶ The water permeability coefficient K_1 was calculated from the following equation:

$$K_1 = \frac{\text{flux} \times l}{\Delta p - \Delta \pi}$$

where flux is the permeate volume collected per unit time and membrane area, l is the membrane thickness, and $\Delta p - \Delta \pi$ is the effective pressure of the system.

Measurement of Water-Vapor Permeability

The water vapor permeability of grafted films was measured by a conventional cup method⁷ at 40°C and 90% R.H.

Measurement of Relative Heat of Fusion of Grafted Nylon Films

The heat of fusion was determined for each grafted film using a Perkin-Elmer DSC-1B differential scanning calorimeter. The temperature was raised at a rate of 5°C/min. The relative heats of fusion were calculated from the areas under the thermograms.

RESULTS

Figure 1 shows the graft copolymerization of sodium styrenesulfonate in water-ethanol solution onto nylon films. In the graft copolymerization onto unstretched nylon films (films A and B), the difference in thickness of the nylon films had almost no effect on the initial rate of graft copolymerization. The distinctive feature of the results shown in Figure 1 is that the rate of graft copolymerization onto biaxially stretched film (film C) was remarkably low.

Figure 2 shows the water vapor permeability of grafted nylon films at 40°C, 90% R.H. The water vapor permeability for these three kinds of grafted films increased with increasing degree of grafting. The permeability of the grafted film prepared from film A was larger than that from film B. This is attributed to the effect of thickness of the original nylon films. The permeability of the grafted film prepared from film C was extraordinarily low compared with those of equal degree of grafting prepared from the unstretched films A and B. The results shown in Figures 1 and 2 suggest that grafting onto film C occurred mostly in the region near the surface and proceeded slightly in the inner part of the film.

Figure 3 shows the increase in length and thickness of the films in dryness induced by the grafting. A remarkable change is the shrinking in length of the grafted film prepared from film C, though the thickness of the film increased by the grafting as much as the other grafted films. The results also indicate that grafting onto film C occurred mostly in the region near the surface of the film, which is consistent with the results shown in Figures 1 and 2.

Figure 4 shows the relative heat of fusion of the grafted films as functions of the percentage of graft. In this figure, ΔH_{f_0} and ΔH_f represent the heat of fusion of original nylon film and that of the grafted film based on unit quantity of nylon. The heat of fusion, which is calculated from the areas under the thermograms, derives from the crystalline region of nylon component. The relative heat of fusion, $\Delta H_f/\Delta H_{f_0}$, decreased with increasing degree of grafting in the case of grafted films from the unstretched nylon films A and B. The marked decrease in $\Delta H_f/\Delta H_{f_0}$ could be attributed to the decrease in the crystalline region of nylon caused by the grafting. On the other hand, $\Delta H_f/\Delta H_{f_0}$ of grafted

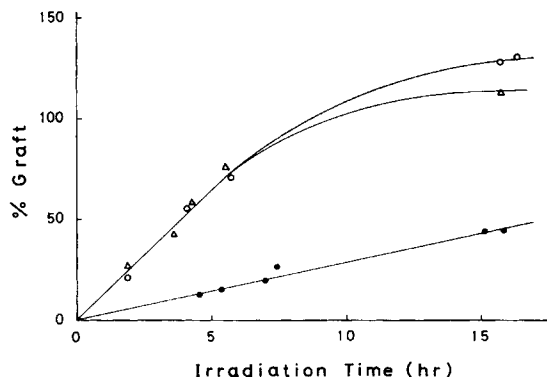


Fig. 1. Graft copolymerization of sodium styrenesulfonate onto nylon 6 films at 22°C, 2.2×10^4 R/hr in water-ethanol 1:1 solution: (O) film A, unstretched, 16.5 μ thick; (Δ) film B, unstretched, 25 μ thick; (\bullet) film C, biaxially stretched, 14 μ thick.

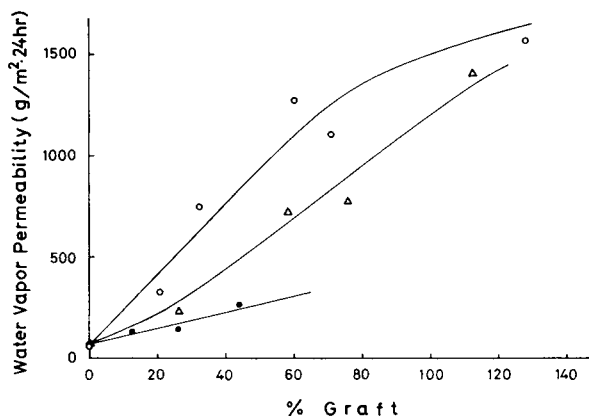


Fig. 2. Water vapor permeability of nylon-*g*-poly(sodium styrenesulfonate) films at 40°C 90% R.H.: (O, Δ, and ●) grafted films prepared from films A, B, and C, respectively. The thickness of these grafted films varies with the degree of grafting and the type of the original films.

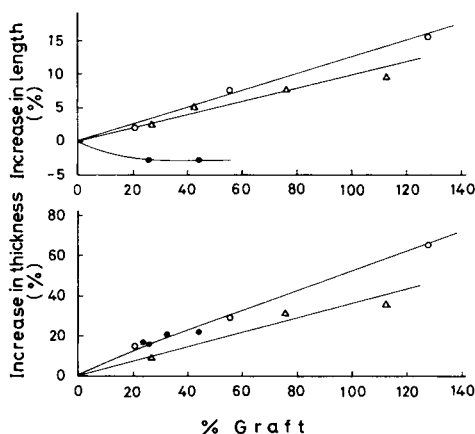


Fig. 3. Increase in length and thickness of grafted films in dryness: (O, Δ, and ●) grafted films prepared from films A, B, and C, respectively.

film from the stretched nylon film C increased slightly with increasing degree of grafting, which indicates that the crystalline region of nylon remained approximately unchanged.

Figure 5 shows some typical examples of flux variation versus time in reverse osmosis experiments at 20°C, 20 atm, using nylon(unstretched)-*g*-poly(sodium styrenesulfonate) membranes. The water flux decreased slightly in the initial stage and then reached a stationary state in each run. The water flux in the stationary state increased with increasing degree of grafting, as is indicated by the numbers in Figure 5, when the same kind of nylon film was used as the backbone polymer. The largest water flux obtained in this series of reverse osmosis experiment was 5.26 l./m² hr using 313.3% grafted film from the unstretched film A. The water flux obtained in the reverse osmosis using the grafted film prepared from film C was extremely small, which confirms that the grafting onto film C occurred mainly in the region near the surface of the film.

Some typical examples of ABS rejection versus time in reverse osmosis are shown in Figure 6. ABS rejection was more than 99.4% in the stationary state and unchanged throughout the operation time thereafter.

Figure 7 shows variation of flux and rejection versus time in reverse osmosis using nylon-*g*-poly(vinylpyrrolidone) membrane. The percentage of ABS rejection in this case was much lower than that in the operation using the nylon-*g*-poly(sodium styrenesulfonate) membrane, which shows that the higher percentage of rejection shown in Figure 6 was brought about by the repulsion between the fixed ionic groups of membrane and solute ions of the same charge.

In Figure 8, the lower line shows variation of the water permeability coefficient K_1 for nylon-*g*-

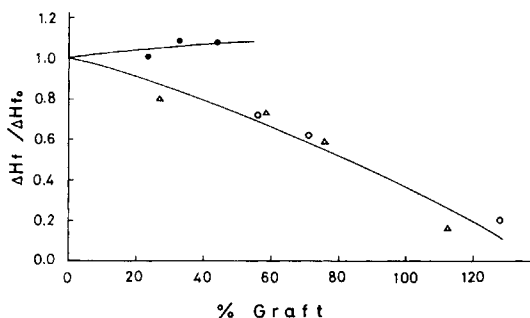


Fig. 4. Relative heat of fusion of nylon-*g*-poly(sodium styrenesulfonate) films: (O, Δ, and ●) grafted films prepared from films A, B, and C, respectively.

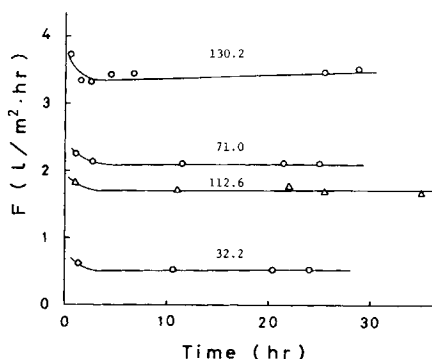


Fig. 5. Typical examples of flux variation vs. time in reverse osmosis with nylon-*g*-poly(sodium styrenesulfonate) membranes at 20°C, 20 atm. Concentration of sodium dodecylbenzenesulfonate (ABS) = 1 g/l. Percentage of graft indicated by numbers in figure. Membranes were prepared by grafting onto nylon films A (O) and B (Δ).

poly(sodium styrenesulfonate) membranes as a function of the percentage of graft. The value of K_1 increased almost linearly with increasing percentage of graft. The upper convex line shows variation of the fraction of water in the swollen membrane, H .

Yasuda et al.⁸ studied the permeability of water in water-swollen polymer membranes and proposed the following equations for the higher hydration:

$$K_1 = K_0 \exp(-\Phi_k \cdot x)$$

$$x = (1 - H)/H$$

where K_0 and Φ_k are constants. Figure 9 shows the dependence of the water permeability coefficient K_1 on $(1/H) - 1$. It is obvious that the experimental data obey the equations shown above, that is, the water permeability coefficient is determined mainly by the extent of hydration.

DISCUSSION

In Figures 1 and 2, comparisons were made between the rate of grafting onto the unstretched films and that onto the stretched film, and also between the water-vapor permeability of grafted films prepared from the unstretched films and that from the stretched film. Marked differences were observed in these comparisons, and they are due to the difference in the swelling characteristic of the backbone polymer film in the monomer solution. The changes in size of the grafted films in dryness shown in Figure 3 indicated that the grafting onto the stretched film C occurred mostly in the region near the surface of the film, since almost no swelling of the film in the monomer solution

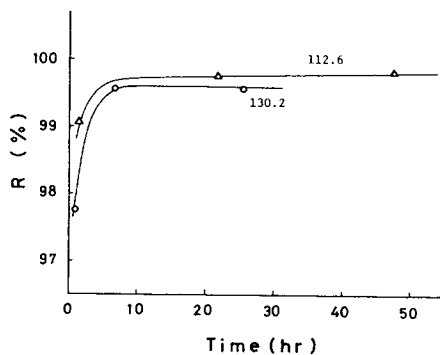


Fig. 6. Typical examples of ABS rejection vs time in reverse osmosis at 20°C, 20 atm. Percentage of graft indicated by numbers in figure. Membranes were prepared by grafting onto nylon films A (O) and B (Δ).

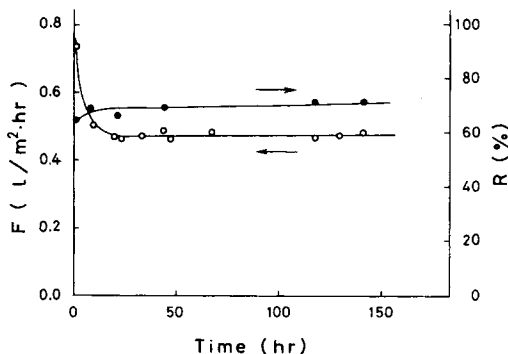


Fig. 7. Variation of flux and rejection vs. time in reverse osmosis with nylon-*g*-poly(vinylpyrrolidone) membrane at 20°C, 20 atm. Percentage of graft = 55.2%, concentration of ABS = 1 g/l.

occurred during the grafting. The difficulty in swelling of the biaxially stretched film is attributable to the high degree of orientation. The results shown in Figures 1 and 2 can be explained from this viewpoint.

The changes in the relative crystallinity of the backbone polymer induced by the grafting (Fig. 4) could be explained similarly as follows: In the grafting onto the unstretched films, the films were swollen in the monomer solution, and the monomer molecules penetrated gradually even into crystalline regions of the films as well as into amorphous regions with the progress of the grafting reaction, which caused the decrease in the relative crystallinity of the backbone polymer. In the grafting onto the biaxially stretched film, however, almost no swelling of the film occurred, and the crystalline region of the film remained almost unchanged since it is difficult for the monomer molecules to penetrate into the highly oriented polymer matrix.

Pegoraro et al.³ reported that 7 l./m²-hr flux and 33.3% ABS rejection were obtained in a reverse osmosis operation at 50 atm using a water-conditioned 5 μ -thick poly(propylene-*g*-acrylic acid) membrane, and that the high flux and the low percentage of rejection were caused by direct permeation of water through passing channels formed by microfibrures in the polypropylene matrix. They also reported that a 0.5 l./m²-hr flux and 100% ABS rejection were obtained using a 23 μ -thick grafted membrane, which were brought about by water permeation through the grafted poly(acrylic acid) hydrophilic regions preferentially by a solution and diffusion mechanism. In our experiment, the maximum flux, 5.26 l./m²-hr, and 99.6% ABS rejection were obtained in a reverse osmosis operation at 20 atm using nylon-*g*-poly(sodium styrenesulfonate) membrane (the degree of grafting was 313.3%). The water permeability coefficient was influenced mainly by the extent of hydration, *H*, under the experimental conditions, as was shown in Figure 9. The rejection of ABS was almost 100%, with the exception of that using nonionic nylon-*g*-poly(vinylpyrrolidone) membranes. These results

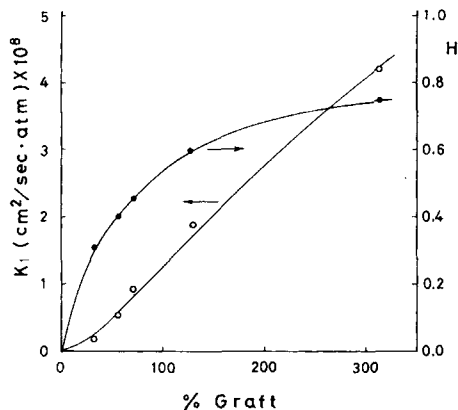


Fig. 8. Variation of water permeability coefficient K_1 and fraction of water in the water-swollen membrane, H , vs percentage of graft. Membranes prepared by graft copolymerization of sodium styrenesulfonate onto nylon film A were used.

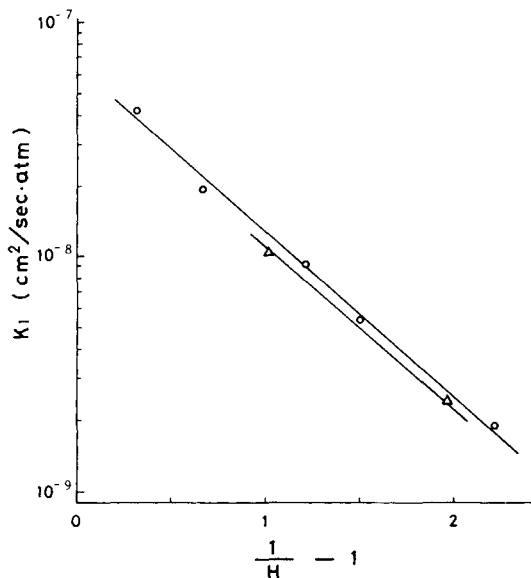


Fig. 9. Dependence of the water permeability coefficient K_1 on $(1/H) - 1$ for membranes prepared by graft copolymerization of sodium styrenesulfonate onto films A (O) and B (Δ).

show that the membranes in this experiment do not have any passing channels which Pegoraro et al. assumed in their experiment but can be treated as a homogeneous hydrophilic polymer matrix through which water permeates.

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