

Properties of Modified Poly(vinyl alcohol) Membranes Prepared by the Grafting of New Polyelectrolyte Copolymers for Water–Ethanol Mixture Separation

Wen-Yen Chiang, Yi-Haw Lin

Department of Chemical Engineering, Tatung University, 40 Chungshan N. Road, 3rd Section, Taipei 10451, Taiwan

Received 12 October 2001; accepted 2 April 2002

ABSTRACT: For the preparation of a water-selective membrane for the pervaporation separation of an azeotropic solution, a series of grafted copolymers were synthesized by the reaction of poly(vinyl alcohol) (PVA) with poly(sodium salt styrene sulfonic acid-co-maleic acid) (PSStSA-co-MA). The esterification was performed between the hydroxyl groups of PVA and the carboxylic groups of the copolymer with a heat treatment. PSStSA-co-MA was prepared with sodium salt styrene sulfonic acid and maleic anhydride copolymerization in dimethyl sulfoxide with azobisisobuty-

ronitrile as an initiator. The reaction mechanism and resultant structure were confirmed with IR spectra. The effect of the heat-treatment time on the gel content was investigated. The permeation flux decreased and the separation factor increased as the crosslinking agent content rose. A membrane containing 15 wt % PSStSA-co-MA was used for water–ethanol azeotropic solution pervaporation at 30°C, and a flux of 0.43 kg/m² h and a separation factor of 190 were obtained. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2854–2859, 2002

INTRODUCTION

Azeotropic solutions have recently been separated with distillation techniques in industry. To avoid the high energy and distillation costs, the pervaporation of azeotropic solutions with membrane techniques has been widely investigated.^{1–5} However, these distillation techniques have not been replaced by pervaporation because of the failure to develop adequate membrane materials. A membrane with high selectivity and ample flux is the goal of current research efforts. Grafting a hydrophilic monomer onto a hydrophobic polymer,⁶ blending a hydrophilic polymer into a hydrophobic polymer,^{7,8} and the copolymerization of a hydrophobic or hydrophilic monomer^{9,10} are widely used techniques for the modification of separating membranes.

Poly(vinyl alcohol) (PVA) is a useful membrane material because of its excellent film-forming ability, its resistance to chemicals, and its good transparency. However, its application in pervaporation is restricted because of its water solubility and high crystallinity. Recently, many researchers^{11–14} have attempted to use hydrophobic monomers or polymers as crosslinking agents to crosslink PVA, thereby improving water insolubility. Modified PVA membranes reveal useful properties for the separation of alcohol–water solutions.

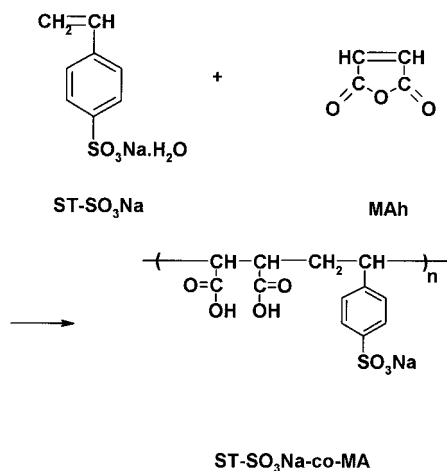
From this perspective, a series of copolymers with hydrophilic and hydrophobic groups were synthesized as PVA crosslinking agents in our laboratory.^{11,12,15} Earlier studies used maleic anhydride (MAh) as the crosslinking agent. Later, to obtain a hydrophilic–hydrophobic balance, MAh was replaced with ST-co-MAh¹¹ and ST-co-MAh-Hz.¹² The purpose of this study was to prepare more hydrophilic copolymers grafted onto PVA and treated for water insolubility and then use them for separating an alcohol–water azeotropic system. Modified membranes were expected to possess high water selectivity and high flux. Comparisons of the separation properties in our research series were also conducted.

EXPERIMENTAL

Materials

PVA BF-17, a product of Chang Chun Petrochemical Co. (Taiwan; degree of polymerization = 1700, degree of saponification of 98.5–99.2 mol %, and viscosity = 25–30 cp), was used. Reagent-grade MAh, methanol, toluene, and dimethyl sulfoxide (DMSO) were purchased from Acros Co. (New Jersey). DMSO was purged with CaH₂ and nitrogen for the removal of water before use. Maleic acid (MA) was purchased from Wako Pure Chemical Industries (Osaka, Japan). Sodium salt styrene sulfonic acid (SStSA) and azobisisobutyronitrile (AIBN) were purchased from Aldrich Co. (Milwaukee, WI). AIBN was recrystallized from methanol and dried in vacuo.

Correspondence to: W.-Y. Chiang (chiang@ttu.edu.tw).



Scheme 1 Reaction mechanism of ST-SO₃Na and MAh.

Synthesis of poly(sodium salt styrene sulfonic acid-co-maleic acid) (PSSStSA-co-MA)

The copolymerization reaction was carried out in a four-necked flask equipped with a stirrer, a thermometer, a condenser, and a nitrogen inlet. After SStSA (10.3 g, 0.05 mol) was dissolved in 35 mL of DMSO, MAh (4.9 g, 0.05 mol) was added. After a homogeneous solution formed, AIBN (0.15 g) was added as an initiator. The reaction was allowed to proceed for 24 h at 65°C. The product was precipitated into a large amount of toluene and stirred for 12 h. Unreacted MAh was dissolved in toluene. The undissolved part was added into a large amount of methanol and stirred for 12 h. Unreacted SStSA was dissolved in methanol. The undissolved part was dried in a vacuum oven at 30°C, and PSSStSA-co-MA was obtained.

Viscosity measurements

An Ubbelohde viscometer was used for measuring the intrinsic viscosity of the prepared PSSStSA-co-MA. The

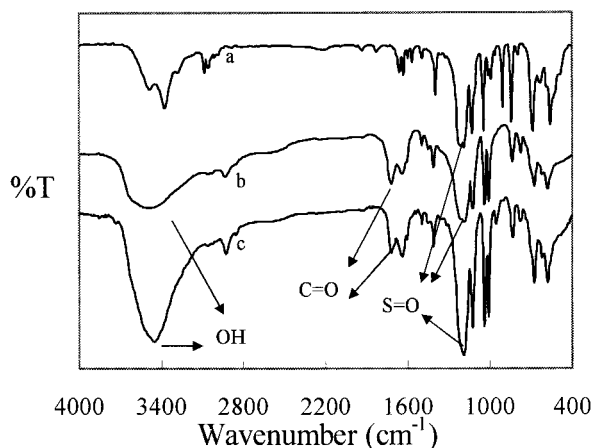


Figure 1 IR spectra of (a) ST-SO₃Na, (b) ST-SO₃Na-co-MAh, and (c) ST-SO₃Na-co-MA.

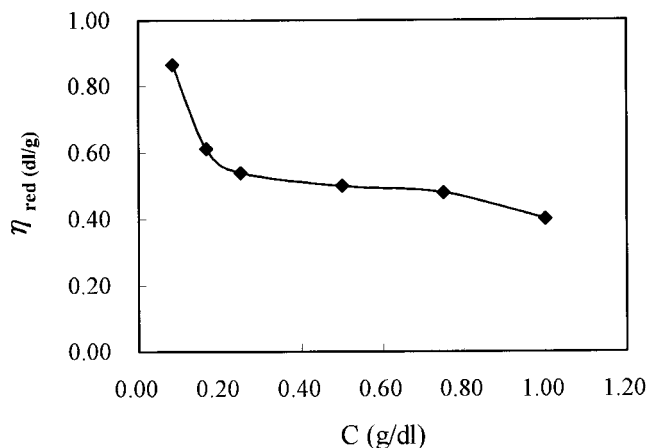


Figure 2 Effect of the concentration on the viscosity of ST-SO₃Na-co-MA.

copolymer solutions were prepared by the dissolution of the polymers in DMSO, and the measurement temperature was adjusted at 30°C. Because the viscosity of the copolymer showed polyelectrolyte characteristics, the intrinsic viscosity was calculated with the following Fuoss equation:¹⁵

$$\eta_{sp}/C = A/(1 + B \times C^{1/2})$$

where η_{sp} is the specific viscosity, A is the intrinsic viscosity, B is a constant related to an interaction of counterions with polyions, and C is the polymeric concentration in the lower polymeric concentration region.

Membrane preparation

After PVA (0.95, 0.90, or 0.85 g) was dissolved in a given quantity of DMSO, PSSStSA-co-MA (0.05, 0.10, or 0.15 g) was added. The homogeneous solution was cast over a clean glass plate and was allowed to dry at 60°C in vacuo to a constant weight to form the membrane.

Membrane heat treatment

All of the prepared membranes were treated in an oven at 170°C for 2 h to obtain a crosslinking structure before the pervaporation test. The membrane thickness was about 105–110 μm .

Swelling measurements

The preweighed membrane was immersed in deionized water, methanol, ethanol, or isopropanol at 30°C for 24 h. After equilibrium was achieved, the surface of the wet membrane was wiped. The swollen membrane was weighed as quickly as possible. The degree of swelling (S) could be calculated with the following equation:

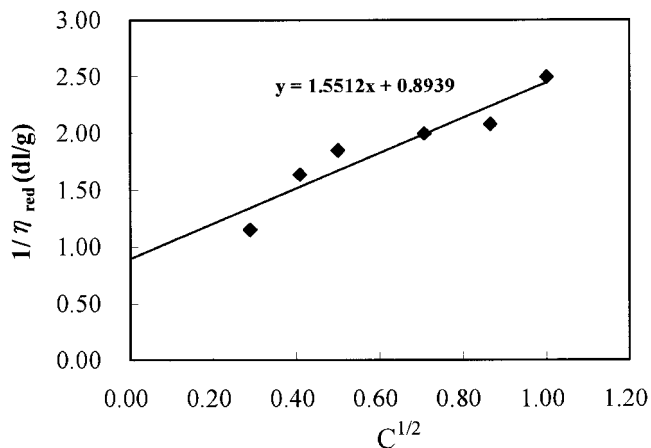


Figure 3 Intrinsic viscosity of ST-SO₃Na-co-MA drawn with the Fuoss equation.

$$S = (M - M_0/M_0) \times 100$$

where M is the weight of the swollen membrane and M_0 is the weight of the dry membrane.

Mechanical property measurements

The tensile strength and elongation at membrane breaking was measured according to ASTM Standard D 638 with an Instron 1130 instrument.

Gel content measurements

The preweighed membranes were immersed in deionized water at 90°C for 24 h. The residual membranes were then dried and weighed. The gel content could be calculated with the following equation:

$$\text{Gel content (\%)} = M/M_0 \times 100\%$$

where M_0 is the weight of the original membrane and M is the weight of the residual membrane.

Pervaporation experiments

The apparatus and procedure for the pervaporation process were essentially the same as those described in a previous report.¹⁵

RESULTS AND DISCUSSION

Synthesis of PSStSA-co-MA

The copolymerization reaction mechanism between SStSA and MAh is shown in Scheme 1. The IR spectrum of the obtained copolymer PSStSA-co-MA is shown in Figure 1(b). The characteristic bands of MAh usually appeared at 1700 and 1800 cm⁻¹. However, the prepared copolymer displayed the characteristic bands at 1738 and 3500 cm⁻¹. These bands were characteristic of the absorption peak for the acid carbonyl (C=O) group and OH group of the MA group (—COOH). These bands formed because of the ring opening of MAh to MA by a small amount of water that absorbed in SStSA to form solvate water as SStSA · H₂O. To prove this result, we prepared SStSA and MA copolymers and confirmed the same IR characteristic absorption bands [Fig. 1(c)].

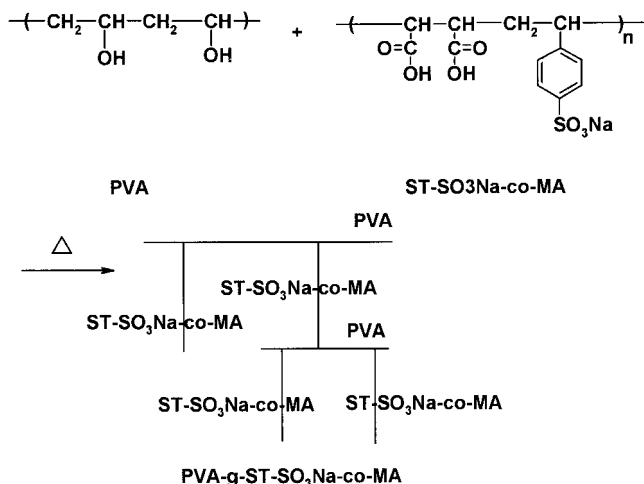
The copolymer showed its polyelectrolyte properties through the viscosity measurements. The reduced viscosity of the copolymer increased with the decrease in concentration, as shown in Figure 2. The intrinsic viscosity of the copolymer was obtained in Figure 3 with the Fuoss equation. The effect of the amount of the initiator on the prepared copolymer properties is shown in Table I. The intrinsic viscosity of the copolymer decreased with the increase in the amount of the initiator. The intrinsic viscosity of the copolymer reached 1.12 when 1 wt % initiator was added. The low yields (ca. 52%) were due to the steric hindrance of the two monomers.

Membrane heat treatment

The PVA-g-PSStSA-co-MA reaction mechanism of the heat treatment for the crosslinking of PVA and PSStSA-co-MA is shown in Scheme 2. The dehydrated reaction between the hydroxyl groups in PVA and the carboxylic groups in the copolymer proceeded. After the heat treatment, all of the membranes formed a crosslinking network structure, which was a result of the interchain ester linkages. Similar ester linkages involving polyacid and PVA have been reported in the literature.^{11,12,16,17} This could enhance the hydrophobic property and increase the mechanical strength. The effect of the time in the heat treatment on the gel

TABLE I
Synthesis of ST-SO₃Na-co-MA copolymer

ST-SO ₃ Na (mol)	MA (mol)	DMSO (mL)	AIBN (wt %)	Temperature (°C)	Time (h)	Yield (%)	[η] (dL g)
0.05	0.05	35	0.5	65	24	10.2	X
0.05	0.05	35	1	65	24	53.7	1.12
0.05	0.05	35	1.5	65	24	51.5	0.93
0.05	0.05	35	2	65	24	53.3	0.71
0.05	0.05	35	2.5	65	24	51.1	0.50



Scheme 2 Reaction mechanism of PVA and ST-SO₃Na-co-MA.

content is shown in Figure 4. Membranes treated at 170°C for 1 h produced a gel content of 90%. The gel content reached 99% as membranes were treated at 170°C for at least 2 h. The effects of PVA on the mechanical strength are shown in Figure 5. The tensile strength and elongation at membrane break increased with the increase in PVA in the feed. The mechanical strength of the graft-modified PVA was greater than that of the original PVA because of the crosslinking structure formed after the heat treatment.

Degree of membrane swelling

Table II shows the results of the swelling measurements for each pure solvent component at 30°C. As the PSStSA-co-MA contents in the membrane increased, the degree of swelling in the membranes from alcohol decreased. This phenomenon was due to the increase in the crosslinking density from the carboxylic acid reaction with poly(vinyl alcohol) (PVA), which caused

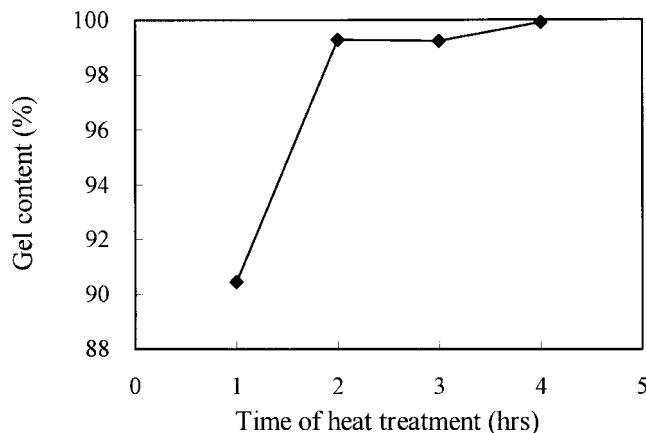


Figure 4 Effect of the heat-treatment time on the gel content of the membranes.

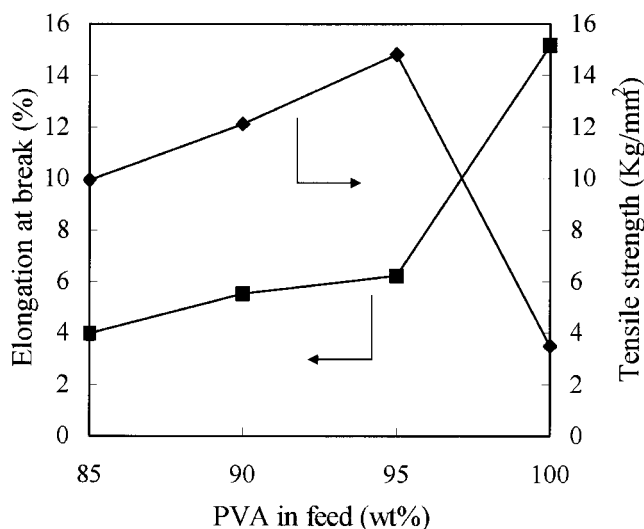


Figure 5 Effect of the content of PVA in the feed on the tensile strength and elongation at break of the membranes.

a decrease in the free volume of the membrane. The same results were also observed in the decrease in the degree of swelling with the increase in the carbon number of the alcohols. The effect of the PSStSA-co-MA content on the degree of swelling in the membranes due to water was greater than the free volume effect, which was due to the hydrophilic PSStSA-co-MA. The degree of swelling in the membranes due to water increased with the increase in the PSStSA-co-MA content. Water causes membrane swelling to a far greater degree than alcohol because of the strength of the hydrogen-bonding interaction. The difference in the strengths of the hydrogen-bonding interactions between the membrane and water and the membrane and alcohol may lead to selective separation by the membrane.

Water-alcohol pervaporation

Figures 6–8 show the separation factor and permeation flux for each alcohol-water solution. All of the results are related to the PSStSA-co-MA feed weight percentage at 30°C. The permeability or flux decreased and the separation factor increased as the PSStSA-co-MA content increased in the membranes. These results reflect the fact that the membrane network had a more compact form because of the crosslinking ef-

TABLE II Swelling Degree Measurement for Each Pure Component at 30°C (wt %)

PVA/copolymer	Water	Methanol	Ethanol	IPA
(8.5/1.5)	155.4	12.3	8.2	6.1
(9.0/1.0)	140.9	13.7	11.9	7.5
(9.5/0.5)	114.7	14.3	13.4	8

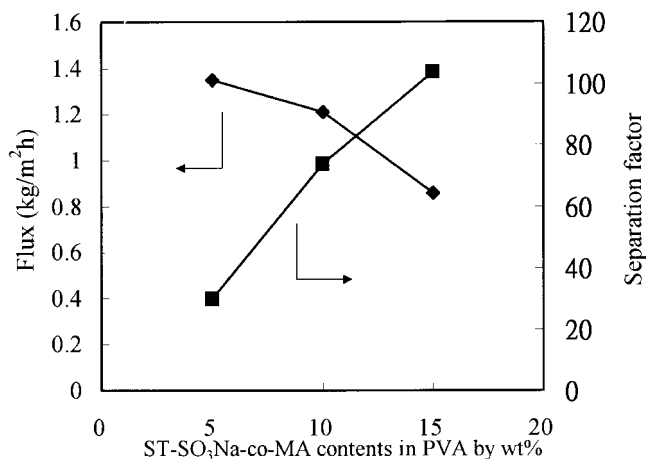


Figure 6 Permeability and separation factors for 1:1 w/w water-methanol mixtures.

fect. The side-chain $-\text{SO}_3\text{Na}$ group showed strong hydrophilic characteristic, and so water selectivity appeared and resulted in an increase in the separation factor. However, because the interaction between water and the polar group of the modified polymer membrane was too strong, water clusters formed to suppress permeation. This phenomenon caused a decrease in the flux with the increased PSSStSA-co-MA content in the membranes. The relationships between the permselectivity and the size of the alcohol molecules with one to three carbon atoms were investigated with 50 wt % alcohol feed mixtures, as shown in Figure 9. The results showed that as the molecular weight of the compounds in a given homologous series increased, the permeation flux decreased and the separation factor increased. In isopropanol-water systems, the separation factor was greater than that in other systems because of the larger cross section. The flux of the isopropanol-water system showed the lowest value.

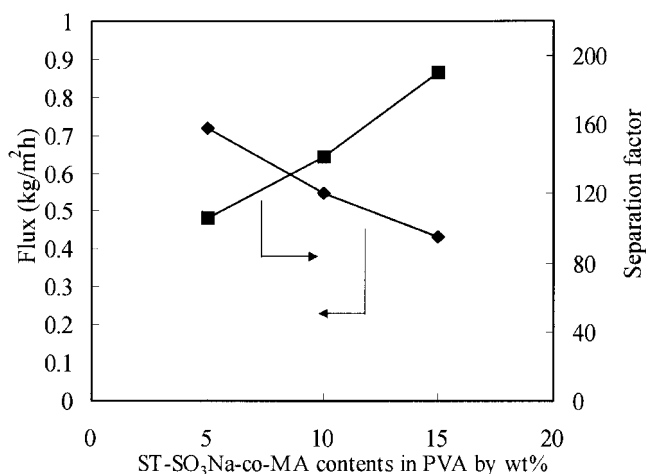


Figure 7 Permeability and separation factors for 1:1 w/w water-ethanol mixtures.

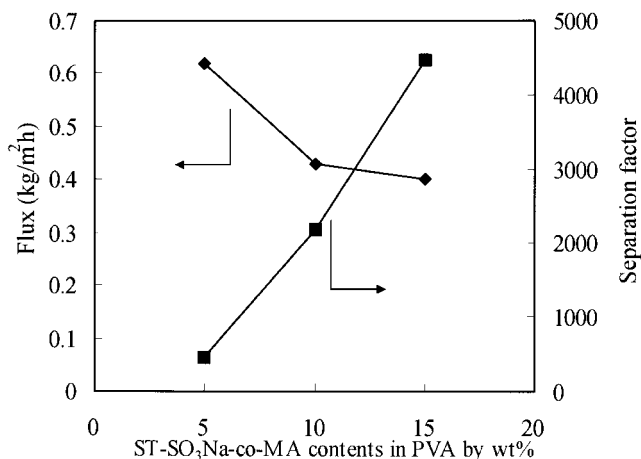


Figure 8 Permeability and separation factors for 1:1 w/w water-isopropanol mixtures.

CONCLUSIONS

After a crosslinking PVA membrane heat treatment, PSSStSA-co-MA was used for the separation of water-alcohol mixed solutions with the pervaporation technique. PVA-g-PSSStSA-co-MA formed a crosslinking network and enhanced the water insolubility and mechanical strength while retaining a high affinity toward water. Because the strong $-\text{SO}_3\text{Na}$ hydrophilic group was introduced, the degree of swelling in the membrane due to water was greater than that due to alcohol. The difference in the hydrogen-bonding interactions between the membrane and water and the membrane and alcohol showed that the modified copolymer was a water-permeable membrane with selective permeability toward water in a water-alcohol solution. Moreover, for a water-ethanol solution, a flux of $0.55 \text{ kg/m}^2 \text{ h}$ and a separation factor of 141 were obtained at 30°C when a PVA membrane crosslinked with 10% PSSStSA-co-MA was used. As shown in Table III,¹² the PVA-g-PSSStSA-

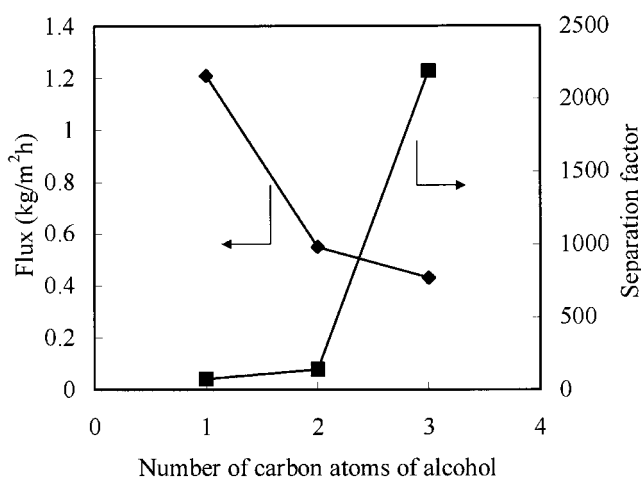


Figure 9 Effect of the size of the permeation species on the flux and separation factor through membrane 2 at 30°C .

TABLE III
Pervaporation Separation with Different Membranes in a 50 wt % Ethanol–Water System^o

Membrane	Separation factor (α)	Flux ($\text{kg m}^{-2} \text{ h}^{-1}$)	$\alpha \times \text{Flux}$
PVA-g-ST-SO ₃ Na-co-MA (95% PVA)	106	0.72	76.3
PVA-g-ST-SO ₃ Na-co-MA (90% PVA)	141	0.55	77.6
PVA-g-ST-SO ₃ Na-co-MA (85% PVA)	190	0.43	81.7
PVA-g-ST/MA-HZ	21	1.19	25.0
Chitosan	13.5	2.92	39.4
Cellulose	4.33	9.02	39.1
PVA/Nafion blend	40	0.8	32.0
PVA-g-AA	80	0.4	32.0
PVA-g-MMA/MA	38	0.8	30.4
PVA-g-ST/MA	24	0.95	22.8
PVA-g-NSMAc/MMA	27	0.65	17.6
Neutralized chitosan	450	0.0039	1.8
PVA-g-NSMI/MMA	20	0.32	6.4
3-(<i>N,N</i> -dimethyl)amino-propylacrylamide-co-AN	528	0.01	5.3
Porous PVA	4.5	1.1	5.0
PAA/nylon 6	30	0.12	3.6
PVA-g-AN	4	0.7	2.8
PAN-EA	75	0.03	2.3
Poly(AA-co-maleimide)	50	0.04	2.0
1-Bu-4-VPiodide-co-AN	50	0.04	2.0
Poly(AA-co-AN)	50	0.03	1.5
ST-co-divinyl benzene	9	0.16	1.4
Nylon-g-AA	30	0.04	1.2
Poly(4-vinyl pyridine-co-AN)	10	0.02	0.2
Poly(AA-co-ST)	15	0.002	0.03

co-MA membranes had a higher separation factor than most membranes. We succeeded in improving the membrane selectivity toward water while maintaining an acceptable flux.

References

- Kusumocahyo, S. P.; Sano, K.; Sudoh, M.; Kensaka, M. *Sep Purif Technol* 2000, 18, 141.
- Chan, W. H.; Ng, C. F.; Lam-Leung, S. Y.; Xumin, H.; Cheung, O. C. *J Appl Polym Sci* 1997, 65, 1113.
- Yeom, C. K.; Lee, K. H. *J Appl Polym Sci* 1998, 67, 949.
- Eli, R.; Fuming, S. *J Membr Sci* 1995, 103, 271.
- Byun, I. S.; Kim, I. C.; Seo, J. W. *J Appl Polym Sci* 2000, 76, 787.
- Ray, S. K.; Sawant, S. B.; Joshi, J. B.; Pangarkar, V. G. *J Membr Sci* 1999, 74, 2645.
- Huang, Y. M.; Shieh, J. J. *J Appl Polym Sci* 1998, 70, 317.
- Jonggeon, J.; Lee, K. H. *J Appl Polym Sci* 1999, 72, 1755.
- Camilla, W.; Maurer, H. J. *Polymer* 1998, 39, 2897.
- Godjevargova, T.; Konsulov, V.; Dimov, A. *J Membr Sci* 1999, 152, 235.
- Chiang, W. Y.; Hsiao, C. Y. *Angew Makromol Chem* 1994, 219, 169.
- Chiang, W. Y.; Chen, C. L. *Polymer* 1998, 39, 2227.
- Katya, C.; Maurizio, C.; Maurizio, V. *J Appl Polym Sci* 1999, 74, 1881.
- Li, X.; Goh, S. H.; Lai, Y. H.; Deng, S. M. *J Appl Polym Sci* 1999, 73, 2771.
- Chiang, W. Y.; Hu, C. M. *J Appl Polym Sci* 1985, 30, 3895.
- Chiang, W. Y.; Hu, C. M. *J Appl Polym Sci* 1988, 36, 1479.
- Gryte, C. C.; Chen, J.; Kevorkian, V.; Gregor, H. P. *J Appl Polym Sci* 1979, 23, 2611.