Chemical Initiated-Grafted Nylon 4 Membranes

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Synopsis

To improve the performance of nylon 4 membranes, this study attempts to utilize chemical initiation which induces different hydrophilicities vinyl monomers grafted onto nylon 4 membranes. Sodium styrene sulfonate, chloromethyl styrene, styrene, and glycidyl methacrylate were used as grafting monomers. The factors that affect the degree of grafting considered were chemical initiators, pH values, kinds and concentrations of monomers, reaction time, and temperatures. The mechanical strength and the transport properties of these chemical-initiated grafted nylon 4 membranes were also investigated. Both the water flux and the salt rejection of sodium styrene sulfonated-grafted membrane were increased significantly, compared to our previous paper,[1] and the casein rejections of all of the four grafted nylon 4 membranes studied exceeded 90%. The quaternized nylon 4-g-poly(chloromethyl styrene) membranes were prepared and possessed high water uptake behavior and high transfer number (0.99) for electrodialysis. The sulfonating process was also applied to improve the hydrophilicity of nylon 4-g-poly(glycidyl methacrylate) membrane so that the water flux and the salt rejection were both increased.

INTRODUCTION

Graft copolymerization of nylon appeared to be a very fascinating field of research with possibilities for improvement of its properties: For instance, nylon grafted with styrene showed good water repellency and significant resistance to weathering[2]; on the other hand, nylon grafted with acrylic or methacrylic acid has been reported to improve the water absorbancy and heat resistance.[3] Radiation initiated process to introduce vinyl monomers to graft onto nylon 4 membranes for desalination purposes has been used by Lai, Chang, Wu, and Hsieh.[1] Although the radiation grafting technique was a simple process for grafting vinyl monomers onto nylon, its commercial application was rather limited because of the need for sophisticated apparatus. The chemical initiation method was simpler and more convenient than the above method since it involved simple equipment and cheap chemicals. The purpose of this study is to utilize chemical initiation to graft different hydrophilic monomers onto nylon 4 membranes. The factors that affect the degree of grafting considered were chemical initiators, pH values, kinds and concentrations of monomers, reaction time, and temperatures. Some properties of reverse osmosis, ultrafiltration, electrodialysis, and mechanical strength of these grafted membranes were tested.

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EXPERIMENTAL

Polymer Synthesis

Nylon 4 was synthesized by the CO_2-initiated polymerization of 2-pyrrolidone using potassium 2-pyrrolidonate as the catalyst.[1,4] The molecular weight of the samples, measured by a Cannon-Fenske viscometer with *m*-cresol as a solvent at 25°C, were about 20,000 and 42,000. The lower molecular weight of nylon 4 was used to prepare ultrafiltration membrane and the higher molecular weight for reverse osmosis membrane.

Membrane Preparation

The membrane was prepared from a formic acid-casting solution of nylon 4 with added *n*-PrOH as a swelling agent.[1,5] The detail procedure of the membrane preparation was carried out according to our previous paper.[1] The casting conditions for ultrafiltration membrane was heat treatment at 40°C for 40 min to evaporate solvent and provide suitable pore size of membranes.

IR Measurement

IR spectra ranging from 4000 to 400 cm^{-1} of the grafted nylon 4 samples in the membrane state were obtained by using the Perkin-Elmer 710B spectrophotometer. The IR spectra of nylon 4-*g*-poly(sodium styrene sulfonate) (nylon 4-*g*-PSSS) showed the new absorption peak ν_{max} 1000 cm^{-1} (salt of $SO_3^-Na^+$); nylon 4-*g*-poly(chloromethyl styrene) (nylon 4-*g*-PCMS) showed ν_{max} 810 cm^{-1} (C—H of 1,4-disubstituted benzene), 780 cm^{-1} (CH_2Cl); after quaternization, the IR spectra of quaternized nylon 4-*g*-PCMS showed the new absorption peak ν_{max} 960 cm^{-1} [salt of $N^+(CH_3)_4Cl^-$]. The IR spectra of nylon 4-*g*-polystyrene (nylon 4-*g*-PSty) showed a new absorption peak ν_{max} 1500 cm^{-1} (C=C), 750 cm^{-1} (C—H of monosubstituted benzene); nylon 4-*g*-poly(glycidyl methacrylate) (nylon 4-*g*-PGMA) showed ν_{max} 1720 cm^{-1} (C=O of unsaturated ester group), 1140 cm^{-1} (C—O—C of cyclic ether group), 890 and 830 cm^{-1} (C—H of epoxy group). After sulfonation, the IR spectra of sulfonated nylon 4-*g*-PGMA showed a new absorption peak ν_{max} 1040 cm^{-1} (salt of $SO_3^-Na^+$), while the intensity of 890 and 830 cm^{-1} (C—H of epoxy group) bands decreased.

Graft Copolymerization

Graft Monomers. The following different compositions of formulas were used: (1) sodium styrene sulfonate (SSS) 10% solution: SSS 10 wt % H_2O/EtOH(1/1, v/v)/$K_2S_2O_8$ 1 wt %; (2) chloromethyl styrene (CMS) 10 wt % solution: CMS 10 vol %/H_2O/EtOH(1/1, v/v)/$(NH_4)_2S_2O_8$ 1 wt %/ polyoxyethylene sorbitan oleate 1 wt %; (3) styrene (Sty) 10% solution: Sty 10 vol %/H_2O/EtOH(1/1, v/v)/$(NH_4)_2S_2O_8$ 1 wt %/polyoxyethylene sorbitan monostearate 1 wt %; and (4) glycidyl methacrylate (GMA) 10% solution: GMA 10 vol %/H_2O/EtOH(1/1, v/v)/benzoyl peroxide 0.5 wt %.

Graft Copolymerization Procedure. Nylon 4 membranes were washed with pure water several times and dried in vacuum for 12 h at room

temperature. Then the nylon 4 membrane was placed in a glass bottle. The required amounts of monomer, solvent, initiator, and emulsifier were added.[6-8] The reactions were carried out under various conditions in a nitrogen atmosphere. The grafted membrane was washed with suitable solvent for 4 h to remove all of the homopolymer and then dried in vacuum. The degree of grafting was calculated by the percentage increase in weight over the original weight of the membrane.

Nylon 4-*g*-PCMS Quaternization. The quaternization of nylon 4-*g*-PCMS membrane can be performed in 30 wt % trimethylamine aqueous solution below 50°C for about 9 h.[9] After quaternization, the nylon 4 membrane was washed with ether and distilled water, and then dried in vacuum and weighed to calculate the increased weights of membrane.

Nylon 4-*g*-PGMA Sulfonation. The sulfonation of nylon 4-*g*-PGMA membrane can be carried out in the aqueous solution which was mixed Na_2SO_3 10 wt % solution with $NaHSO_3$ 7 wt % solution until the pH value was about 6.5–7.0.[10,11] The sulfonation was carried out at 70°C for 2 h. The sulfonated membrane was washed with distilled water, and then dried and weighed to calculate the increased weights of membrane.

Measurement of Transfer Number

The Na^+ form of the nylon 4-*g*-PSSS membrane and the Cl^- form of the quaternized nylon 4-*g*-PCMS membrane equilibrated in NaCl solution to be used in this experiment was clamped between two half-cells in the rubber gaskets. Each half-cell was filled with a different concentration of NaCl solution and carried an Ag–AgCl electrode. The steady potential of the cell Ag,AgCl/NaCl(a_1)/membrane/NaCl(a_2)/Ag,AgCl was measured by potentiometer and the transfer number could be calculated in terms of the following equations[12]:

$$E_0 = RT/F \ln(a_1/a_2) \qquad (1)$$

$$\bar{t} = E_m/2E_0 + 0.5 \qquad (2)$$

where E_0 is the cell potential, E_m is the membrane potential, a_1 and a_2 are the activities of the electrolyte solution, and $\bar{t}$ is the transfer number of counterions in the membrane phase.

Measurement of Water Content

The clean and dried membranes with known weights were immersed in distilled water at room temperature for at least 1 h to reach equilibrium swelling. The membranes were removed and blotted quickly with absorbent paper to remove the liquid attached on their surface, and weighed quickly. The degree of water content was calculated by the following equation:

$$\text{water content } (\%) = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{wet}}} \times 100\% \qquad (3)$$

where W_{dry} and W_{wet} represent the weights of dry and wet grafted membranes, respectively.

Measurement of Transport Properties

Reverse Osmosis Properties. The reverse osmosis[1,5] (RO) runs were carried out in RO high-pressure testing equipment (Schleicher and Schüll Co., Type RO-03). The apparatus consists of three testing cell that can test three membranes at the same time. The permeate which flowed down from the cell was collected for measurements of volume and conductivity. All of the reverse osmosis runs were conducted under 41 kg/cm^2 at the room temperature with 0.1 wt % sodium chloride aqueous solution. The water flux (WF) and the salt rejection (SR) were determined by the following equations:

$$WF = \frac{V \times \rho}{A \times t} \quad (g/cm^2 \ s) \tag{4}$$

$$SR = \frac{Cf_1 - Cf_2}{Cf_1} \times 100\% \tag{5}$$

where V is the permeate volume, ρ is the density of permeate solution, A is the effective membrane area, t is the operation time, and Cf_1 and Cf_2 are the feed and permeate concentrations, respectively. The sodium chloride concentrations were determined by a conductivity meter (Suntex Model SC-15).

Ultrafiltration Properties. Urea solution (0.1 wt %) and casein solution (0.05 wt %) were used as two feed streams, respectively. The water flux was determined by the same procedure as those used in the reverse osmosis runs, except that the pressure used was 7 kg/cm^2. The casein concentration was determined from absorption peak at λ_{max} 289 nm by using UV-visible double beam spectrophotometer (Shimadzu UV-160).[13] The urea permeate was added with urease to hydrolyze to NH_4^+ ion and CO_3^{-2} ion. Ion concentrations, NH_4^+ and CO_3^{-2}, were also determined by a conductivity meter (Suntex Model SC-15).[14]

Measurement of Mechanical Strength

The tensile strengths of nylon 4 and grafted nylon 4 membranes were measured by the Toyo Baldwin type TENSILON/UTM-III-100 instrument at ambient temperature. The tensile strengths and elongations of membranes in their dry states were measured according to ASTM D638[15] method.

RESULTS AND DISCUSSION

Effects of pH Value and Emulsifier on Grafting Yield

The grafting yields of each monomer onto nylon 4 membranes under different pH values are shown in Figure 1. The results indicated that the grafting yields of nylon 4-*g*-PSSS and nylon 4-*g*-PCMS both increased more in acidic or basic conditions than they did under neutral conditions. Owing to the great reactivity of the epoxy group of GMA monomer to open the highly strained three-membered ring easily under acidic or basic conditions, grafting GMA onto nylon 4 membranes proceeded in neutral conditions. Initiator, potassium persulfate, was used in nylon 4-*g*-PSSS graft copolymerization, and
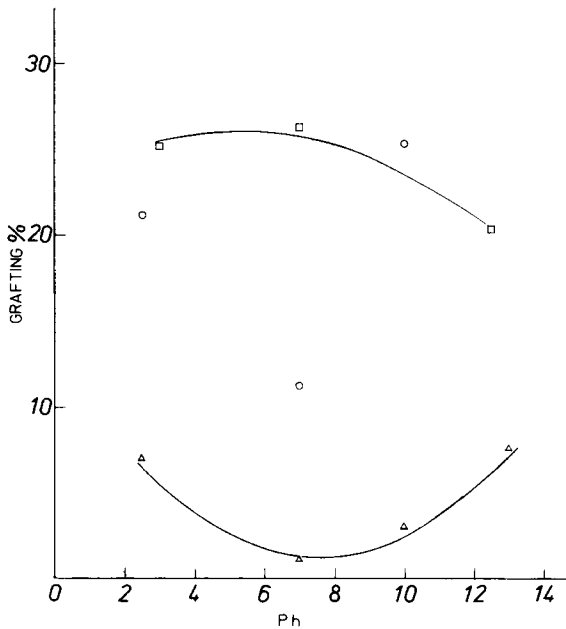
Fig. 1. Effect of pH on grafting yield: (□) nylon 4-*g*-PGMA; GMA 10%/H$_2$O/ EtOH(1/1, v/v)/BPO 0.5%/60°C, 60 min; (○) nylon 4-*g*-PSSS; SSS 20%/ H$_2$O/EtOH(1/1, v/v)/K$_2$S$_2$O$_8$ 2%/65°C, 2 hr; (△) nylon 4-*g*-PCMS; CMS 10%/ H$_2$O/(NH$_4$)$_2$S$_2$O$_8$ 1%/polyoxyethylene sorbitan oleate 1%/65°C, 50 min.

ammonium persulfate was used in nylon 4-*g*-PCMS and nylon 4-*g*-PSty graft copolymerization, respectively. In nylon 4-*g*-PGMA, thermally sensitive and easily decomposed initiators, such as peroxide type (BPO) and redox type [BPO–Fe(NH$_4$)$_2$(SO$_4$)$_2$], were used. Higher grafting yield of nylon 4-*g*-PGMA could be obtained by using the above initiators due to the ring-unopening addition of the epoxy group of GMA monomer. Since CMS is a hydrophobic monomer, emulsifiers, such as nonionic surfactants, sorbitan oleate (HLB = 6.4, W/O type), polyoxyethylene sorbitan oleate (HLB = 15.0, O/W type), were selected. When polyoxyethylene sorbitan oleate emulsifier is used, a higher degree of grafting can be obtained. The enhancement of grafting yield by polyoxyethylene sorbitan oleate could be ascribed to the fact that it was an oil in water type, which caused monomer to be easily soluble in solvent, and increased both the affinity to water and the swelling property of nylon 4 membrane. In order to obtain a higher degree of grafting, emulsifier poly-oxyethylene sorbitan monostearate (HLB = 14.9, O/W type) was used in nylon 4-*g*-PSty graft copolymerization, like polyoxyethylene sorbitan oleate in nylon 4-*g*-PCSM described above.

As shown in Figure 2, the reaction medium plays an important role in grafting SSS monomer onto nylon 4 membranes. The grafting yield decreased according to the following order: H$_2$O–EtOH, H$_2$O. From the experimental results, higher grafting depended on the nature of the solvent. It is suggested that EtOH could swell the nylon 4 membranes and cause the monomer to diffuse more easily.
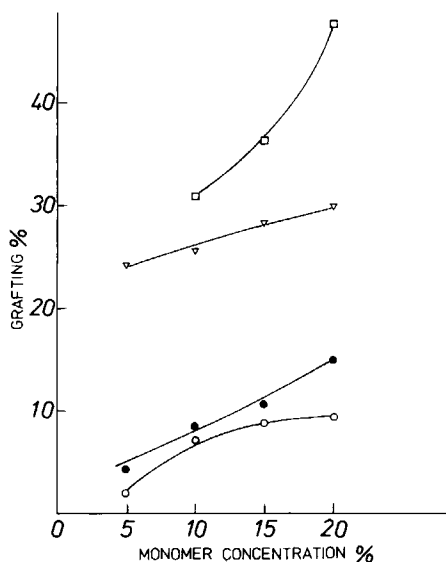
Fig. 2. Effect of monomer concentration on grafting yield: (□) nylon 4-g-PGMA; H_2O/ EtOH(1/1, v/v)/BPO 0.5%/pH = 6/60°C, 80 min; (∇) nylon 4-g-PSty; H_2O/ EtOH(1/1,v/v)/$(NH_4)_2S_2O_8$ 1%/polyoxyethylene sorbitan oleate 1%/pH = 2/60°C, 60 min; nylon 4-g-PSSS; $K_2S_2O_8$ 1%/pH = 2/65°C, 60 min; (●) solvent = H_2O/EtOH(1/1,v/v); (○) solvent = H_2O.

Effect of Monomer Concentration on Grafting Yield

The grafting yield of nylon 4 with different concentrations of monomers (SSS, CMS, GMA, and Sty) are shown in Figure 2. Obviously, for a given set of reaction conditions, the higher the grafting yield, the higher the monomer concentration. It was possible to assume that the nature and efficiency of the free radical would be the same. Hence, the above fact could be attributed to the following reasons: (a) increasing the rate of swelling of the nylon 4 membranes; (b) complexing of nylon 4 with monomer; (c) gel effect, i.e., increase in the solubility of homopolymer in its own monomer; and (d) the same species, which are either present or generated during the copolymerization reaction, act as an efficient radical scavenger.[6]

Effect of Temperature on Grafting Yield

The results of different monomers grafted onto nylon 4 membranes under various temperature are shown in Figure 3. The results indicated that the grafting percentage increased with the increase of temperature; similar results have also been reported by Nayak and co-workers.[6] The enhancement of grafting yield with the increase of temperature could be ascribed to the greater activation energy, the swellability of membrane, the solubility of monomer, and its diffusion rate.

Effect of Reaction Time on Grafting Yield

The graft copolymerization of nylon 4 membranes was carried out at different reaction time in the range from 30 to 120 min. The grafting yield
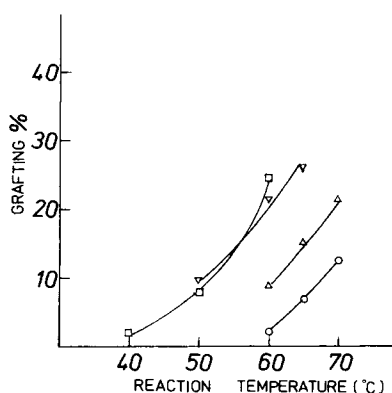
Fig. 3. Effect of temperature on grafting yield. Solvent = H_2O/EtOH(1/1, v/v); (□) nylon 4-*g*-PGMA; GMA 10%/BPO 0.5%/pH = 6.5/60 min; (∇) nylon 4-*g*-PSty; Sty 10%/$(NH_4)_2S_2O_8$ 1%/polyoxyethylene sorbitan monostearate 1%/pH = 2/30 min; (△) nylon 4-*g*-PCMS; CMS 10%/$(NH_4)_2S_2O_8$ 1%/polyoxyethylene sorbitan oleate 1%/pH = 2.5/60 min; (○) nylon 4-*g*-PSSS; SSS 10%/$K_2S_2O_8$ 1%/pH = 2/60 min.
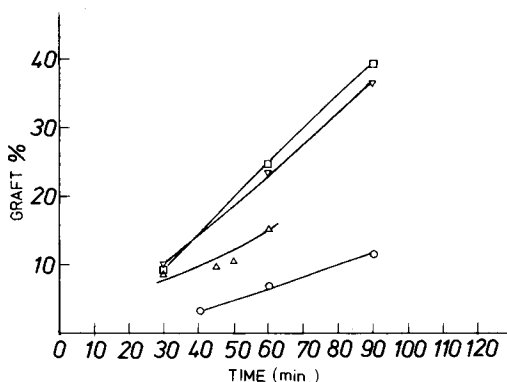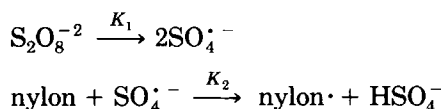

Fig. 4. Effect of reaction time on grafting yield. Solvent = H_2O/EtOH(1/1, v/v); (□) nylon 4-*g*-PGMA; GMA 10%/BPO 0.5%/pH = 6.5/60°C; (∇) nylon 4-*g*-PSty; Sty 10%/$(NH_4)_2S_2O_8$ 1%/polyoxyethylene sorbitan monostearate 1%/pH = 2/50°C; (△) nylon 4-*g*-PCMS; CMS 10%/$(NH_4)_2S_2O_8$ 1%/polyoxyethylene sorbitan oleate 1%/pH = 2.5/65°C; (○) nylon 4-*g*-PSSS; SSS 10%/$K_2S_2O_8$ 1%/pH = 2/65°C.

increased with an increase of grafting time, as shown in Figure 4. The increased grafting by prolongation of the polymerization time could be anticipated in view of the favorable effect of time duration on: (a) decomposition of initiator; (b) diffusion and adsorption of the monomer into the nylon 4 membranes; (c) number of the growing homopolymer chains in the vicinity of nylon 4; (d) diffusion of low molecular weight growing homopolymer chains; and (e) initiation and propagation of the graft.[8]
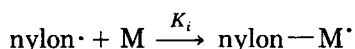
Mechanism of Graft Copolymerization

The successful grafting of vinyl monomers onto nylon 4 involves the creation of free radical on the backbone of nylon 4. The persulfate is known to produce free radicals by homolytic dissociation. The radicals may abstract one labile hydrogen atom from the carboxyl or amino group of nylon 4, creating a

macroradical which starts the graft copolymerization. In a system containing of persulfate, monomer (SSS, or CMS, or Sty), and nylon 4, the proposed mechanism is given as below[16]:
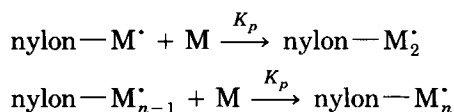
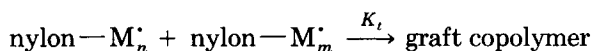$$S_2O_8^{-2} \xrightarrow{K_1} 2SO_4^{\cdot -}$$

$$\text{nylon} + SO_4^{\cdot -} \xrightarrow{K_2} \text{nylon}\cdot + HSO_4^-$$

Initiation:

$$\text{nylon}\cdot + M \xrightarrow{K_i} \text{nylon} - M^{\cdot}$$

where M is monomer.

Propagation:

$$\text{nylon} - M^{\cdot} + M \xrightarrow{K_p} \text{nylon} - M_2^{\cdot}$$

$$\text{nylon} - M_{n-1}^{\cdot} + M \xrightarrow{K_p} \text{nylon} - M_n^{\cdot}$$

Termination:

$$\text{nylon} - M_n^{\cdot} + \text{nylon} - M_m^{\cdot} \xrightarrow{K_t} \text{graft copolymer}$$

Owing to the reactivity of the epoxy group of GMA monomer, thermally sensitive and easily decomposed initiator, such as peroxide type (BPO) and redox type [BPO–Fe(NH$_4$)$_2$(SO$_4$)$_2$], were used in nylon 4-*g*-PGMA graft copolymerization. In a system consisting of BPO, GMA, and nylon 4, BPO reacts with nylon 4 forming nylon 4 macroradical, which reacts with the vinyl monomer resulting in the formation of the graft copolymer on the nylon 4 backbone:

BPO
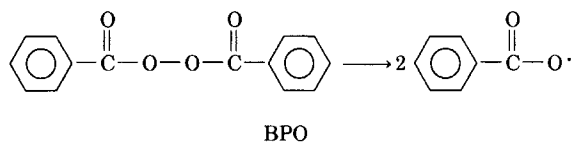
While in another initiating system that contains redox type [BPO–Fe(NH$_4$)$_2$(SO$_4$)$_2$], the oxidation of ferrous ion, Fe^{+2}, to ferric ion, Fe^{+3}, with benzoyl peroxide can be represented by the overall equation (6)[17]:
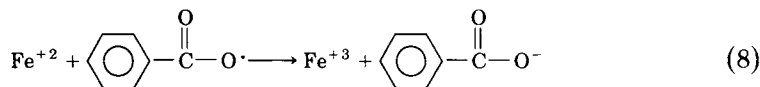

$$(6)$$
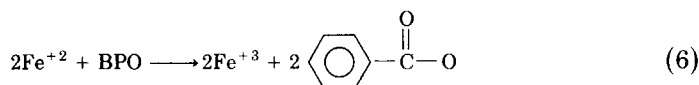
A kinetic study of this reaction revealed that it consists of two steps: (a) the donation of an electron from one Fe^{+2} to the BPO molecule, which is converted into a benzoate radical and a benzoate ion [eq. (7)]; and (b) the donation of another electron from another,
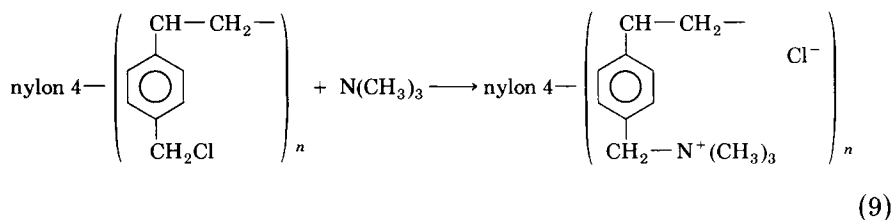

$$(7)$$
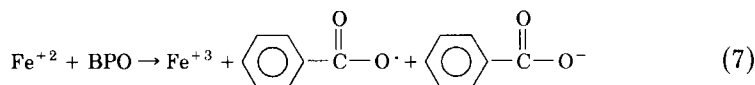
Fe^{+2} to the benzoate radical to give another benzoate ion [eq. (8)]:

$$Fe^{+2} + \langle\bigcirc\rangle - \overset{\overset{\text{O}}{\|}}{\text{C}} - \text{O} \cdot \longrightarrow Fe^{+3} + \langle\bigcirc\rangle - \overset{\overset{\text{O}}{\|}}{\text{C}} - \text{O}^- \tag{8}$$

The commonly used temperature ranges of redox type initiator (40°C) is lower than peroxide type (80–100°C); it is observed that initiation with redox type may occur rather rapidly. The mechanism of nylon 4-*g*-PGMA graft copolymerization is similar to that described in persulfate initiation method.

Quaternization of Trimethylamine with the Nylon 4-*g*-PCMS Membrane

The quaternization of the grafted membranes improved the properties of the water uptake and swelling behaviors made them acceptable for handling and practical use as anion-exchange membranes.[9] The alkyl halide reaction with a tertiary amine is a well-known method to prepare a quaternary ammonium salts. Higher trialkylamines failed to do such quaternization, probably due to the decrease in nucleophilicity, caused by the increasing steric hinderance of the product. The nylon 4-*g*-PCMS quaternization can be expected as follows:[18]

$$\text{nylon 4} - \left(\begin{array}{c} \text{CH} - \text{CH}_2 - \\ \bigcirc \\ \text{CH}_2\text{Cl} \end{array} \right)_n + \text{N(CH}_3)_3 \longrightarrow \text{nylon 4} - \left(\begin{array}{c} \text{CH} - \text{CH}_2 - \\ \bigcirc \qquad \text{Cl}^- \\ \text{CH}_2 - \text{N}^+(\text{CH}_3)_3 \end{array} \right)_n \tag{9}$$

After quaternization, the weights of membranes increased with an increase of the degree of CMS grafting, reaction time and reaction temperature, as seen in Figure 5.
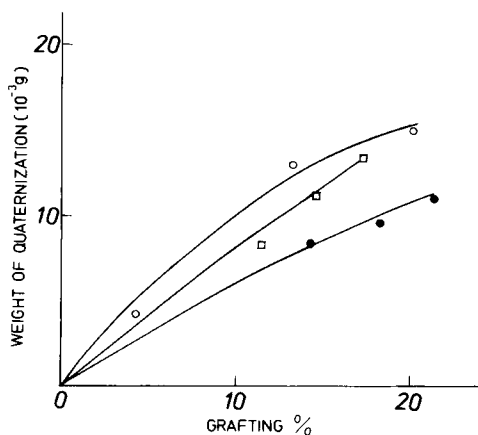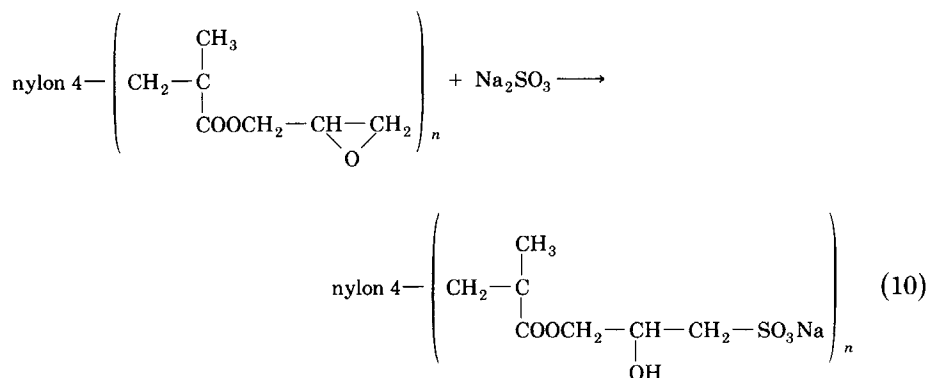

Fig. 5. The increased weights of membrane in nylon 4-*g*-PCMS after quaternization vs. degree of grafting. Quaternization conditions: (○) 50°C, 9 h; (□) 30°C, 18 h; (●) 30°C, 9 h.

Sulfonation of Na_2SO_3–$NaHSO_3$–H_2O Solution with Nylon 4-g-PGMA Membrane

Anion-exchange and cation-exchange membranes can be prepared by using the chemical reactivity of glycidyl methacrylate-grafted membranes. It is well-known that sodium oxysulfonate is produced by the ring-opening addition of epoxy and Na_2SO_3, and using $NaHSO_3$ to adjust the pH of solution, to obtain the cation-exchange membrane.[10] The sulfonated nylon 4-g-PGMA membrane was prepared via the epoxy-opening addition with 10 wt % Na_2SO_3 and 7 wt % $NaHSO_3$ aqueous solution. The nylon 4-g-PGMA sulfonation occurs as shown in the following reaction[10]:

$$\text{nylon 4}\!-\!\left(\begin{array}{c} CH_3 \\ | \\ CH_2\!-\!C \\ | \\ COOCH_2\!-\!CH\!-\!CH_2 \\ \diagdown\!O\!\diagup \end{array}\right)_n + Na_2SO_3 \longrightarrow$$

$$\text{nylon 4}\!-\!\left(\begin{array}{c} CH_3 \\ | \\ CH_2\!-\!C \\ | \\ COOCH_2\!-\!CH\!-\!CH_2\!-\!SO_3Na \\ | \\ OH \end{array}\right)_n \qquad (10)$$

After sulfonation, the weights of membranes increased with an increase of GMA grafting yield, as shown in Figure 6. Comparing the same grafting yield of nylon 4-g-PGMA membranes with redox or peroxide type initiator, it was found that the weights of membrane initiated with redox type were greater than those initiated with peroxide type after sulfonation. It was assumed that initiation with redox type may occur rather rapidly and keep more unopening epoxy group for sulfonation even at relatively low temperature.
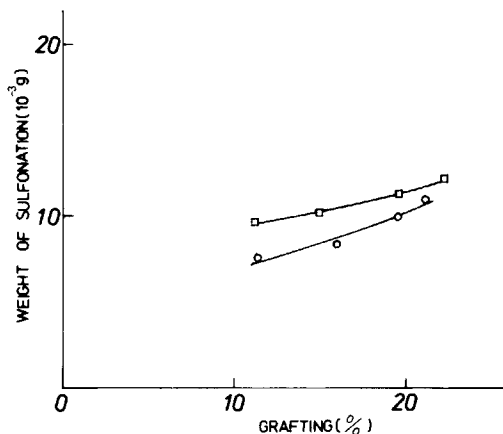

Fig. 6.   The increased weights of membrane in nylon 4-g-PGMA after sulfonation vs. degree of grafting: (□) initiator = BPO–Fe$(NH_4)_2(SO_4)_2$; (○) initiator = BPO.
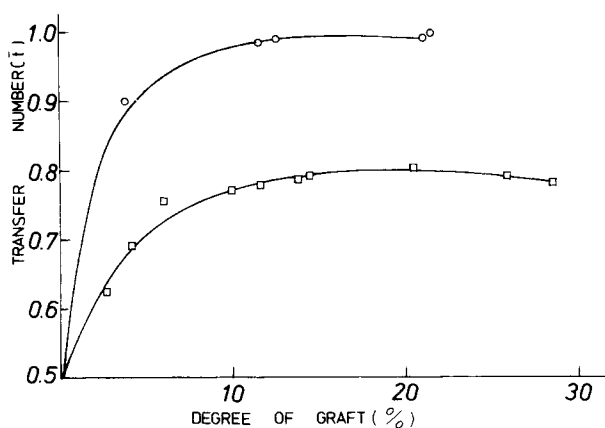
Fig. 7. Transfer number of counterion in nylon 4-*g*-grafted membranes vs. degree of grafting: (○) quaternized nylon 4-*g*-PCMS membranes; (□) nylon 4-*g*-PSSS membranes.

Transfer Number Test

The cation-selective membranes for electrodialysis practically are all made from polystyrene with sulfonate groups attached. The corresponding anion-selective membranes are constructed on a framework of the polymer poly(vinyl benzyl chloride) with the quaternary ammonium ion such as trimethylammonium.[19] When the membrane system containing different concentrations of NaCl solution on either side of the membrane was electrolyzed, the rate at which ions through the membrane was controlled by their transfer numbers. From Figure 7, it is obvious that the transfer number ($\bar{t}$) in nylon 4-*g*-PSSS or quaternized nylon 4-*g*-PCMS membranes increased with an increase of grafting yield. The transfer number of Cl^- counterion obtained from quaternized nylon 4-*g*-PCMS membrane was 0.996, which is close to the value 1, as expected in a perfect anion-exchange membrane.

The Water Content of the Nylon 4 Grafted Membranes

The water content of the membranes reflected the volume fraction of water in the membrane, as shown in Figure 8. The higher water content means that the macromolecule segments could be separated further in the presence of water. Therefore, the water permeate from the membrane would be influenced by the water content of the membrane. Increasing the degree of grafting of nylon 4 membranes grafted with polystyrene or poly(chloromethyl styrene) indicated a decrease of water content, since these polymers were less hydrophilic. Since poly(glycidyl methacrylate) is a slightly hydrophilic polymer, it was shown that the water content of nylon 4-*g*-PGMA membrane was unchanged as the increasing of grafting yield. In all of the grafted membranes, the nylon 4-*g*-PSSS membranes had the greatest water content. Similar results have been mentioned in our previous paper.[1] Moreover, the quaternized grafted and sulfonated grafted nylon 4 membranes possessed much higher water content than unquaternized grafted and unsulfonated grafted membranes, respectively.
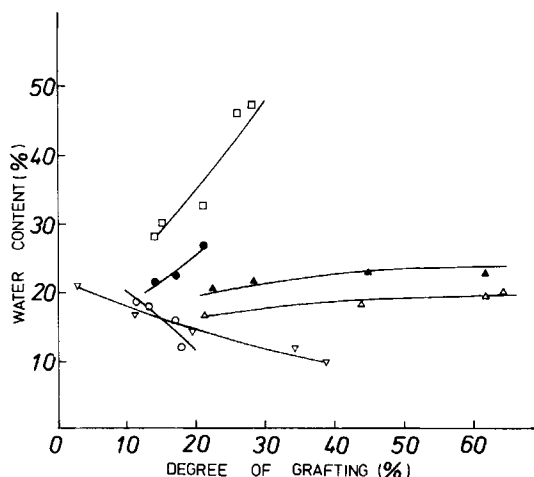
Fig. 8. Water content of nylon 4-*g*-grafted membranes vs. degree of grafting: (□) nylon 4-*g*-PSSS; (●) quaternized nylon 4-*g*-PCMS; (○) nylon 4-*g*-PCMS; (▽) nylon 4-*g*-PSty; (▲) sulfonated nylon 4-*g*-PGMA; (△) nylon 4-*g*-PGMA.

Effect of Degree of Grafting on the RO Performance of the Grafted Nylon 4 Membranes

The RO membranes performance of nylon 4-*g*-PSSS, nylon 4-*g*-PCMS, and nylon 4-*g*-PSty are summarized in Table I. The grafted nylon 4 membranes possessed much less water flux than those of ungrafted membranes did. With both nylon 4-*g*-PCMS and nylon 4-*g*-PSty membranes having higher degrees of grafting, the water flux decreased and the salt rejection increased. The decrease of the water flux could be attributed to the decreasing of the membrane hydrophilicity and water content. The increase of salt rejection was due to the fact that the surface pores of the membranes had been masked

TABLE I
The Performance of Nylon 4-*g*-Grafted RO Membranes[a]

Nongrafted membranes		Grafted membranes			
WF [(g/cm^2 s) $\times$ 10^5]	SR (%)	Monomer	Grafting (%)	WF [(g/cm^2 s) $\times$ 10^5]	SR (%)
0.60	50.6	SSS	11.43	2.85	72.9
0.69	50.0	SSS	14.20	2.30	76.0
0.43	38.8	SSS	14.84	3.40	72.7
0.40	39.2	SSS	17.60	2.75	71.8
0.57	48.9	SSS	19.90	2.53	76.1
0.75	28.9	CMS	11.60	0.53	41.1
0.44	31.8	CMS	16.50	0.39	34.0
0.38	23.7	CMS	17.40	0.31	38.0
0.36	44.1	Sty	5.47	0.32	64.6
0.51	43.6	Sty	10.62	0.39	67.4
0.33	49.5	Sty	11.93	0.29	64.5
0.35	49.1	Sty	19.64	0.26	76.3

[a] Thickness = 55–65 μm.

TABLE II
The Performance of Nylon 4-g-PGMA RO Membranes and Nylon 4-g-PGMA Sulfonated RO Membranes[a]

Nongrafted membranes		Grafting condition	Grafting membranes			Sulfonated membranes	
WF $[(g/cm^2\ s) \times 10^5]$	SR (%)	Initiator	Grafting (%)	WF $[(g/cm^2\ s) \times 10^5]$	SR (%)	WF $[(g/cm^2\ s) \times 10^5]$	SR (%)
0.35	43.29	BPO	8.47	0.31	52.17	0.63	56.52
0.31	52.48	BPO	10.43	0.32	56.88	0.68	77.33
0.43	48.91	BPO	28.35	0.36	61.42	0.50	77.04
0.51	39.68	BPO–	29.71	0.17	41.41	0.38	71.04
0.21	42.17	$Fe(NH_4)_2(SO_4)_2$	21.29	0.20	56.54	0.38	77.57
0.29	35.59	$Fe(NH_4)_2(SO_4)_2$	28.25	0.20	52.50	1.15	63.66
0.22	44.71	$Fe(NH_4)_2(SO_4)_2$	29.72	0.13	48.60	0.66	72.99

[a] Thickness = 55–65 μm.

by grafted molecules. Both water flux and salt rejection increased significantly for nylon 4-*g*-PSSS membranes. The ratio of water flux and salt rejection of membrane between the grafted and ungrafted was calculated. It was found that the values of this work are higher than those corresponding values of our previous paper.[1]

The performance of nylon 4-*g*-PGMA and sulfonated nylon 4-*g*-PGMA RO membranes are listed in Table II. The water fluxs of these nylon 4-*g*-PGMA having higher degree of grafting membranes decreased slightly, while the salt rejection all increased. Sulfonated nylon 4-*g*-PGMA membranes exhibited higher water flux and salt rejection than those of unsulfonated membranes. Moreover, the ratio of water flux between the grafted and ungrafted GMA monomer onto nylon 4 membranes initiated by redox type initiator was higher than those of membranes by peroxide type initiator. The reason was the enlargement of sulfonation by using redox type initiator. Although the water flux and the salt rejection increased in nylon 4-*g*-PSSS membrane, the commercial application of this method is rather limited because of the expensive chemicals and a lower degree of grafting in nylon 4-*g*-PSSS graft copolymerization. The method of sulfonated nylon 4-*g*-PGMA membrane was more convenient and easier in graft copolymerization, and it involved cheaper chemicals. Thus, to achieve the desires of both higher water flux and salt rejection, this study suggests utilization of the preparation of sulfonated nylon 4-*g*-PGMA membranes.

Effect of the Degree of Grafting on the UF Performance of Grafted Nylon 4 Membranes

The UF membranes performance of nylon 4-*g*-PSSS, nylon 4-*g*-PCMS, nylon 4-*g*-PSty, and nylon 4-*g*-PGMA in urea solution are shown in Table III. The water flux of the other three grafted membranes decreased with increas-

TABLE III
The Performance of Nylon 4-*g*-Grafted UF Membranes in Urea Solution

Nongrafted membranes			Grafted membranes			
WF [(g/cm^2) × 10^5]	Thickness (μm)	Urea rejection (%)	Monomer	Grafting (%)	WF [(g/cm^2) × 10^5]	Urea rejection (%)
29.03	14	2.56	SSS	11.56	56.92	4.59
25.61	14	7.09	SSS	10.73	38.42	2.69
27.96	14	14.62	SSS	13.47	48.79	8.09
31.62	14	17.24	SSS	14.90	92.69	9.49
45.92	12	10.71	CMS	6.27	32.32	19.04
35.48	13	6.75	CMS	7.20	16.89	15.24
38.45	12	4.89	CMS	13.88	21.36	17.78
43.26	12	4.12	CMS	14.90	26.56	5.35
17.08	17	23.97	GMA	17.94	2.67	28.29
21.35	14	26.00	GMA	18.91	10.21	17.48
12.45	18	8.22	Sty	11.87	4.14	18.77
10.80	19	10.10	Sty	13.59	2.83	23.60
23.80	15	2.50	Sty	22.66	4.88	12.98

TABLE IV
The Performance of Nylon 4-g-Grafted UF Membranes in Casein Solution

Nongrafted membranes			Grafted membranes			
WF $[(g/cm^2) \times 10^5]$	Thickness (μm)	Casein rejection (%)	Monomer	Grafting (%)	WF $[(g/cm^2) \times 10^5]$	Casein rejection (%)
13.23	14	65.6	SSS	10.73	19.10	98.4
12.79	14	55.0	SSS	11.56	15.83	98.0
17.02	14	57.0	SSS	14.90	39.37	98.4
10.34	16	58.0	CMS	6.97	1.83	93.3
14.77	14	60.0	CMS	7.98	2.14	93.4
25.56	13	60.5	CMS	13.75	4.13	94.4
31.97	12	68.0	CMS	14.90	4.66	97.0
30.58	14	65.6	GMA	18.91	3.57	97.0
14.30	15	65.6	GMA	21.29	5.72	97.6
27.75	13	68.0	GMA	37.32	5.43	96.0
45.35	11	61.0	Sty	11.19	8.15	91.6
32.22	12	58.0	Sty	14.22	11.28	90.6
47.27	12	68.0	Sty	22.66	4.59	98.4
34.99	13	66.0	Sty	29.21	3.70	96.6

ing grafting yield except the nylon 4-g-PSSS membranes, while the urea rejection all increased slightly. Thus the nylon 4-g-PSSS membranes possessed both the higher water flux and the lower urea rejection.

The performance of nylon 4-g-PSSS, nylon 4-g-PCMS, nylon 4-g-PSty, and nylon 4-g-PGMA UF membranes in the case of casein solution are shown in Table IV. The water flux of these four grafted membranes coincided with the case of urea solution. All of the grafted membranes showed excellent casein rejection (over 90%) and high water flux.

Effect of Grafting on the Tensile Properties of Nylon 4 Grafted Membranes

The tensile strengths of nylon 4 membranes are shown in Table V. On the average, the tensile strength of ungrafted nylon 4 membranes is 717.5 kg/cm^2, and the elongation at break is about 60.83%. The tensile strengths and elongations of nylon-4-grafted membranes slightly decreased with the increasing of grafting yield. The decrease of tensile strength of the grafted membranes could be attributed to the decrease of crystallinity of grafted membranes. But the tensile strengths of grafted nylon 4 membranes using chemical initiation method was higher than that of using γ-ray irradiation method in our previous paper.[1] The decrease in elongation of grafted nylon 4 membranes was similar to that described in γ-ray irradiation method.

CONCLUSION

Grafted membranes prepared by utilizing chemical initiation which induced vinyl monomers grafted onto nylon 4 membranes for reverse osmosis and ultrafiltration application have been studied. Water flux in nylon 4-g-PSSS and sulfonated nylon 4-g-PGMA membranes are both significantly improved,

TABLE V
The Tensile Properties of Nylon 4 Membranes[a]

Species	Grafting (%)	Tensile strength (kg/cm^2)	Elongation (%)
Nylon 4	—	717.50	60.83
Nylon 4-g-PSSS	6.45	626.00	66.67
Nylon 4-g-PSSS	11.43	591.67	56.67
Nylon 4-g-PSSS	21.14	595.67	51.67
Nylon 4-g-PSty	1.93	579.46	51.67
Nylon 4-g-PSty	11.93	578.46	46.67
Nylon 4-g-PSty	19.64	578.75	31.67
Nylon 4-g-PGMA	9.23	653.33	55.00
Nylon 4-g-PGMA	16.57	644.61	45.83
Nylon 4-g-PGMA	21.49	649.30	40.83
Nylon 4-g-PGMA sulfonation	12.32	641.30	48.33
Nylon 4-g-PGMA sulfonation	16.20	622.58	46.67
Nylon 4-g-PGMA sulfonation	21.29	646.52	45.00
Nylon 4-g-PCMS	11.90	612.50	38.33
Nylon 4-g-PCMS	17.20	530.71	21.67
Nylon 4-g-PCMS	10.40	605.71	31.67
Quaternization	16.80	512.00	43.33

[a] Drawing rate: 5.0 mm/min; drawing temperature = room temperature; load cell = 5 kg.

compared to ungrafted nylon 4 membranes. The salt rejection and casein rejection are all increased significantly, and the mechanical strengths of grafted membranes are not seriously decreased. The quaternized nylon 4-g-PCMS membranes were also prepared and possessed high water uptake behavior and high transfer number (0.99) for electrodialysis. This shows that it is feasible to improve the transport properties of nylon 4 membranes by inducing vinyl monomers with chemical initiation method, and which is better than that does with γ-ray irradiation method.

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