

Ionic Reverse Osmosis Membranes of Grafted Polyethylene

C. E. LAMAZE and H. YASUDA, *Camille Dreyfus Laboratory, Research Triangle Institute, Research Triangle Park, North Carolina 27709*

Synopsis

Membranes of graft copolymers of polyethylene with poly(sodium styrene sulfonate), poly(4-vinylpyridinium methyl bromide), and poly(sodium acrylate) were prepared by using the technique of peroxide grafting. The reverse osmosis characteristics of the membranes were examined as a function of grafting yield. In these membranes, the grafting can be considered as a process of introducing ionic sites, and it depends on the conditions of the grafting reaction, such as monomer concentration and temperature. However, the overall reverse osmosis characteristic is not only dependent on the number of ionic sites introduced but also on the swelling capability of the membrane. Consequently, the salt rejection of grafted membrane of a fixed graft yield depends on the conditions of the grafting reaction. All grafted membranes which have grafting yields above a certain value behave as normal ionic polymer membranes, and their interrelationship of salt rejection and water permeability follow the general dependence found for ionic polymer membranes.

INTRODUCTION

Graft copolymerization of hydrophilic polymers onto hydrophobic semi-crystalline polymer films provides an interesting means of preparing membranes which can be used in many important processes such as dialysis, reverse osmosis, and electro dialysis. The crystalline phase of the film provides the mechanical strength which otherwise is incorporated by crosslinking of hydrophilic polymers. Therefore, this graft copolymerization bypasses the major difficulties of forming crosslinked networks in thin film form from hydrophilic polymers (or from monomers). This aspect of graft copolymerization is particularly useful to prepare ionically charged polymer membranes in relatively thin form. In this respect, they are quite nice for reverse osmosis evaluation and were included as part of a study of salt rejection by ionic polymer membranes.¹

The relationship between the salt rejection (R_s) and water permeability (K_1) of ionic membranes was found to be an exponential one, of the form

$$K_1 = A_{\text{exp}} (-BR_s), \quad (1)$$

where A and B are constants. This unique relationship was explained as a transport depletion of salt flux relative to water flux due to different transport volumes available to the water and the mobile ions (which are re-

pulsed by the fixed ion charges). This relationship was found valid regardless of the chemical nature or charge of the membrane (various block and graft copolymers, both anionic and cationic, were investigated).

That is, unlike the relationship found between R_s and K_1 for nonionic membranes (where the size of the hydrated ions and their solubility in the membrane determine their transport depletion relative to water through the membrane), for ionic membranes the transport depletion of salt and the water permeability are both determined by the water sorbed by the fixed ionic sites and therefore are related as described in eq. (1).

The solution-diffusion mechanism used to explain the salt rejection of nonionic polymers can only play a role in ionic membranes when there is so little swelling due to ionic sites that the movement of water in the film is by diffusion, and hence this becomes the limiting factor for movement of salt.

Interpretation of these results obtained with various kinds of ionic membranes showed some fascinating aspects of the graft copolymer system that warranted further study and explanation.

Thus, the charged graft copolymer membranes not only provided an interesting form of membrane to examine the mechanism of salt rejection by ionic membrane in reverse osmosis, but it would seem possible to distinguish the sieve effect (if any) of crosslinking on the salt rejection, since the polyelectrolytes in these films are not crosslinked though they are confined within the matrix of trunk polymer. It seems also possible to gather some insight into the mechanism of the grafting reaction, since water transport and salt rejection entirely depend on the grafted phase of the copolymers, if hydrophobic (water-impermeable) polymer is selected as the starting film.

For this study, low-density polyethylene was chosen as the starting film material, and peroxide grafting was used to prepare the graft copolymers of both cationic and anionic membranes.

EXPERIMENTAL

The Preparation of the Graft Samples

Peroxidation of the Polyethylene Film. A low-density polyethylene film, 15 μ thick, was used in the study. The film was wound loosely in a large tube adapted with an O-ring seal with stopcock. The air in the tube was replaced by oxygen, then sealed. Several tubes were prepared in this manner and then irradiated in a ^{60}Co gamma source at a low dose rate, 0.01 Mrad/hr, for various times yielding samples of 3, 5, 10, 16, and 20 Mrad total dose. The films were then stored in the dark and at room temperature until used.

The stability of the diperoxide groups is quite good in the absence of light and at room temperature, and the peroxidized films have been found to have a shelf life of over a year.² The efficiency of the peroxidized graft system is quite good and was found quite versatile, because large numbers of samples could be conveniently produced under any desired set of conditions within the laboratory itself rather than at a radiation source.

Polyethylene-Sodium Polystyrene Sulfonate Copolymers. The grafting of the styrene onto the preirradiated films was carried out in excess monomer at 60° and 80°C. Tared squares of the peroxidized polyethylene film were placed in specially designed reaction tubes having a double constriction and an O-ring assembly. The diluted or undiluted monomer (styrene/toluene 90/10, or styrene) was added to fill the tube above the lower constriction, assuring the film would remain immersed in the monomer at all times. The samples were then degassed and, under vacuum, were sealed at the second constriction. The samples were then totally submerged in a constant-temperature bath for various periods of time. Three main series of samples were prepared in this manner: one using undiluted styrene at a reaction temperature of 60°C, one using a 90/10 ST/TOL mixture at a 60°C reaction temperature, and a third one using a 90/10 ST/TOL mixture at an 80°C reaction temperature, with the reaction times ranging from 1 to 48 hr. The samples are described in Table I. The films were visibly affected by the grafting from early in the reaction, with translucency developing sometimes after 1 hr of heating, and opacity and swelling increasing with time. After the films were removed from the baths, the tubes were cut open and the samples underwent multiple washings in toluene, with no more elaborate extraction found necessary. The films were then dried in a vacuum oven and weighed to determine their weight increase, from which the graft yield, Y_G , was calculated as $Y_G = (W - W_0)/W_0$, where W is the weight of the film after grafting and W_0 is the weight of the original polyethylene film.

In order to convert the polyethylene-polystyrene (PE-ST) graft copolymers to the polyethylene-sodium polystyrene sulfonate (PE-SSS) copolymers, the films were first sulfonated in a mixture of $\text{CCl}_4:\text{SO}_3:(\text{C}_2\text{H}_5)_3\text{PO}$ (20:1:1 volume ratio) for 5 hr at room temperature. Then, after a series of consecutive CCl_4 , MeOH, and H_2O washings to remove traces of the sulfonation solution, the films were placed in a 4% NaOH solution for 5 hr for conversion to the sodium salt form. The reaction times for sulfonation and salt formation were quite long to secure as high a conversion as possible. After thorough washings in water, the films were ready for testing in the reverse osmosis test loop.

Polyethylene-4-Vinylpyridinium Methyl Bromide Copolymers. These samples were prepared analogously to the PE-SSS series, using 3 Mrad preirradiated PE film and 4-vinylpyridine/ethanol monomer mixtures. The reaction time ranged from 1 to 7.5 hr at a temperature of 80°C.

The films were washed with methanol, dried, and weighed to determine graft yield. The films were then quaternized with methyl bromide gas to obtain the polyethylene-4-vinylpyridinium methyl bromide (PE-4-VPMeBr) copolymer.

Polyethylene-Sodium Acrylate Copolymers. These samples were prepared by mutual irradiation. Tared squares of untreated polyethylene were placed in reaction tubes which were then filled with a mixture of acrylic acid monomer and a saturated cupric chloride solution (in a 1:1 volume ratio). The cupric chloride retards polymerization of the acrylic acid in

TABLE I
Polyethylene-Sodium Styrene Sulfonate Graft Copolymer Films

Film no.	Preirrad. dose, Mrad	Reaction time, hr	Graft yield	Rejection	Hydration	H'
Monomer solution: $\frac{90 \text{ Styrene}}{10 \text{ Toluene}}$; reaction temperature: 60°C						
1	3	1.0	.110	.06	.20	.58
2	3	3.5	.102	.50	.14	.49
3	3	7.0	.285	.79	.33	.59
4	3	16.0	.371	.70	.45	.66
5	3	24.0	.304	.50	.08	.18
6	3	40.5	.761	.55	.50	.63
7	5	3.5	.117	—	.36	.75
8	5	7.0	.201	—	—	—
9	5	16.0	.344	.78	.34	.56
10	5	24.0	.417	—	—	—
11	5	40.5	.588	.60	.61	.74
12	10	1.0	.050	.26	.12	.60
13	10	4.0	.206	.62	.47	.75
14	10	16.0	.494	.70	.43	.60
15	10	40.5	.971	.49	—	—
Monomer solution: $\frac{90 \text{ Styrene}}{10 \text{ Toluene}}$; reaction temperature: 80°C						
16	3	1.0	.079	.52	.14	.55
17	3	2.2	.149	.82	.22	.50
18	3	3.0	.134	.80	.09	.32
19	3	4.0	.199	.66	.20	.46
20	3	20.0	.352	.56	.49	.70
21	5	1.0	.040	.25	.09	.57
22	5	3.5	.075	.32	.33	.79
23	5	6.2	.123	.27	.45	.81
24	5	8.0	.207	.50	.19	.45
25	5	20.0	.245	.54	.24	.47
26	5	31.5	.492	.53	.53	.69
27	10	1.2	.086	—	.19	.63
28	10	3.0	.186	—	.29	.61
29	10	15.5	.673	.40	.71	.81
30	10	24.0	.623	.03	.61	.74
Monomer: styrene; reaction temperature: 60°C						
1	3	1.0	.040	.12	.11	.63
2	3	3.0	.089	.65	.33	.77
3	3	5.0	.395	.73	.55	.73
4	3	15.0	.258	.17	.60	.81
5	3	23.2	.417	.67	.30	.49
6	3	43.5	.855	—	—	—
7	20	1.0	.193	—	—	—
8	20	3.0	.244	—	—	—
9	20	5.0	.366	—	—	—
10	20	15.5	.708	—	—	—
11	20	24.0	1.05	—	—	—
12	20	38.5	1.18	—	—	—

solution phase. The solutions were degassed and sealed as described earlier. At room temperature, the samples were then irradiated at a dose rate of 0.01 Mrad/hr. Total doses varying from 0.3 to 6 Mrads were obtained in this series. After irradiation, the films were washed in water and then converted to the polyethylene-poly(sodium acrylate) (PE-SA) form using 4% sodium hydroxide solution.

The Reverse Osmosis Testing

The measurements were made in a test loop consisting of four stirred cells pressurized by an air-driven pump. The Amicon Model 500 high-pressure cells have an effective membrane area of 37.5 cm², and are operated independently at relatively low feed solution flow rates at 1500 psi. Concentration polarization and feed concentration build-up in each cell is minimized by internal stirring and regulated feed solution flow rate for each cell.

Pressurization and circulation of the feed solution is maintained by a system consisting of a Sprague air-driven pump (S-440-CS35-SS) used with a laboratory 100-psi air line, a Greer bladder accumulator (which eliminates pressure pulse due to pumping), and a Culligan Filter Gard (which filters the feed before recirculating through the pump).

The pressure can be maintained within ± 20 psi at 1500 psi applied pressure. All measurements were made at 1500 psi and 24–25°C, and using a 3.5 wt-% NaCl solution. Salt rejection is calculated on the basis of the relative concentration of the feed solution to the effluent of each cell. The conductivity measurements are made with a Type CDM2e conductivity meter manufactured by Radiometer of Copenhagen. The rejection can be expressed as

$$R_s = \frac{(\text{concentration of feed}) - (\text{concentration of effluent})}{\text{concentration of feed}}$$

Water permeability K_1 is represented (with approximation) using the membrane flux, membrane thickness, and the total pressure of the system by using the relationship

$$K_1 = \frac{(\text{flux}) (l)}{(\Delta P - \Delta \pi)}$$

where the flux is the effluent 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 (applied pressure — osmotic pressure of feed solution).

Hydration Determination

The weight fraction of water in the film was determined by drying weighed samples of the wet films in a vacuum oven at 60°C. The dry films were then weighed and the weight fraction calculated as

$$H = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{wet}}}$$

RESULTS AND DISCUSSION

Irradiation of polyethylene in the presence of oxygen results in the formation of various peroxides, mainly hydroperoxides or diperoxides. The high permeability of polyethylene allows even relatively thick samples to be peroxidized with ease, and at room temperature and low dose rates the formation of diperoxides is generally expected.³ Several factors, e.g., preirradiation dose, the reaction temperature and time, and monomer concentration will affect the graft yield.

The grafting yields obtained with the various grafting conditions described earlier are shown in Figure 1. The effect of total dose was as expected, with the higher preirradiation dose samples achieving the higher graft yields for a given reaction time and temperature.

The effect of grafting temperature on graft yield was much more noticeable in the high preirradiation dose films. Little difference was observed in 3-Mrad sample graft yields obtained using reaction temperatures of 60°C and 80°C, but the grafting yields obtained at 80°C were significantly higher than at 60°C for 10-Mrad samples. This observation is no doubt reflecting a combination of several simultaneous and sometimes opposing processes affected by temperature, e.g., the decomposition rate of the peroxides, the increased swelling of the polyethylene matrix in styrene at the higher temperature, the graft-versus-thermal homopolymerization competition, and determination of the chain length.⁴

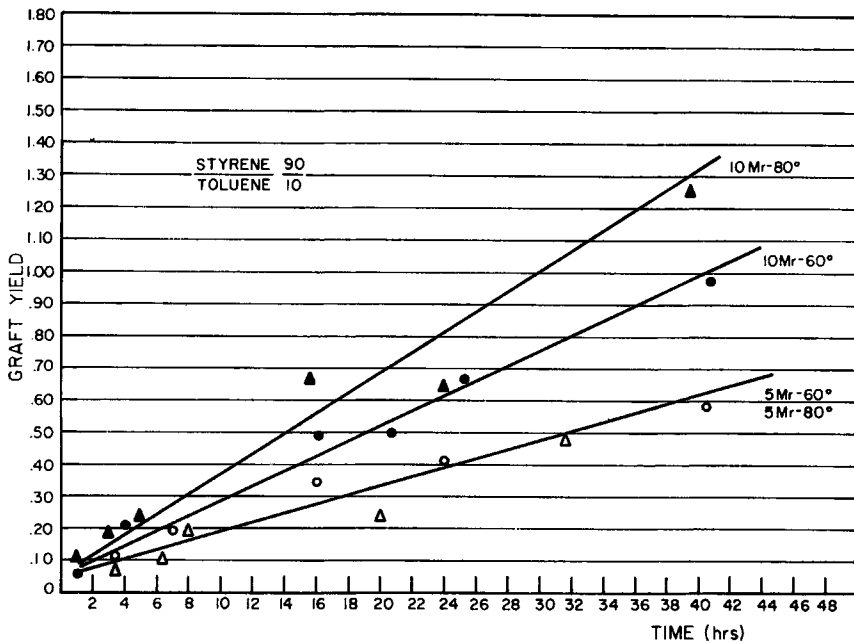


Fig. 1. Effect of preirradiation dose and reaction temperature on the graft yield-vs.-time relationship for peroxidation grafting of styrene onto polyethylene.

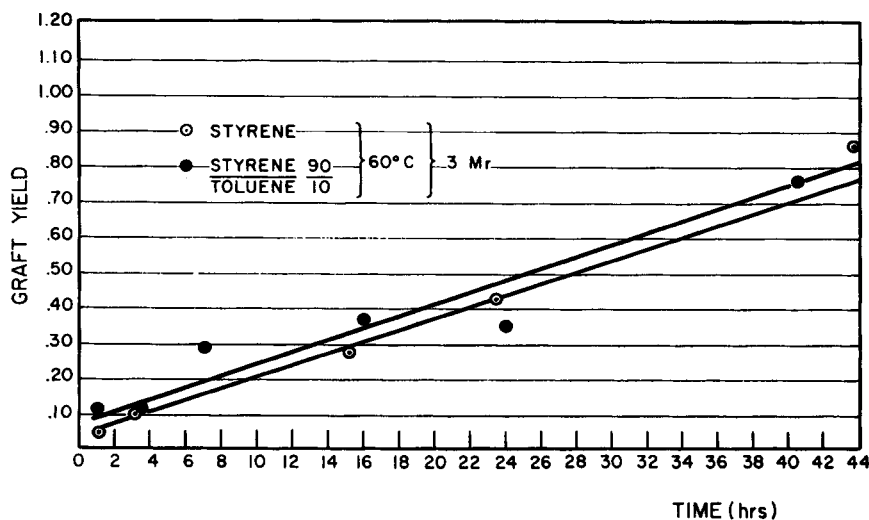


Fig. 2. Effect of monomer dilution on graft yield-vs.-time relationship for peroxidation grafting of styrene onto polyethylene.

The effect of monomer dilution on graft yield was examined only briefly and can be seen in Figure 2. For these samples of low preirradiation dose and using a 10% dilution with toluene, no large difference was seen.

Films of graft yields up to 1.00 were successfully prepared and evaluated. Graft yields even greater than 1.00 were obtained in a system using 20-Mrad film and undiluted styrene monomer. The films, however, disintegrated upon sulfonation, the polyethylene matrix not being strong enough to withstand the swelling of the PE-SSS system.

One of the important features that seemed clear on examining the reverse osmosis behavior of graft copolymers is that a basic understanding of the reverse osmosis characteristics cannot be obtained as a straightforward relationship between graft yield and performance (though this is the most common approach used in interpretation of grafting experiments reported in the literature).

In Figure 3, the rejection data is shown as a function of the graft yield for the various series of samples prepared. In each case, the rejection increases rapidly with graft yield (up to Y_G of 10–20%), after which the salt rejection decreases steadily with continued increase of graft yield. Although the initial increase in rejection versus graft yield is quite similar for the three series of samples, the rate of decrease in rejection as the graft increases from the value $Y_G = 0.20$ is quite different for each sample series.

The salt rejection of ionic membranes is generally described in terms of the exclusion of ions of the same charges as those of the fixed charge of the membrane. The concentration, then, of ionic sites in the swollen membrane is very important in determining its characteristics. This concentration of ionic sites, C^* , is dependent on the concentration of ionic sites in the

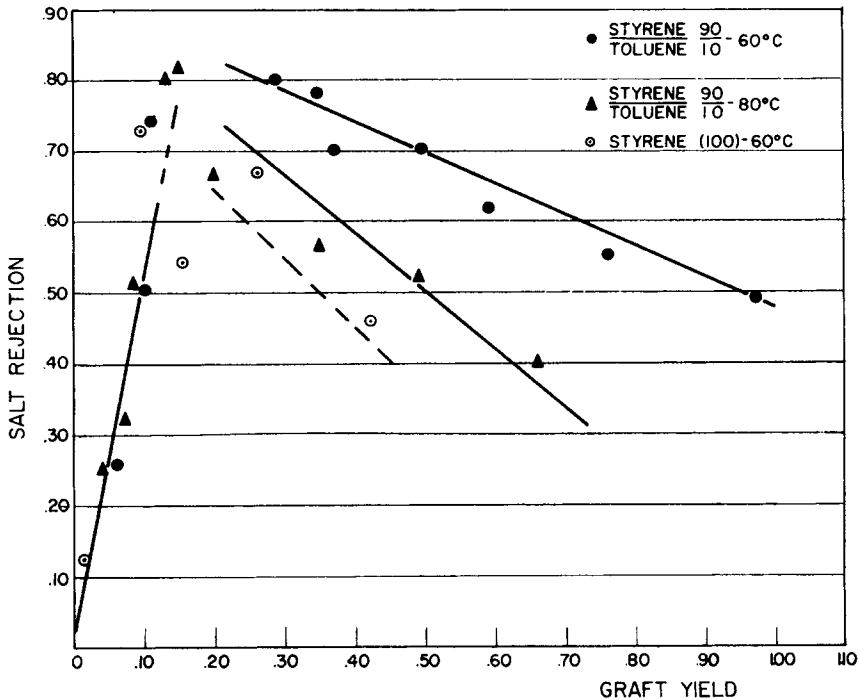


Fig. 3. Salt rejection (obtained in reverse osmosis tests) of various series of polyethylene-poly(sodium styrene sulfonate) graft copolymer membranes as a function of graft yield.

dry film, C^{**} , and the amount of swelling that is experienced by the particular sample (determined by crosslinking, morphology, etc.).

The swelling (hydration) of the membranes is therefore an important factor in characteristic membrane behavior. When graft yield is plotted as a function of hydration (Fig. 4), a linear relationship is apparent, hydration increasing with graft yield. (The significant scatter of data points is to be expected in view of the uncertainties in both Y_G and H determinations.) Although the hydration of the samples prepared in undiluted styrene seem consistently high, no great differences in the H -versus- Y_G values are observed between the various sample series. Some differences should be apparent since the different grafting conditions should result in different membrane morphology.

These hydration values, however, actually represent an average hydration of both the polyethylene and the graft portions of the membrane. A more direct value, termed H' , is the hydration corrected for the permeable (ionic polymer) portion of the film. H' can be calculated as

$$H' = \frac{(1 + Y_G a)H}{Y_G a + H}$$

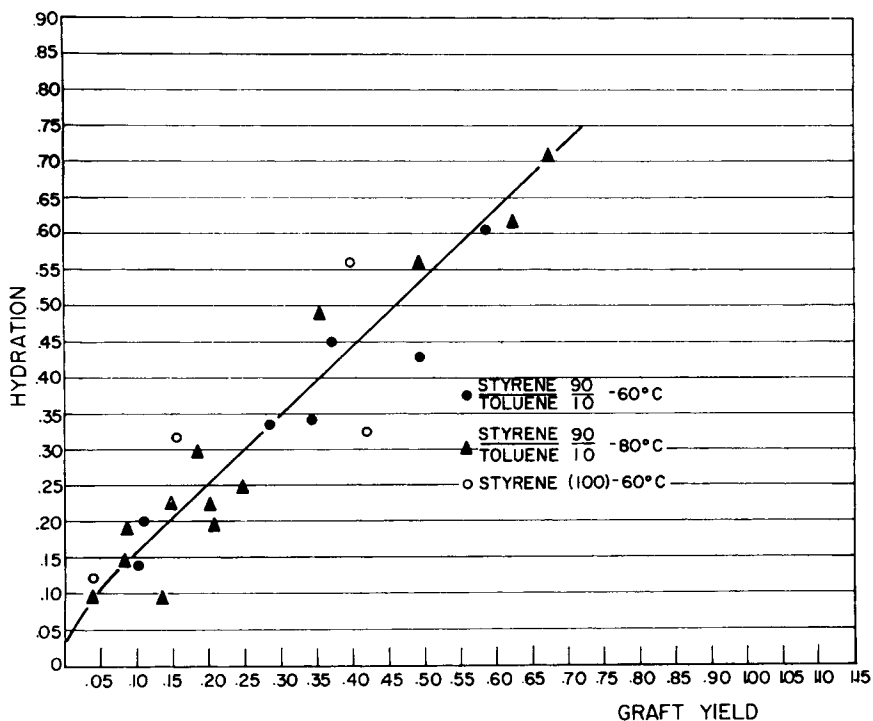


Fig. 4. Hydration of the polyethylene-poly(sodium styrene sulfonate) graft copolymer membranes as a function of the graft yield.

where Y_G is the graft yield and a is the ratio

$$\frac{\text{gram-mol. wt. of ionic polymer}}{\text{gram-mol. wt. of polymer before sulfonation}}$$

For example, consider a particular PE-SSS membrane whose hydration was determined to be 0.50 and graft yield 1.00. The value a is equal to

$$\begin{aligned} a &= \frac{\text{gram-mol. wt. St SO}_3\text{Na}}{\text{gram-mol. wt. styrene}} \\ &= \frac{207}{104} = 2. \end{aligned}$$

The H' value can then be calculated as follows:

$$\begin{aligned} H' &= \frac{[1 + 1(2)]0.5}{1(2) + 0.5} \\ &= \frac{1.5}{2.5} = 0.6. \end{aligned}$$

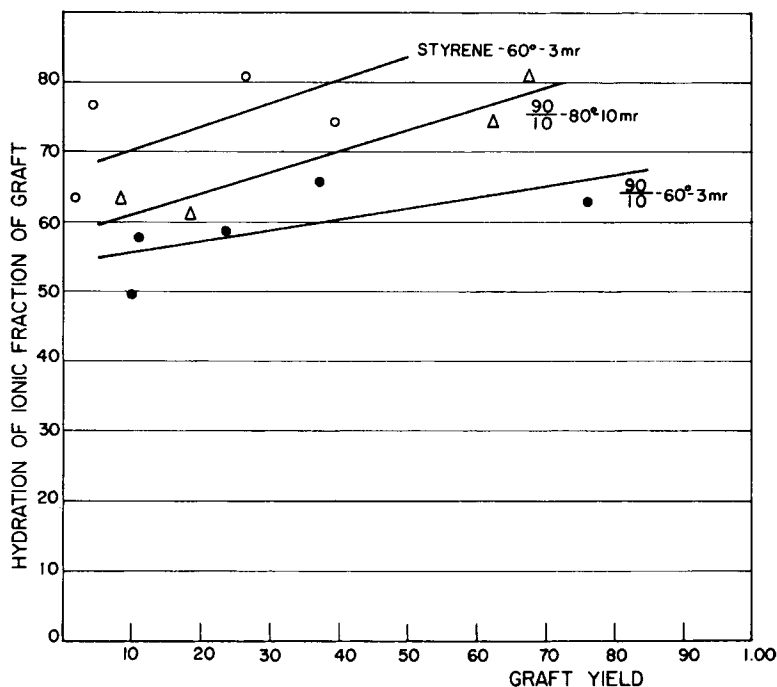


Fig. 5. Hydration of the ionic fraction of the polyethylene-poly(sodium styrene sulfonate) graft copolymer membranes as a function of graft yield.

Here, mention should be made of the fact that this calculation assumes complete sulfonation of the styrene graft and complete conversion to the Na form of the polystyrene sulfonic acid. Therefore, the H' values will include not only the uncertainties of the graft yield and hydration determinations but also the undetermined errors due to incomplete sulfonation and hydrolysis.

The plot of H' versus Y_G , shown in Figure 5, is limited to three sets of samples for which the results were expected to give a significant difference in graft yield versus hydration. When the H' values were calculated and H' versus Y_G was plotted, the following aspects seemed important in interpretation of the graft-hydration-rejection relationships.

First of all, the various sets of graft conditions each give a distinct slope. The 100% styrene series exhibits the highest H' versus Y_G , with the styrene/toluene 90/10 10-Mrad 80°C series showing the intermediate values and the styrene/toluene 90/10 3-Mrad 60°C series showing the lowest values. This relationship was reflected in the rejection-versus-graft plot shown earlier in Figure 3. The styrene samples, which show the highest H' -versus- Y_G values, show the most rapid decrease in salt rejection with increasing Y_G , the styrene/toluene 90/10 10-Mrad 80°C series samples show an intermediate rate of rejection decrease with increasing G , and the styrene/toluene 90/10 3-Mrad 60°C samples, which show the lowest H' -ver-

sus- G values, show the slowest rate of rejection decrease. Note also that the slopes extrapolate back to fairly high hydration, indicating the ionic or "working" part of the membrane is exhibiting the high hydration expected for ionic polymer.

Increase in H' , then, seems correlated to a decrease of salt rejection and can be seen clearly in terms of the interdependence of the membrane hydration H , the concentration of ionic sites in the dry polymer C^{**} , and the concentration of ionic sites in the membrane at equilibrium swelling C^* . For the range of hydration $0 < H < 1$, the relationship can be expressed as

$$C^* = (1 - H)C^{**}.$$

It has been demonstrated¹ that salt rejection by ionic membranes is proportional to C^* .

Therefore, the effect of grafting is only to increase C^{**} . That is, the calculated graft yield is proportional to the concentration of ionic sites in the dry polymer. Rejection, however, is governed not by C^{**} but by C^* which is not uniquely dependent on C^{**} but is a function of H as well. The swelling, or hydration, of the membrane is governed not only by C^{**} but also by the morphology of the graft copolymer. The amorphous regions distributed among crystalline regions of polyethylene are utilized to make networks of hydrophilic-hydrophobic dispersed phases. The extent of the crystalline regions and radiation-induced crosslinks which serve as a restraint against swelling and the composition of the graft phase then jointly determine the overall swelling that will occur.

The results obtained with a series of samples prepared using 20-Mrad (preirradiation dose) film resulted in very high graft yields, well above 1.00, and certainly substantiate this argument. When these samples were sulfonated, they literally disintegrated into small bits, the result of the swelling pressure generated by the sulfonation of the large fraction of graft within the restraining polyethylene framework (which is highly crosslinked by the high preirradiation dose).

Looking again at Figure 3, we can interpret the results in terms of these relationships. At the very low graft yields, as C^{**} (Y_G) increases, the rejection is also increasing, implying that C^* is also increasing. In this range we are dealing not only with the observable effects of an increase in ionic site concentration C^{**} , but also with the change from PE to the graft copolymer. The initial increase of salt rejection with grafting yield may be interpreted as a consequence of increasing C^* in the early stage of copolymerization. Consider the "starting point," $C^{**} = 0$. Here, C^* must also be zero. Any increase in C^{**} will be reflected by an increase in C^* until the system reaches the point where the effect of additional swelling overtakes the effect of increasing C^{**} and C^* begins to decrease. This point will depend upon membrane morphology, as discussed earlier.

Then, as this point is passed, we observe a decline in rejection as C^* decreases. By considering both Figures 3 and 5, we can see that the faster the hydration of the graft portion increases with graft yield, the faster the

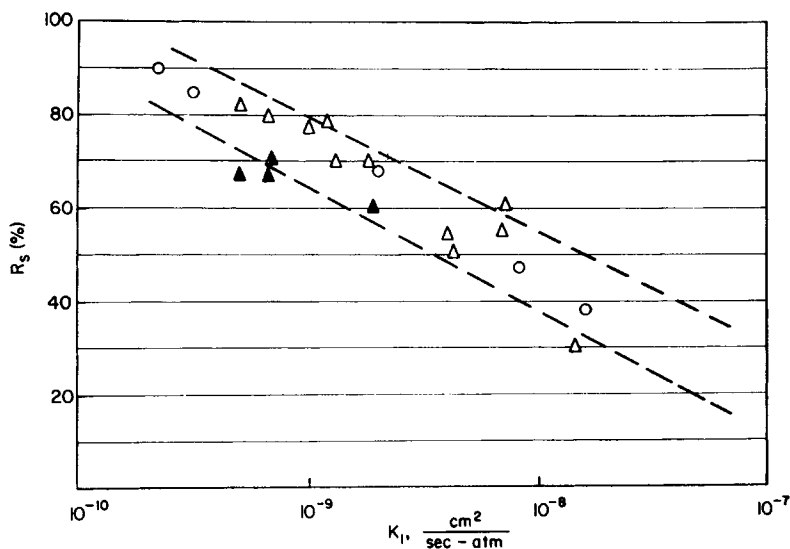


Fig. 6. Interrelationship of salt rejection (R_s) and water permeability (K_1) for three types of graft copolymers: (Δ) PE-SSS; (\blacktriangle) PE-SA; (\circ) PE-4VPMeBr.

salt rejection of the membrane decreases. In other words, films grafted under different conditions will exhibit different interdependence of C^{**} versus swelling (hydration) and therefore exhibit different rejection-versus-graft yield relationships.

These trends observed in Figures 3 and 5 indicate some important factors which might give more insight into the mechanism of salt rejection and graft copolymerization. These factors are as follows: (a) The salt rejection occurs as a consequence of the existence of charged sites in membrane phase and does not seem to be related to the sieve mechanism which is often interpreted as a consequence of crosslinking. It is very unlikely that the grafted side chains are highly crosslinked and that the crosslinking is responsible for the salt rejection. (b) The salt rejection of such graft copolymers (ionic grafted polymer in water-impermeable semicrystalline polymer) reflects the variation of factors (such as molecular weight, morphologic distribution, etc.) involved in the grafted side chain. Most properties (such as sorption and gas permeability) observed with graft copolymers depend on the total volume or weight fraction of grafted polymer and do not reflect the changes in these factors. For instance, no clear distinction can be made between graft copolymers prepared in different conditions in their relationship of total water pickup versus grafting yield as shown in Figure 4.

The aspects of graft copolymerization reaction discussed with the PSSS-PE system are also valid to the rest of systems, though details are not presented here. Once the grafting yield reaches a certain value, all grafted membranes behave as typical ionic membranes and the interrelationship of salt rejection and water permeability of all three types of graft copolymers is nearly identical, as seen in Figure 6.

In examining the reverse osmosis characteristics, given by eq. (1), of grafted ionic membranes, the inhomogeneous nature of the grafting reaction should be taken into account. Namely, R_s observed in reverse osmosis test is straightforward, particularly with water-impermeable starting polymer films; however, the value of K_1 depends on the effective thickness of the membrane in the actual condition of the test, which is not always equal or close to the gross thickness of the membrane. Considering that most grafting reactions proceed from the surface of the starting film, the values, such as grafting yield and water content, based on the gross membrane may not represent the characteristics of the actual (effective) membrane layer. Consequently, K_1 calculated with the gross thickness may vary in orders of magnitude depending on the heterogeneous nature of grafting reaction. Grafted membranes which show relatively high swelling are expected to follow the general relationship; however, grafted membranes which have conspicuously low apparent swelling may appear to deviate greatly from the relationship due to the inhomogeneity of the grafting.

This study was supported in part by the U.S. Department of Interior Office of Saline Water, Contract No. 14-01-0001-1785. The authors' special thanks are due Dr. Anton Peterlin, Director, Camille Dreyfus Laboratory, Research Triangle Institute, for his stimulating discussion and creative criticism.

References

1. H. Yasuda, C. E. Lamaze, and A. Schindler, *J. Polym. Sci. A-2*, in press.
2. A. Chapiro, *J. Polym. Sci.*, **29**, 321 (1958).
3. A. Chapiro, *Radiation Chemistry of Polymeric Systems*, Interscience, New York, 1962.
4. H. Sack, *J. Polym. Sci.*, **34**, 434 (1959).

Received January 21, 1971