Vinyl Monomer Irradiation-Grafted Nylon 4 Membranes

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Synopsis

To improve the performance of Nylon 4 membranes, this study attempts to utilize ^{60}Co γ-ray irradiation which induces vinyl monomers to be grafted onto Nylon 4 membranes for desalination purposes. Sodium styrene sulfonate, acrylamide, vinylacetate, and styrene are the grafting monomers. The transport properties and mechanical strength of the γ-ray irradiation-grafted Nylon 4 membranes are studied. Both the water flux and salt rejection of sodium styrene sulfonate-grafted membrane increase significantly, compared to Huang's results. The other grafted membranes also show increased salt rejection.

INTRODUCTION

Nylon 4 (polypyrrolidone) has been regarded as a promising membrane material for separation purposes because of its excellent strength and inherent affinity to water. Previous work on Nylon 4 membranes had been carried out by Lonsdale et al. and by Orofino (cited in Huang et al.[1,2]) but they found that Nylon 4 membranes behaved erratically in terms of their transport fluxes. By using the improved polypyrrolidone synthesis and membrane preparation method, a better performance of Nylon 4 membranes was reported by Huang et al.[1,2] The results of their membranes still showed poor salt rejection of NaC[1] solution with low permeability.

Graft copolymerization is a well known method which can modify the chemical and physical properties of polymers.[3,4] Reverse osmosis, (RO) characteristics of membranes prepared by grafting of hydrophilic polymers onto hydrophilia polymers have been examined by several workers.[5-8] In the present study we have varied the conditions of Nylon 4 membrane preparation to improve the performance of Nylon 4 (RO) membranes. We are the first to attempt to utilize ^{60}Co γ-ray irradiation inducing the hydrophilic monomers to be grafted onto Nylon 4 membranes for desalination purposes.

The membranes with different hydrophilicities such as sodium styrene sulfonate (SSS), acrylamide (AAm), vinyl acetate (VAc), and styrene (Sty) were chosen as the grafting monomers and the graft copolymerization was carried out by the simultaneous irradiation method. The transport properties and mechanical strength of the γ-ray irradiation-grafted Nylon 4 membranes were studied.

EXPERIMENTAL

Polymer Synthesis

The Nylon 4 was synthesized by the CO_2-initiated polymerization of 2-pyrrolidone using potassium 2-pyrrolidonate as the catalyst.[1,9,10] The molecular

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weight is measured by the viscosity method to be about 20,000–25,000 for most of the runs. To synthesize the higher molecular weight Nylon 4, we altered the catalyst system to CO_2/KOH/Crown-ether system by adding 18 crow-6 ether into the above catalyst system.[11]

Membrane Preparation

The membrane was prepared from a formic acid-casting solution of Nylon 4 with added *n*-PrOH as swelling agent. The composition of casting solution is

Nylon 4 10 wt%
formic acid (90%)/*n*-PrOH = 4/1 (v/v) 90 wt%

The membrane was formed by casting the solution on a glass plate to predetermined thickness. Then the glass plate was evaporated for specified different times (5, 20, 40 min) at ambient temperature and heated for 10 min at predetermined different temperatures (70, 80, 90°C) in the oven and cooled for 10 min. Then the glass plate with the film was immersed in a methanol nonsolvent bath for 10 min at room temperature. The membrane was then peeled off and stored in distilled water for at least 12 hr before subsequent use. The membrane thickness was in the range of 64–74 μm.

Reverse Osmosis Properties

The reverse osmosis (RO) runs were carried out in RO high-pressure testing equipment (Schleicher & Schiill 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 to be measured. All the reverse osmosis runs were conducted at 41 kg/cm^2 at laboratory temperature with 0.1 wt% sodium chloride aqueous solution. The water flux (WF) and the salt rejection (SR) were determined by the following equations:

$$\mathrm{WF} = \frac{V \times \rho}{A \times t}\,(\mathrm{g/cm^2\text{-}s}) \tag{1}$$

$$\mathrm{SR} = \frac{Cf_1 - Cf_2}{Cf_2} \times 100\% \tag{2}$$

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.

Graft Copolymerization

Nylon 4 membranes were washed with pure water and dried in vacuum at room temperature. Then the Nylon 4 membrane was placed in a glass bottle. The grafting monomer solution was poured into it to completely soak the membrane. The compositions of different monomers used were

Sodium styrene sulfonate (SSS): 10 g SSS + 100 mL H_2O + 100 mL EtOH
Acrylamide (AAm): 10 wt% aqueous solution
Vinyl acetate (VAc): VAc/EtOH/H_2O = 1/3/2 (v/v)
Styrene (Sty):
a. pure styrene
b. styrene/EtOH = 90/10 (v/v)

Graft copolymerization was carried out by irradiation with γ-rays from ^{60}Co at room temperature, dose rate 1.2×10^4 rad/hr. After irradiation, the grafted membrane was washed with suitable solvent several times to remove all the homopolymer and then dried in vacuum. The degree of grafting was calculated from the weight increase of the grafted membrane.

Measurement of Water Content

The wet membranes were placed in distilled water for at least 1 hr to reach equilibrium swelling. The water content of Nylon 4 membranes was determined by drying weighed samples of the wet membranes in vacuum at room temperature. The dry membranes were then weighed and the water content (H) was calculated as

$$H(\%) = \frac{W_{wet} - W_{dry}}{W_{wet}} \times 100\%$$

where W_{wet} and W_{dry} are the weight of wet and dry membranes, respectively.

Measurement of Tensile Strength

The tensile strength measurement of Nylon 4 and grafted Nylon 4 membranes were carried out on the Toyo Baldwin type TENSILON/UTM-III-100 instrument at ambient temperature. The membranes were tested by ASTM D638[12] method, for their tensile strengths and elongations in their dry states.

RESULTS AND DISCUSSION

Effect of Solvent Evaporation Time and Heat Treatment Temperature on Membrane Performance

Table I shows the effect of solvent evaporation time at ambient temperature and heat-treatment temperature on Nylon 4 RO membrane performance in terms of water flux (WF) and salt rejection (SR). As can be seen, the WF decreased slightly with increasing solvent evaporation time, the SR increased with increasing solvent evaporation time. The WF and SR increased slightly with increasing heat-treatment temperature. The results of this research have better WF and SR than the results reported by Huang[2]. The best condition from this study for preparation of Nylon 4 membrane is the combination of 20 min solvent evaporation time and 80°C heat-treatment temperature. The

TABLE I
Effect of Solvent Evaporation Time and Heat Treatment Temperature on Nylon 4 RO Membrane Performance

Evap. time (min)	Heating temp. (°C)	Gelation[a] time (min)	Water[b] flux (WF) (g/cm²-s) × 10^5	Salt rejection (SR) (%)	Salt retention rate (WF × SR)
5	80	10	1.97	31.6	62.3
20	80	10	1.78	38.8	69.1
40	80	10	1.71	39.4	67.4
5	70	10	1.68	27.6	46.4
5	90	10	2.12	33.7	71.4

[a]Gelation solution: MeOH, at room temperature.
[b]Feed: 0.1 wt% NaCl. Op. press.: 41 kg/cm^2 Op. temp.: room temp. Effective membrane area: 19.52 cm^2.

TABLE II
The Effect of the Amount of 18 Crown-6 Ether on the Degrees of Polymerization of Nylon 4

Run no.	Mole ratio of reactant: Monomer	Catalyst (KOH)	Initiator (CO_2)	18 Crown −6 ether	Product[b]: [η]	M_v[a]	Conversion (%)
1	1	0.1	0.04	0.000	5.74	48900	66.1
2	1	0.1	0.04	0.001	6.20	54700	65.7
3	1	0.1	0.04	0.002	6.80	62400	68.9
4	1	0.1	0.04	0.004	7.62	73500	67.2
5	1	0.1	0.04	0.0085	8.25	82300	71.1
6	1	0.1	0.04	0.017	7.80	76000	68.9
7	1	0.1	0.04	0.035	7.69	74400	72.2
8	1	0.1	0.04	0.070	6.58	59600	76.1
9	1	0.01	0.006	0.007	—	—	—

[a]The molecular weight is measured by viscosity method with m-cresol as solvent at 25°C. $[\eta] = 2.99 \times 10^{-3} M_v^{0.7}$ (25°C).
[b]The reaction conditions: reaction time: 120 hr, reaction temperature: 50°C.

TABLE III
Effect of Nylon 4 Molecular Weight on Membrane Performance

Molecular[a] weight (MW)	Evap. time (min)	Heating temp. (°C)	Gelation time (min)	WF (g/cm²-s) × 10^5	SR (%)
25,000	20	80	10	1.78	38.8
49,000	20	80	10	1.04	47.1
65,000	20	80	10	0.76	51.1

[a]Measured by viscosity method.

highest salt retention rate is obtained for the membranes prepared by the above conditions.

Effect of Nylon 4 Molecular Weight on Membrane Performance

The conditions for synthesizing the higher molecular weight Nylon 4 are listed in Table II. The amount of 18 crown-6 ether does affect the molecular weight of synthesized Nylon 4.

Table III shows the effect of Nylon 4 molecular weight on Nylon 4 RO membrane performance. Considering the molecular weight range of 25,000 and 65,000, membranes which are prepared from higher molecular weight polymers shows increased salt rejection and decreased water flux.

Influence of Membrane Water Content

Figure 1 shows the water content of Nylon 4 membranes. The water content of membrane reflects the volume fraction of water in the membrane. The high water content means that the macromolecular segments could be separated

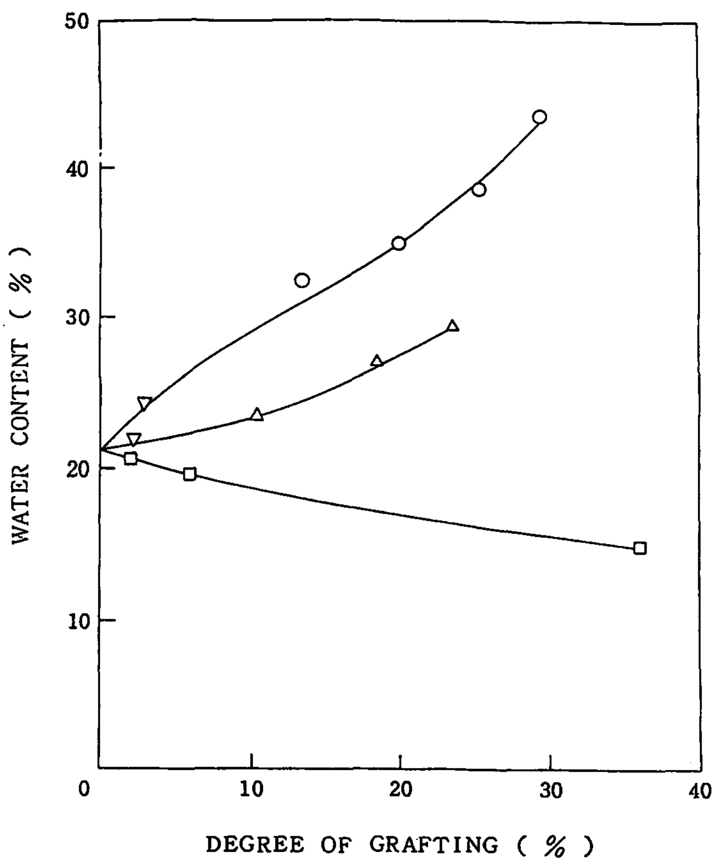

Fig. 1. Water content of Nylon 4-grafted membranes vs. degree of grafting. ○: sodium styrene sulfonate-grafted membrane; △: acrylamide-grafted membrane; ▽: vinyl acetate-grafted membrane; □: styrene-grafted membrane.

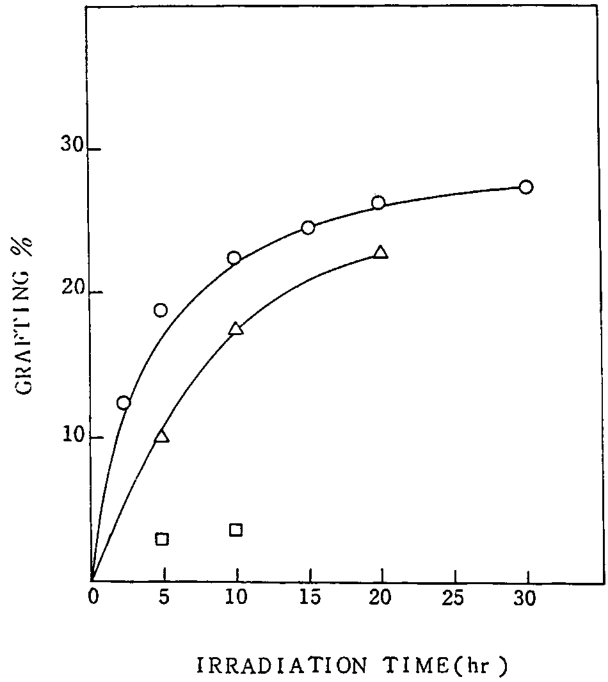

Fig. 2. Plot of degree of grafting vs. irradiation time. ○: Nylon 4-g-PSSS; △: Nylon 4-g-PAAm; □: Nylon 4-g-PVAc.

further by the presence of water. Therefore, the water permeated from the membrane would be influenced by the water content of membrane. Except for the Nylon 4-g-polystyrene membranes, the water content of the other three grafted membranes all increase with increasing degrees of grafting. The Nylon 4-g-poly(sodium styrene sulfonate) membranes have the greatest water content. Polystyrene is a less hydrophilic polymer, it results in a decrease of water content of Nylon 4-g-polystyrene membranes with increasing degree of grafting.

Effect of Irradiation Time on the Degree of Grafting of the Grafted Nylon 4 Membranes and their Performances

From Figure 2 we can see that the degree of grafting increased with increasing γ-ray irradiation time. The Nylon 4-g-poly (sodium styrene sulfonate) has the highest degree of grafting for the same irradiation time.

Table IV shows the effect of grafted poly(sodium styrene sulfonate) on the performances of Nylon 4 membranes. As can be seen, both the water flux and salt rejection increased significantly, with grafted sodium styrene sulfonate membranes with higher degree of grafting showing better WF and SR. For example, a best result of 8.26×10^{-5} g/cm^2-s with 75.9% can be obtained.

Table V shows the performance of Nylon 4-g-poly(acrylamide), Nylon 4-g-poly(vinyl acetate), and nylon 4-g-polystyrene RO membranes. For the Nylon 4-g-polyacrylamide membranes, at higher degrees of grafting, the water flux and the salt rejection of these membranes all increased. This could be

TABLE IV
The Performances of Nylon 4-g-PSSS RO Membranes

	Nongrafted membranes			Grafted membranes		
	WF $(g/cm^2\text{-}s) \times 10^5$	SR (%)	Radiation time[a] (hr)	SSS degree of grafting (%)	WF $(g/cm^2\text{-}s) \times 10^5$	SR (%)
5 min	2.01	31.7	5	18.2	5.83	49.3
80°C	2.87	21.1	10	21.3	8.43	37.3
	1.87	32.8	20	22.5	8.77	49.5
	1.94	37.7	30	27.1	7.81	67.0
20 min	1.98	36.0	5	17.9	3.99	51.6
80°C	1.54	44.3	10	21.3	8.26	75.9
	2.09	34.7	15	24.8	6.56	64.2
40 min	2.19	36.1	5	19.3	0.888	51.9
80°C	2.34	37.1	10	22.5	8.09	69.8
5 min	1.52	39.7	5	18.5	6.56	70.8
90°C	2.13	35.1	10	24.5	6.28	56.2
	1.48	42.2	20	28.2	12.3	72.8
5 min	2.56	23.0	3	12.0	2.88	45.2
70°C	1.51	34.2	10	24.3	6.68	69.3
	1.40	32.4	20	26.9	16.2	56.0

[a] Dose rate: 1.2×10^4 rad/hr, at room temperature.

attributed to the increase of the membrane hydrophilicity and water content, and the result of the masking effect of grafted molecules on the membrane surface pores. Vinyl acetate grafted membranes do not show better water flux, but do increase salt rejection. The phenomenon of the low degree of grafting of Nylon 4-g-poly(vinyl acetate) is similar to the results of Hayakawa et al.[13] who used nylon 6. The water flux of Nylon 4-g-polystyrene membranes is decreased compared to the nongrafted membranes. It agrees with the results of water content, and the salt rejection of these grafted membranes increased. There is irregular change between irradiation time and degree of grafting when using the pure styrene as grafting monomer, and the degree of grafting is low. This might be due to the presence of O_2 in the glass bottle during γ-ray irradiation. As we change the grafting monomer to the composition of styrene/EtOH = 90/10(v/v), there is much higher degree of grafting, because the interaction of styrene and EtOH enhance the styrene molecules to diffuse into the Nylon 4 backbone polymer. The highest salt rejection of Nylon 4-g-polystyrene membrane reaches 85.6%, and its water flux is 4.07×10^{-5} g/cm^2-s.

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

Table VI shows the tensile properties of Nylon 4 membranes. The ultimate tensile strength of nongrafted Nylon 4 membranes is 410 kg/cm^2 on average,

TABLE V
The Performances of Nylon 4-g-polyacryamide, Nylon 4-g-Polyvinyl Acetate and Nylon 4-g-Polystyrene RO Membranes

Nongrafting membranes			Grafted membranes				
Casting condition	WF (g/cm²-s) × 10^5	SR (%)	Monomer	Rad time (hr)	Grafting (%)	WF (g/cm²-s) × 10^5	SR (%)
40 min 80°C	4.01	20.6	Aam	5	9.30	2.33	26.0
	1.30	46.7	″	5	8.72	1.17	47.5
	1.52	43.0	″	5	9.69	1.29	45.2
	1.40	39.1	″	5	10.5	1.48	42.5
	1.30	42.0	″	10	15.5	1.82	42.5
	1.46	42.1	″	10	19.2	1.95	52.1
	1.54	41.7	″	10	19.1	1.75	47.1
20 min 80°C	1.76	36.3	″	20	22.8	2.47	42.0
	1.46	39.2	″	20	21.4	2.05	43.5
	1.32	44.7	″	20	20.9	1.40	48.4
	1.37	43.1	″	20	20.4	1.54	47.8
5 min 80°C	1.28	44.2	VAc	5	2.26	1.47	45.0
	1.23	44.4	″	5	2.18	1.05	56.0
	1.41	34.0	″	5	2.06	1.40	50.0
5 min 90°C	1.31	35.8	″	5	1.66	1.28	43.5
	1.41	35.2	″	5	2.24	1.44	40.0
	2.11	28.1	″	5	1.13	2.19	45.4
	2.05	38.5	″	5	1.58	2.40	52.5
	2.49	31.8	″	10	2.60	2.57	44.8
	2.80	30.6	″	10	2.84	2.22	50.7
	3.56	19.1	″	10	2.46	2.34	51.9
	3.27	24.9	″	10	2.60	3.25	28.9
5 min 80°C	1.91	17.1	Sty	10	4.97	0.752	47.0
	2.01	16.2	″	10	5.40	0.871	45.0
	1.74	40.7	Sty/EtOH	10	36.3	0.724	84.3
20 min 80°C	1.85	33.9	Sty	10	1.09	1.21	44.5
	1.46	42.1	Sty/EtOH	10	36.0	0.724	85.6
	2.61	28.0	″	10	30.6	0.985	61.2
5 min 90°C	2.54	26.7	Sty	10	5.01	2.01	41.8
	3.42	11.8	Sty/EtOH	10	39.5	3.25	16.1

and the elongation at break is about 100%. When the γ-ray irradiation time is increased, the absorption of radiation dose for the membrane increased, and the degree of grafting increased gradually, the tensile strength and elongation all decreased. From Figures 2 and 3 we can clearly see the relationship of the degree of grafting and the tensile strength decay between γ-ray irradiation time for grafted Nylon 4 membranes. The decrease of tensile strength for the grafted membrane could be attributed to the decrease of crystallinity of grafted membrane. The effect of γ-ray irradiation on the mechanical strength of nongrafted Nylon 4 membrane has been studied. The tensile strength of

TABLE VI
Tensile Properties[a] of Nylon 4 Membranes

Nongrafted Membranes				Grafted membranes			
Tensile Strength $(TS)_0$ (kg/cm^2)	Elongation (%)	Rad[b] time (hr)	Grafting monomer	Degree of grafting (%)	Tensile strength $(TS)_g$ (kg/cm^2)	Elongation (%)	$(TS)_g/(TS)_0$
415	109.2	5	SSS	18.9	362	108.5	0.873
399	104.8	10	"	21.8	327	94.2	0.819
449	109.0	15	"	24.0	356	93.3	0.794
382	110.2	20	"	25.7	294	97.2	0.768
395	79.3	30	"	26.7	288	61.1	0.724
408	111.6	5	Aam	9.56	367	101.4	0.900
433	105.4	10	"	17.9	368	97.5	0.849
391	104.1	20	"	22.7	314	97.6	0.802
424	112.4	5	VAc	2.17	395	108.4	0.930
401	104.3	10	"	2.63	370	99.1	0.922
435	113.3	10	Sty	2.99	370	93.0	0.850
464	115.5	15	"	1.52	372	85.7	0.803
386	102.2	10	Sty/EtOH	34.9	326	18.1	0.844

[a] Drawing rate: 50 mm/min; Drawing temperature: room temperature; load cell: 5 kg.
[b] Dose rate: 1.2×10^4 rad/hr, at room temperature.

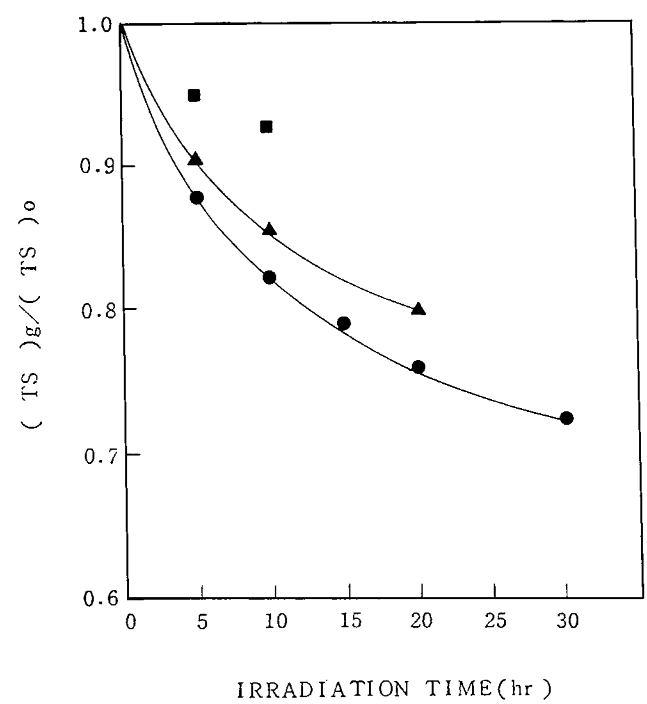

Fig. 3. Plot of tensile strength decay vs. irradiation time. ●: Nylon 4-g-PSSS; ▲: Nylon 4-g-PAAm; ■: Nylon 4-g-PVAc.

Nylon 4 membrane has no appreciable change up to a total irradiation dose of 6.0×10^5 rad. The elongation is also observed to have no change up to a total dose of 3.6×10^5 rad, but it then slightly decreased at higher doses. The decrease of elongation for all nongrafted membranes with 6.0×10^5 rad total dose are in the range of 10 to 15%.

CONCLUSION

Grafted membranes prepared by utilizing ^{60}Co γ-ray irradiation which induces vinyl monomers to be grafted onto Nylon 4 membranes for reverse osmosis have been studied. Both water flux and salt rejection are significantly improved compared to nongrafted Nylon 4 membrane. The mechanical strength of grafted membrane is not seriously decreased in the dose range used in this study. This shows that it is feasible to apply a vinyl monomer irradiation-grafting method to improve the reverse osmosis properties of Nylon 4 membrane.

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