Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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**To cite this Article** Martin, E. C. , Dietert, R. D. and Hamil, H. F.(1971) 'Irradiation-Grafted Polymeric Films. III. Development of Improved Anion-Selective Membranes for Desalting Water', Separation Science and Technology, 6: 5, 637 — 644

**To link to this Article: DOI:** 10.1080/00372367108057959

**URL:** http://dx.doi.org/10.1080/00372367108057959

SEPARATION SCIENCE, 6(5), pp. 637–644, October, 1971

# Irradiation-Grafted Polymeric Films. III. Development of Improved Anion-Selective Membranes for Desalting Water

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## Summary

Experimental anion-selective membranes have been prepared and evaluated as electrodialysis membranes. The membranes were prepared by grafting tertiary amines onto polyethylene films. After grafting, the membranes were made ionic in character by conversion to the corresponding hydrochloride or by quaternizing with 1-bromobutane.

Evaluation demonstrated the feasibility of preparing membranes having acceptable transport numbers, dialysis coefficients, and electrical resistances for use in electrodialysis processes.

## INTRODUCTION

Advances made in the synthesis of polymeric films have led to the development of processes based on transport through ion selective membranes (*1*). Desalination processes based on electrodialysis (*2–4*) as well as methods for the removal or concentration of substances from liquid mixtures by electrodialysis (*5, 6*) across ion selective membranes are known examples.

The transport processes that occur across ion-exchange membranes separating different solutions are of continuing interest, and the transport phenomena (*7, 8*), properties (*9, 10*), and preparation (*7, 10, 11*) of a large variety of anion-exchange and cation-exchange membranes have been investigated.

In recent years, graft polymerization has been a useful technique for preparing ion-exchange membranes (*12*). Thin films having good mechanical and electrochemical properties are prepared by this technique. Cellophane and polyethylene have been the base polymers selected by many investigators for modification by irradiation graft polymerization (*2*, *13*). The procedure usually consists of impregnating the base polymer with a monomer such as styrene or vinyl pyridine prior to $\gamma$-irradiation using a $^{60}$Co source. Cross-linking is performed either concurrently or sequentially with grafting by reaction with a difunctional monomer such as divinylbenzene. To prepare anion exchange membranes, the resulting styrene-grafted membrane can be chloromethylated and quaternized. The vinyl pyridine-grafted membrane can be used as is, or it can be quaternized to form a strong anion exchange membrane.

In this study, the electrodialysis characteristics were determined for several anion-exchange membranes prepared by grafting tertiary amine monomers onto polyethylene films using $\gamma$-irradiation from a $^{60}$Co source. The transport properties used to describe these anion-exchange membranes were the transport number, electrical resistance, and dialysis coefficient.

The transport number of a membrane, $t^+$ or $t^-$, designates the fraction of the ionic current through a membrane that is carried by cations ($t^+$) or by anions ($t^-$). Thus, if the value of $t^+$ is near unity, the membrane is highly selective toward cations. Conversely, if $t^+$ is near zero (or $t^-$ is near unity, since $t^+ + t^- = 1$), the membrane is highly selective toward anions.

The electrical resistance of an ion-selective membrane is a measure of the ease of ion movement through the membrane. A low electrical resistance increases the electrical efficiency in demineralizing water by electrodialysis.

The dialysis coefficient of a membrane is a measure of the rate of transfer of salt through the membrane due to a concentration difference across the membrane. Since the electrodialysis process moves ions from a dilute stream to a concentrated stream, dialysis tends to reverse this process and reduce the separation efficiency. Therefore, a good membrane must have a low dialysis coefficient.

## EXPERIMENTAL PROCEDURE

In this study, 1-mil Dow 560 polyethylene film was used as the base material. The grafting monomers were 2-vinylpyridine, 4-vinylpyridine,

TABLE 1

Monomer Solutions Used for Grafting Polyethylene

| Membrane prepared[a] | Composition of grafting solution | |
|---|---|---|
| | Material | Wt% |
| 2-VP | 2-Vinylpyridine | 25 |
| | Methanol | 75 |
| 4-VP | 4-Vinylpyridine | 25 |
| | Methanol | 75 |
| DMAM | Dimethylaminoethyl methacrylate | 25 |
| | Benzene | 70 |
| | Carbon tetrachloride | 5 |
| TBAM | *t*-Butylaminoethyl methacrylate | 25 |
| | Benzene | 70 |
| | Carbon tetrachloride | 5 |

[a] 2-VP = 2-Vinylpyridine-grafted polyethylene film. 4-VP = 4-Vinylpyridine-grafted polyethylene film. DMAM = Dimethylaminoethyl methacrylate-grafted polyethylene film. TBAM = *t*-Butylaminoethyl methacrylate-grafted polyethylene film.

dimethylaminoethyl methacrylate, or *t*-butylaminoethyl methacrylate. The vinylpyridine grafted polyethylene films were prepared by irradiation in a methanol solution of the monomer, and the substituted aminoethylmethacrylate grafts were prepared in a benzene solution containing carbon tetrachloride as the terminator. Table 1 lists the composition of the grafting solutions used in this study.

The procedure used to prepare the grafted films was to roll the polyethylene film on a $\frac{1}{4}$-in. aluminum pipe (capped on one end) using a filter paper backing between the layers of polyethylene. The rolls of polyethylene film were placed in glass cylinders, and the cylinders were sealed with rubber stoppers having inlet and outlet valves. Oxygen was excluded by repeatedly evacuating and refilling the cylinders with nitrogen. The monomer solutions were introduced into the cylinders while maintaining a blanket of nitrogen above the liquid. The containers were then subjected to $\gamma$-irradiation at an intensity of 0.012 Mrad/hr until a total dosage of 0.815 Mrad was obtained. The samples were then removed from the cylinders and washed with solvent to remove the homopolymer. A detailed description of the irradiation procedure will appear in another publication (*14*).

The quaternized membranes were prepared by placing approximately 5 g of the grafted membrane, 15 g of 1-bromobutane, and 500 ml of isopropyl alcohol in a 1-liter resin flask equipped with a condenser. The mixture was heated at reflux for 16 to 20 hr. During the reflux period, the film was weighted with a glass rod to assure complete immersion. The quaternized film was washed several times in acetone and then water.

A portion of the 4-vinylpyridine-grafted polyethylene film was crosslinked by placing it in a benzene solution containing 5 wt% divinylbenzene. The dose rate was 0.025 megarads per hour applied for 22 hours. The total dose was 0.55 megarads. The irradiation procedure was similar to that described above.

Another portion of the 4-vinylpyridine-grafted polyethylene film was converted to the corresponding hydrochloride by placing the membrane in 10% hydrochloric acid at approximately 95°C for 1 to 2 hr. The film was then washed with deionized water until neutral.

The transport numbers for the membranes were initially determined by the concentration potential method as outlined in the "Test Manual for Permselective Membranes" (*15*). This method has the advantage of being rapid and functions over a wide range of salt concentrations. The cell used in this study was similar to that described in the test manual; however, a simpler design was employed. Instead of a flow system to sweep fresh salt solution across the membrane surface, the cell was designed so that the membrane would divide the chamber into two compartments. A 250-ml solution was placed in each compartment, and the solutions were rapidly stirred by means of Teflon-coated magnetic stirring bars. The calomel electrodes were inserted directly into the solutions through a hole in the top of each compartment. Measurements were made using three concentration pairs of potassium chloride solution: 0.100–0.050 molal concentration for dilute solutions; 0.200–0.100 molal concentration for intermediate solutions; and 1.00–0.500 molal concentration for concentrated solutions.

A single membrane electrolysis cell was used to measure the transport numbers under conditions of actual ion flux (*16*). The Plexiglas cell consisted of two half-cells. Each half-cell had a recess 1-in. wide, 8-in. long, and $\frac{1}{8}$-in. deep for circulation of the potassium chloride solution and was equipped with an independent circulation loop. These recesses contained a strip of silver gauze which had been plated with silver chloride in order to have an electrochemically reversible electrode.

The transport number was obtained by making a material balance on each side of the membrane before and after the experiment. The cation transport number is the ratio of the moles of $K^+$ ion transferred through the membrane to the number of farads of electricity transferred.

The same cell was used to obtain the dialysis coefficient. The cell was used without current flowing, with the membrane in place, and with a 0.30-*N* potassium chloride solution circulating through one compartment and distilled water through the other. After 3 hr of circulation, the amount of salt that had dialyzed into the distilled water compartment was determined.

The electrical resistance of the membranes was obtained with a cell identical to that described in Section 601.1 of the "Test Manual for Permselective Membranes" (*15*). All of the resistance measurements were made in a 0.1-*N* potassium chloride solution. It is important to note that the recorded electrical resistances are the resistances of the membranes in excess of the resistance of an equivalent thickness of the test solution. To obtain these data, a blank was run with a piece of the same membrane as that being tested; however, a hole was cut in the membrane to match the film surface area exposed by the test cell. Thus, the electrodes were separated by the same distance as when the film measurements were made. Using this technique, it is possible to have a negative resistance value for the membrane if the membrane resistance is less than the resistance of an equivalent thickness of the test solution.

## RESULTS AND DISCUSSION

The transport numbers of the membranes as determined by the concentration potential method and their electrical resistances are given in Table 2. This method was used as a screening technique to justify further evaluation in the single membrane electrodialysis cell. For comparative purposes, a commercial membrane Ionac MA 3475 Q was evaluated by the same method. The transport numbers for all of the membranes evaluated by the concentration potential method were about the same as that obtained for the commercial membrane. However, the electrical resistances of the 4-VP-Q, 4-VP-H, and 4-VP-X-Q membranes were much lower than that of the commercial membrane.

Table 3 lists the cation transport numbers and dialysis coefficients at different current densities and solution concentrations using the single membrane electrodialysis cell. A transport number of 0.0 was obtained with the 2-VP-H, 4-VP-H, and 4-VP-Q membranes when the potassium chloride solution concentration was 0.03 *N*. At a solution concentration of 0.3 *N*, the 2-VP-H and 4-VP-H membranes had much higher transport numbers, and the transport numbers had a tendency to increase with increasing current density. The 4-VP-Q membrane had a much lower transport number than the 4-VP-H membrane in the 0.3 *N* potassium chloride solution.

The dialysis coefficient is an important factor for a good electrodialysis membrane. This coefficient should be at least as low as $1.0 \times 10^{-5}$ cm/sec for an electrodialysis plant demineralizing brackish water. This coefficient is most important in the last stages of demineralization where the current density is the lowest and the effect of dialysis becomes more serious. With the quaternized 4-VP membranes, it was found that cross-linking the grafted membrane significantly reduced the dialysis coefficient. The coefficients for 4-VP-Q and 4-VP-X-Q were $1.71 \times 10^{-5}$ and $4.5 \times 10^{-6}$ cm/sec, respectively. Furthermore, cross-linking did not have a detrimental effect on the electrical resistance or transport number of the membrane.

TABLE 2

Cation Transport Numbers for Membranes for 3 Molal Concentration Pairs of KCl Solution

| Membrane[a] | Cation transport numbers (molal) | | | Electrical resistance[b] (ohm-cm$^2$) |
|---|---|---|---|---|
| | 0.10–0.05 | 0.20–0.10 | 1.00–0.50 | |
| 2-VP-H | 0.007 | 0.06 | 0.09 | 15.5 |
| 4-VP-Q | 0.030 | 0.04 | 0.10 | 0.48 |
| 4-VP-H | — | — | — | −0.1 |
| 4-VP-X-Q | — | — | — | 0.95 |
| DMAM-H | 0.003 | 0.05 | 0.08 | 730 |
| DMAM-Q | — | — | — | 525 |
| TBAM-H | 0.020 | 0.07 | 0.11 | >750 |
| TBAM-Q | — | — | — | 126 |
| Ionac MA 3475 Q | 0.006 | 0.05 | 0.16 | 18.0 |

[a] Q: Membrane was quaternized with 1-bromobutane after grafting. X: Membrane was crosslinked with divinylbenzene after grafting. H: Membrane was converted to the hydrochloride after grafting.

[b] Measured in 0.1 *N* KCl solution. Expressed as resistance in excess of the resistance of an equivalent thickness of KCl solution.

TABLE 3

Cation Transport Numbers, Current Densities, and Dialysis Coefficients for Membranes in the Single Membrane Cell

| Membrane | Current density (ma/cm) | Transport number (moles/farad) | Dialysis coefficient (cm/sec) | Solution concentration (*N*) |
|---|---|---|---|---|
| 2-VP-H | 6 | 0.00 | $7.22 \times 10^{-6}$ | 0.03 |
| | 3 | 0.03 | | 0.30 |
| | 6 | 0.11 | | 0.30 |
| | 16 | 0.13 | | 0.30 |
| | 30 | 0.25 | | 0.30 |
| 4-VP-H | 6 | 0.00 | $2.4 \times 10^{-5}$ | 0.03 |
| | 3 | 0.12 | | 0.30 |
| | 6 | 0.16 | | 0.30 |
| | 16 | 0.19 | | 0.30 |
| | 30 | 0.15 | | 0.30 |
| 4-VP-Q | 3 | 0.00 | $1.71 \times 10^{-5}$ | 0.03 |
| | 3 | 0.05 | | 0.30 |
| | 6 | 0.03 | | 0.30 |
| 4-VP-X-Q | 3 | 0.02 | $4.5 \times 10^{-6}$ | 0.30 |
| | 6 | 0.02 | | 0.30 |
| | 12 | 0.03 | | 0.30 |
| DMAM-Q | 3 | 0.00 | $4.5 \times 10^{-7}$ | 0.30 |
| | 6 | 0.00 | | 0.30 |
| | 12 | 0.00 | | 0.30 |
| TBAM-Q | 3 | 0.03 | $6.5 \times 10^{-7}$ | 0.30 |

The DMAM and TBAM membranes had very low transport numbers and dialysis coefficients; however, the electrical resistances were too high for electrodialysis membranes.

## CONCLUSIONS

The data obtained to date indicate that the graft polymerization of polyethylene films is a promising technique for the production of superior electrodialysis membranes. The best transport properties in this study were obtained when the grafted membranes were quaternized with 1-bromobutane. In the case of the 4-VP-X-Q membrane, the dialysis coefficient was significantly reduced by cross-linking the membrane after grafting. Factors such as degree of grafting and cross-linking are subjects of future study. It is realized that the transport properties of electrodialysis membranes containing aromatic rings usually deteriorate with time; however, long duration tests of these membranes are being considered.

## REFERENCES

*1.* S. D. Tuwiner, *Diffusion and Membrane Technology* (American Chemical Society Monograph Series, No. 156), Reinhold, New York, 1962.

*2.* J. M. Shackelford, K. A. Kase, F. C. DiLuzio, W. S. Gillam, and A. Kotch, "Bibliography of Membrane Technology Pertaining to Saline Water Desalination, Part II," Office of Saline Water Research and Development Progress Report No. 153, 1965.

*3.* J. R. Wilson (ed.), *Demineralization by Electrodialysis*, Butterworths, London, 1960.

*4.* H. J. Cohan, *Chem. Eng. Progr.*, *57*, 72 (1961).

*5.* S. Katz and F. Ellinger, *Biochemistry*, *2*, 406 (1963).

*6.* A. G. Van Studen and W. A. G. Hoeting, *T. N. O. Nieuws*, *23*(3), 165 (1968).

*7.* N. Lakshminarayanaiah, *Chem. Rev.*, *65*, 491 (1965).

*8.* P. Laüger, *Angew. Chem. Int. Ed.*, *8*, 42 (1969).

*9.* H. P. Gregor, *Pure Appl. Chem.*, *16*; 239 (1968).

*10.* F. G. Helfferich, *Ion Exchange*, McGraw-Hill, New York, 1962.

*11.* H. Niehuus, R. Stephan, F. Wolf, F. Tränkel, and M. Morgner, Ger. Patent 1,056,103 (1958); *Chem. Abstr.*, *54*, 21545 (1960).

*12.* W. K. Chen, R. B. Mesrobian, D. S. Ballantine, D. J. Metz, and A. Glines, *J. Polym. Sci.*, *23*, 903 (1957).

*13.* W. C. Sheehan, F. C. DiLuzio, J. A. Hunter, and M. E. Mattson, "Development of Improved Ion-Selective Membranes for Desalting Water, Part I," Office of Saline Water Research and Development Progress Report No. 202, 1965.

*14.* H. F. Hamil, L. M. Adams, W. W. Harlowe, Jr., and E. C. Martin, *J. Polym. Sci., Part A-1*, *9*, 363–376 (1971).

*15.* U. S. Bureau of Reclamation, "Test Manual (Tentative) for Permselective Membranes," Office of Saline Water Research and Development Progress Report No. 77, 1064.

*16.* M. S. Mintz, "Transport of Electrolytes Through Membrane Systems," Office of Saline Water Research and Development Progress Report No. 182, 1966.

*Received by editor December 22, 1970*