

Modification of Membrane Permselectivity by Graft Copolymerization

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Synopsis

The permselectivity and other performance characteristics of a polyethylene-graft-poly(potassium acrylate) copolymer membrane were considerably enhanced by subsequent grafting of polystyrene to the membrane. Careful control of the conditions of the grafting procedure, using cobalt-60 gamma radiation initiation, allowed the preparation of membranes with prescribed graft compositions. The permeation behavior of the components of a silver oxide salt and concentrated potassium hydroxide solution were found to be very dependent on the graft content and its distribution in the membrane. The use of optimum polymerization conditions produced membranes in which the transport of the silver salt was reduced more than was that of the electrolyte, i.e., the ratio of silver salt flux to electrolyte flux was decreased by at least an order of magnitude. In addition, the resistance of the membrane to the degradation action of the two penetrating species was significantly increased. A structure model has been proposed which accounts for the observed property changes. These effects suggest that similar modifications may be useful for other polymer-penetrant systems and applications.

INTRODUCTION

Graft copolymerization is a well-recognized general method for modification of the chemical and physical properties of polymeric materials.^{1,2} Recently, such techniques have been applied to the preparation of permselective membranes.³⁻⁶ If it is desired to use this type of modification procedure to achieve specifically prescribed membrane properties, then it is essential that the conditions of the chemical treatment be very carefully controlled. For example, the diffusion and solution behavior of small molecules in membrane materials is very sensitive to graft copolymer composition and, especially, to the composition distribution within the membrane. Variations in the local domain structure of the membrane can have marked effects on the distribution of a sorbed penetrant, the nature of the diffusion mechanism, and the permselectivity of the membrane. An appropriate selection of a grafting monomer whose solution and diffusion behavior in the base polymer are known, as well as its basic polymerization characteristics, allows a degree of control to be exercised over the graft copolymerization process. An appreciation of the many factors which may affect the overall polymerization, such as diffusion control, monomer clustering, and surface polymerization, permits a more realistic

appraisal to be made of the dependence of membrane permselectivity on the resultant polymer composition and structure.

An area of particular interest regarding the potential utilization of carefully controlled specific grafting techniques is concerned with the development of an effective separator membrane for use in a rechargeable alkaline silver-zinc battery. The purpose of such a separator membrane is to physically isolate the two half-cells of the battery in order to prevent contact or contamination of the electrodes. Contamination arises from the fact that silver salts, formed owing to a low solubility of the silver electrode in the highly concentrated potassium hydroxide electrolyte, can migrate through the battery to the zinc electrode, causing self-discharge and loss of function. The separator membrane must retard this permeation of the silver salts, while maintaining simultaneous high electrolyte permeation properties.

An associated problem is that the concentrated alkaline medium and the oxidizing effect of silver salts in this medium lead to chemical degradation of most polymeric separators, accompanied by simultaneous deposition of metallic silver and silver(I) oxide within the membrane.⁴ This evidence, plus other work by Cuddihy et al.,⁷ substantiates the conclusion that the degradation is a redox reaction, involving an oxidative attack of the membrane by the soluble silver salt, while the silver deposition results from the complementary reduction of the silver salt to its lower valence states.

This study is concerned with the modification of an existing membrane material in order to enhance its permselectivity and degradation resistance. The membrane used was a grafted copolymer consisting of crosslinked polyethylene base film with poly(potassium acrylate) grafted to it. It was felt that the susceptibility of the polyethylene-type separator to silver salt permeation and deposition could be significantly retarded by suitable treatment, without adversely affecting the electrolyte flux.

EXPERIMENTAL

The polyethylene-graft-poly(potassium acrylate) (PE-PKA) membrane material was provided by the Jet Propulsion Laboratory of the California Institute of Technology. Its JPL identification code was 5-399GX, and it was reported to contain an average acrylate graft content of between 20% and 30% by weight, an average thickness of 0.0013 in., and a polyethylene crystallinity content of 50%. The polyethylene base material was radiation crosslinked and had a density of 0.926 g/cm³.

The as-received PE-PKA was washed in hot methanol for 48 hr in order to remove impurities prior to being equilibrated with the grafting solution, which consisted of 30% styrene monomer and 70% methanol (by weight). Graft copolymerization of the monomer onto the PE-PKA material was initiated by exposure of the membranes, while immersed in the grafting solution, to cobalt-60 gamma irradiation. The irradiations were carried out at room temperature in an air atmosphere at a dose rate of approxi-

mately 250,000 rads/hr for the times required to achieve the desired irradiation dose. The grafted films were then extracted with two successive room-temperature benzene baths, in which the treated membranes were immersed for a total of 24 hr, with stirring. The processes described yielded membranes in which the grafting yield within a set varied by less than 5% from the average value. Grafted membranes were stored dry in desiccators prior to characterization. Note that, following the initial hot methanol wash, the PKA component of the membranes was converted by ion exchange to the acrylic acid form to facilitate handling (PKA is hygroscopic, acrylic acid is not). After the grafting treatment was completed, the membranes were changed back to the PKA salt.

Two series of membranes were prepared by varying the grafting procedure. In one series, continuous grafting was used, i.e., the membranes were irradiated to the total required dose without interruption. In the second series, the irradiation step was performed in a cyclic fashion. The membranes were irradiated in the usual manner until a total dose of 1.0 Mrad was achieved. They were then removed from the grafting solution and allowed to reequilibrate with a fresh quantity of the same grafting solution for 12 hr before being irradiated for an additional 1.0-Mrad dose. This intermittent process was repeated as often as needed in order to obtain the desired dose.

The grafted membranes were characterized by four techniques, the first of which was simply the per cent change in weight based on the initial membrane weight, effected by the treatment. The weight change data were then used to classify the results of the successive characterization procedures, which were all carried out at 25°C.

Electrolyte flux measurements on the membranes were carried out using a specially constructed Lucite cell. With this apparatus, the permeation from an aqueous 45% (by weight) potassium hydroxide (KOH) solution through the membrane into distilled water was monitored by measuring the pH of the solution in the receiving volume side of the cell. The pH values were continuously recorded on a strip chart recorder, from which the thermodynamic activity of the hydroxyl ion-versus-time curves were calculated. The steady-state flux was then calculated from the steady-state slopes of the curves, using a simple form of Fick's first law:

$$J = \frac{Q}{At} = \frac{SV_a}{A} \quad (1)$$

where Q is the total amount of electrolyte which passes through an area A in a time period t , S is the steady-state slope, and V_a is the downstream solution volume.

Silver salt flux measurements were performed using a radioactive isotope tracer technique. The membranes were mounted in a second Lucite permeation cell, and the flux from a saturated solution of silver(I) oxide in 45% KOH through the membranes into pure 45% KOH was measured,

using aliquots of solution removed from both sides of the cell at known intervals of time. The silver content of the solution samples was measured via liquid scintillation counting, using a Radiation Instrument Development Laboratory Model 49-23 scintillation counter and a Harshaw Chemical Company Type 7F8 thallium-activated sodium iodide well-type scintillation crystal. Each sample was counted for 30 min to get an average counts-per-minute reading. Counting error was ± 10 cpm. Counter output was calibrated in terms of silver concentration units via standardized EMF measurements. Plots of downstream concentration versus time gave the steady-state flux as calculated from the slopes using eq. (1). The radioactive ($\text{Ag}^{110\text{m}}$) silver salt solutions, of silver concentrations of about 2×10^{-5} molal, were prepared after a method outlined by Dirkse.⁸

The final characterization technique used in this study was the silver deposition rate. As outlined above, deposition rate is a measure of the degradation resistance properties of the membrane. This experiment was conducted on films which had been exposed to the silver salt flux experiment and which, therefore, had low-valence silver salts deposited within them. The membranes were removed from the permeation cell and rinsed in distilled water in order to remove excess KOH and unreacted silver salts. Then the membrane was packed into a scintillation vial, and concentrated nitric acid was added to dissolve the deposited silver. This sample was then counted with the liquid scintillation counter, and the quantity of silver present was calculated as before.

The rate at which this quantity of silver deposited in the films per unit exposed area per unit time was calculated via eq. (2),

$$R = \frac{G}{(\Delta T)(A)} \quad (2)$$

where G is the quantity of silver deposited in the membrane.

RESULTS AND DISCUSSION

The effect of the irradiation dose, and the manner in which it was administered, on the grafting yield is listed in Table I and shown graphically in

TABLE I
Effect of Irradiation Dose on Yield

Type of experiment	Dose, Mrad	Yield, %
Dose	0.5	2.5
Dose	1.0	8.5
Dose	1.5	11.3
Dose	2.0	16.5
Dose	3.0	19.6
Dose-cyclic	1.0	8.5
Dose-cyclic	2.0	14.9
Dose-cyclic	3.0	41.8

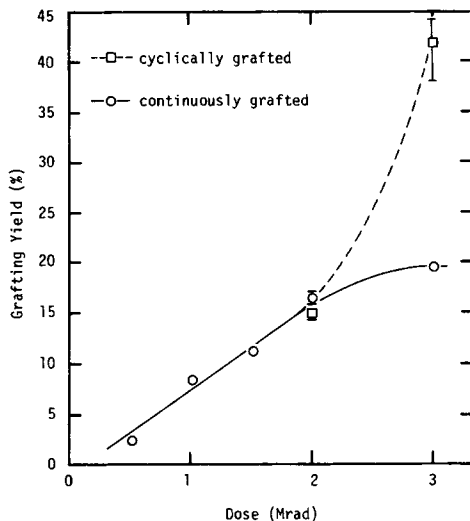


Fig. 1. Grafting yield as a function of irradiation dose.

Figure 1. For the continuous irradiation series, grafting yield increases in a linear fashion in the dose range between 0.5 and 2.0 Mrad, but tails off toward an asymptotic grafting yield above an irradiation dose of 3 Mrad. For the cyclic irradiation series, the 1.0- and 2.0-Mrad irradiation levels resulted in comparable yields to those obtained at the same dose level with continuous irradiation. However, above the 2.0-Mrad dose level, the cyclic grafting exhibits an acceleration effect like that found in the grafting of several vinyl monomers to polyethylene under similar conditions.⁹

In most radiation graft copolymerization experiments, two types of grafting can occur: grafting onto the substrate surface from the surrounding solution and grafting into the substrate interior. Internal grafting is often limited by the quantity of monomer absorbed by, and therefore contained in, the membrane. As the reaction proceeds, the supply of absorbed monomer is depleted and the reaction rate becomes dependent on the rate by which fresh monomer can diffuse into the membrane to the active polymerization sites. Surface grafting does not exhibit this diffusion control limitation. When the membrane is immersed in a monomer solution, a constant supply of monomer can be available to the surface to feed the growing grafted chains.

In the case of the continuously grafted membranes, it is probable that during the membrane treatment both internal and surface reactions are taking place simultaneously. Thus, the grafting yield would be directly proportional to the dose. However, as the total received dose increases above the 1.5- to 2.0-Mrad level, the internally absorbed supply of monomer may be depleted, and the internal grafting process can then become diffusion controlled. Since the diffusion of styrene into polyethylene is slow,⁹ the internal reaction rate will slow or stop altogether. The surface grafting

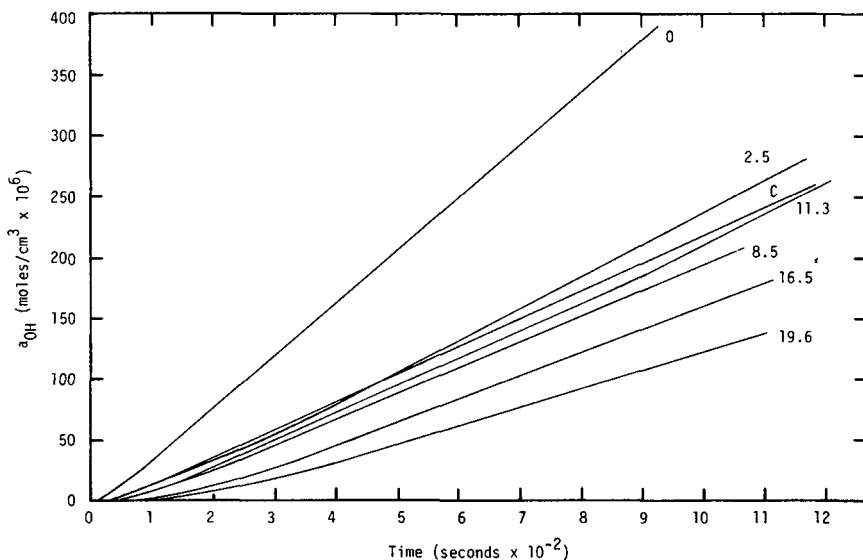


Fig. 2. KOH permeation curves for continuously grafted membranes. Numbers on curves represent graft content.

reaction will continue, but the overall grafting rate will be reduced. The surface reaction eventually also will be slowed and stopped if the radiation is carried out long enough, owing to depletion of the monomer supply from the grafting solution. Such a sequence of events would explain the behavior of the grafting yield-versus-dose curve found for this series of membranes.

As described above, the membrane apparently absorbs a sufficient quantity of monomer to sustain the internal grafting up to the 2.0-Mrad dose level. Hence, intermittent grafting with monomer reequilibration below the 2.0-Mrad dose level should not affect the grafting yield results, as indeed it does not. However, at higher levels of irradiation, the reequilibration step will replenish the monomer supply absorbed in, and external to, the membrane, allowing continued grafting both internally and on the surface. This accounts for the elevated grafting yields found for the high dose-level membranes in the cyclic series.

Electrolyte permeation curves, obtained from the pH measurements, are shown in Figures 2 and 3 for the two series of membranes. Included for purposes of comparison are curves for unmodified PE-PKA materials (labeled with an "O"), tested as received, and for the control films (labeled with a "C"), which were treated in the same manner as a 2.0-Mrad continuously grafted film, except that monomer was omitted from the grafting solution. From these curves, the steady-state slopes are seen to decrease as the graft content increases. This indicates that the electrolyte flux also generally decreases with increasing graft content.

Typical silver salt permeation curves, obtained from the downstream concentration-versus-time data, are shown in Figures 4 and 5. As in the

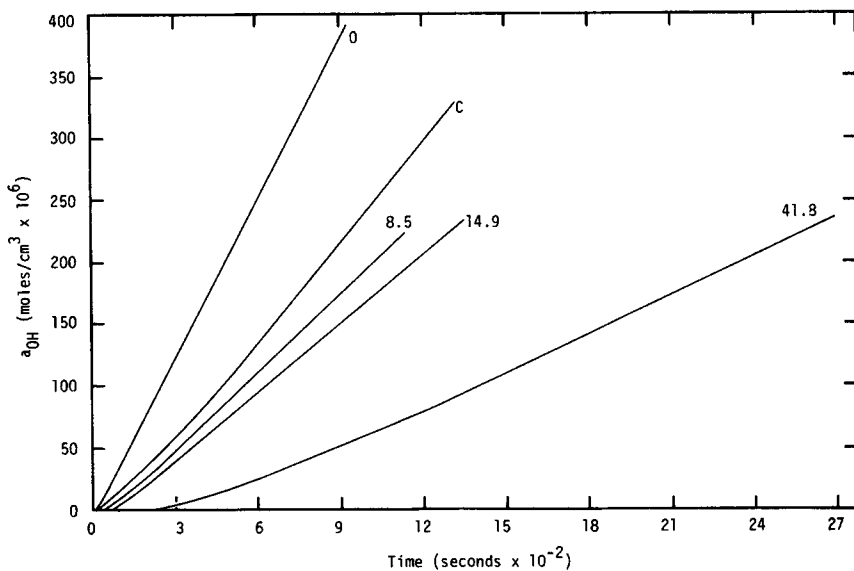


Fig. 3. KOH permeation curves for cyclically grafted membranes. Numbers on curves represent graft content.

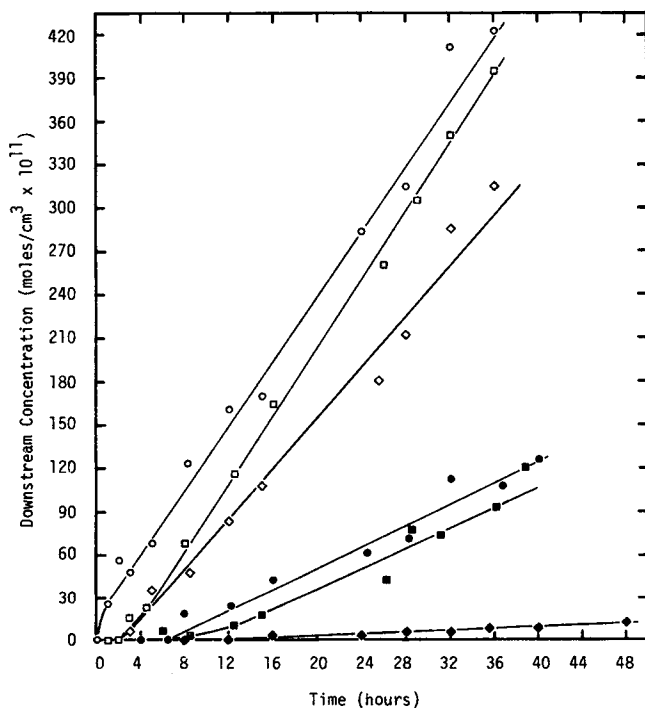


Fig. 4. Silver salt permeation curves for continuously grafted membranes: (O) control; (□) as-received; (◇) 2.5% graft; (●) 8.5% graft; (■) 11.3% graft; (◆) 16.5% graft.

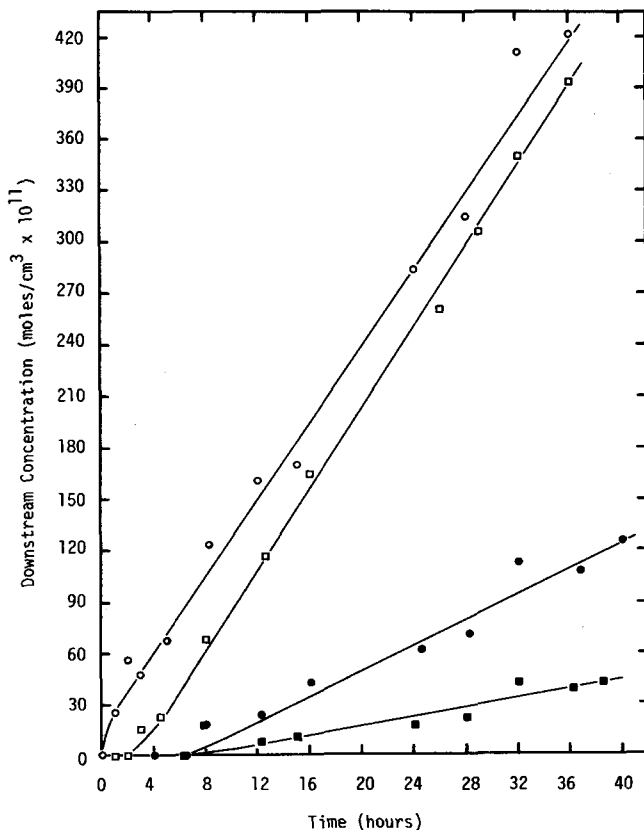


Fig. 5. Silver salt permeation curves for cyclically grafted membranes: (O) control; (□) as-received; (●) 8.5% graft; (■) 14.9% graft.

case of the electrolyte data, the steady-state slopes of the curves decrease as the graft content increases, again illustrating that the flux has been decreased by the modification procedure.

It should be noted that in the transient stages of the salt flux, two types of anomalous behavior are evident. In the case of the control film, the curve does not exhibit the usual concave shape found in the other curves. Secondly, most of the curves have points which are abnormally high, compared to the overall trend, in the transient region of flux. Whether these two effects are real or artifacts due to the measuring technique is uncertain. If they are real, they may be related to similar phenomena found by other investigators for gas and vapor permeation.¹⁰ One explanation offered for this behavior¹¹ is that initial rapid penetration takes place through microcracks, internal pores, or regions of low density within the dry membrane. As sorption and permeation proceed, these imperfections are eliminated by swelling or some other rearrangement of polymer structure, leading to a subsequent decay in the observed permeation rate to a more "normal"

TABLE II
Effect of Styrene Graft Modification on Membrane Properties

Grafting yield, %	KOH, flux, (moles/cm ² -sec) × 10 ⁶	Silver salt Flux, (moles/ cm ² -hr) × 10 ⁹	Silver deposition rate, (g/cm ² -hr) × 10 ⁸	Flux ratio, (J_{Ag^+}/J_{OH^-}) × 10 ⁸
0 (As-received)	6.48	1.53	2.63	6.56
0 (Control)	3.94	1.40	2.14	9.87
2.5	5.34	1.32	1.49	6.87
8.5 ^a	3.66	0.51	1.48	3.85
11.3	4.45	0.51	2.11	3.17
14.9 ^a	3.62	0.24	1.73	1.80
16.5	3.57	0.13	1.29	1.04
19.6	2.49	0	2.53	0
41.8 ^a	1.61	0	1.00	0

^a Cyclically grafted membranes.

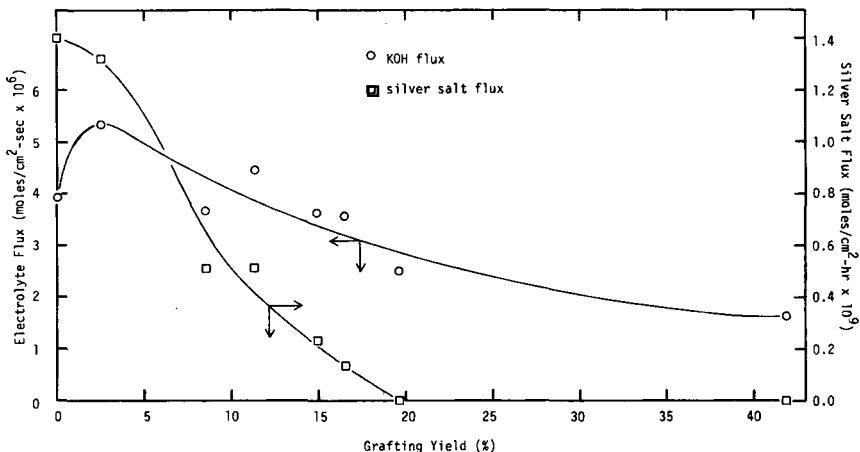


Fig. 6. Electrolyte and silver salt flux as functions of grafting yield.

value. Regardless of the source of these effects, steady-state stage of permeation, which is of interest for application uses, is not affected by the early anomalous behavior.

The calculated flux data for both components, obtained from curves such as those illustrated in Figures 2 through 5, is tabulated in Table II and shown graphically in Figure 6. In the case of the electrolyte transport, the flux values go through a maximum at low grafting yields, then decrease in a generally linear fashion as graft content increases before seeming to approach a lower limiting magnitude at high grafting yields. This limiting value is 41% of the flux found for the ungrafted control material.

The origin of the maximum in the flux curve can be explained by considering the experimental technique used to prepare the membranes for

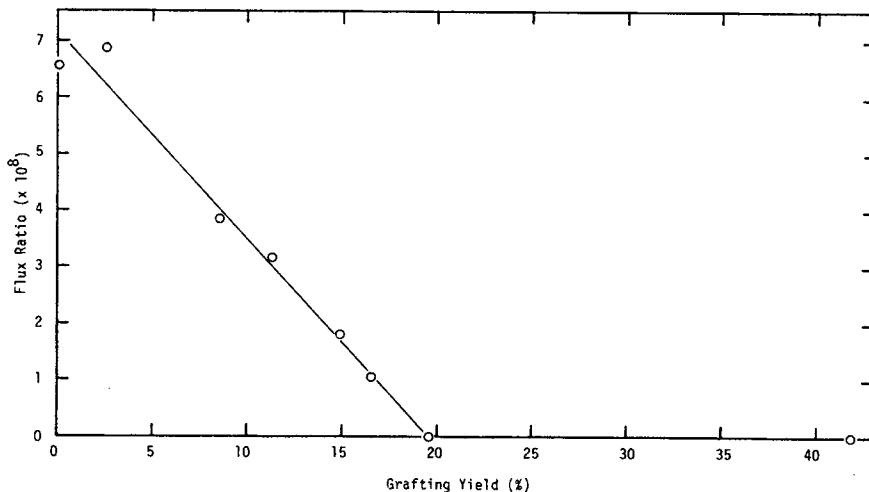


Fig. 7. Flux ratio as a function of grafting yield.

grafting. They were washed in a methanol solvent extractor at 60°C, resulting in an average weight loss of 7%. This extracted material consisted of a high percentage of PKA homopolymer, which then would lower the density of, or leave voids in, the amorphous PKA-grafted regions of the membrane. However, since the extraction was carried out at 60°C, the polymer chains in the membrane should have the opportunity to relax, thus closing up the voids and densifying the amorphous graft phase. This would tend to lower the flux properties of control membranes with respect to those of the as-received material.

In samples prepared at the lowest grafting yield, the polystyrene present in the membrane can act as a "solid state" swelling agent for the PKA domains. Its effect is primarily to disrupt the relatively close-packed regions without providing effective physical blockage to permeation of small penetrants. As the graft content increases, the swollen PKA domains become more tightly packed, and permeation through them decreases. The packing disruption at low yield may be of such a magnitude that it allows the electrolyte species to permeate relatively freely while blocking the penetration of the much larger silver salt species.

Flux data for silver salt permeation were found to decrease gradually with increasing graft content. This decrease is much steeper than was found for the electrolyte data, and the flux was decreased to zero at a graft level of 19.6%. The lowest measurable flux was less than 10% of the initial values, a decrease by at least a factor of 10.

In the case of the silver salt flux, the experimental time scale was 50 hr, so it should be kept in mind that a longer-term experiment may have resulted eventually in a measurable permeation, so little emphasis will be put on the zero flux data.

TABLE III
Features Affecting Permselectivity

Quantity	Electrolyte	Silver salt
Penetrating ionic species	K^+ or $K(H_2O)_n^+$	$[Ag_3O(OH)_2]^-$ or $Ag(OH)_2^-$
Solution concentration	15 <i>m</i>	$2 \times 10^{-5}m$

Also listed in Table II are the silver deposition rate data for both series of membranes. Some of these data are scattered, but the scatter is common to the technique used, and similar results were found by Cuddihy et al.⁷ in their studies on unmodified PE-PKA membranes. However, it can be stated that a general trend is observed in which the lowest graft-content membranes prepared exhibited a drop in rate to about 70% of the rate of the control samples. This is followed by a slow decrease with increasing graft content to less than one half of the initial value at the highest graft level.

A final, important characterization term is the ratio between the silver salt flux and electrolyte flux. This will relate the relative change in one factor to the other and, as such, is a prime key to the effectiveness of the membrane to act as a semipermeable barrier. These data are listed in Table II and Figure 7. The fact that the ratio of the silver salt flux to the electrolyte flux is about 10^{-8} shows that even the starting material is a good semipermeable barrier. Grafting treatment improves the selectivity and lowers the flux ratio by at least an order of magnitude. For both series of films plotted in Figure 7, the flux ratio decreases linearly with increasing graft content, becoming zero at the 19.6% graft level.

When all of the data are compared, it becomes evident that the two series of films exhibit virtually identical properties. As graft content increases, the flux of the two species in question decreases uniformly, with the transport of the soluble silver salts being significantly reduced without seriously decreasing the flow of electrolyte. In addition, the silver deposition rate drops sharply at even the lowest graft level produced and decreases slowly as grafting is continued.

These results suggest the following model. It seems reasonable that the effects of the two types of grafting that occur are separate, to a degree. The internally grafted polystyrene has some effect on the transport properties, but acts primarily as a blocking agent to protect the poly(potassium acrylate) from the oxidative degradation action of the silver salt. The surface graft presents a relatively dense layer to the penetrating species, thus retarding their flux through the membrane on the basis of differences in physical dimension and concentration (Table III). The hydroxylated anionic silver complexes, believed to be formed in highly concentrated alkaline media,^{12,13} are larger in size than the free or slightly hydrated potassium cation present in the same environment.^{14,15} The six orders of magnitude difference in solution concentration creates a correspondingly higher driving force for transport of the electrolyte than of the silver salts.

The model for the two effects on properties is based on the following considerations. At low grafting yields, e.g., less than 5%, the internal graft should exhibit its strongest influence. In this range, the flux data for both species undergoes only a slight change, while the silver deposition rate decreases significantly. At high grafting levels, e.g., above 10%, the surface layer effect becomes more predominant, leading to a continued, slow decline in flux properties, with little change in the deposition rate.

Prior to grafting, the membranes are allowed to equilibrate in the styrene-methanol grafting solution. Diffusion of the styrene will occur preferentially into the amorphous regions of the membrane.¹⁶ The selective diffusion will be enhanced by the presence of the methanol, because it is a good swelling agent and solvent for poly(potassium acrylate) and is a non-solvent for polyethylene. Thus, the irradiation exposure should graft the polystyrene into the same amorphous regions where the PKA is found. The probable close proximity of the two grafted polymers would magnify the protective blockage effect of the polystyrene and allow it to improve the silver degradation resistance properties of the membrane at relatively low concentration levels.

CONCLUSIONS

The grafting treatment of the PE-PKA membrane material decreased the KOH electrolyte flux to a value about 55% of that found for the as-received membrane, while, at the same graft content, the silver salt flux was decreased by a factor of 12. Accompanying this change was a decrease by a factor of 2 in the silver deposition rate of the membrane. Hence, the permselectivity of the membrane and its degradation resistance have been significantly increased by both the intermittent or continuous radiation grafting methods.

These data led to a structural model for the grafted membrane. The copolymerization reaction occurs both inside the film, owing to grafting of the internally absorbed monomer, and on the surface. The primary effect of the internal graft is to protect the poly(potassium acrylate) from oxidation by the silver salts, thus retarding silver deposition. The effect of the surface graft is to present a dense layer to the penetrating species, thus slowing their permeation through the membrane. Permeation is influenced by the presence of the internal graft, but the surface layer would appear to be more effective.

The combined results indicate that a tailoring of membrane properties, for battery separator membranes and potentially other applications, can be achieved by utilizing controlled specific grafting techniques.

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