

Dynamic Deposition of Polyacids on Porous Membrane Supports

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Synopsis

Poly(acrylic acids), poly(styrenesulfonic acid), and their block and random copolymers were tested for their ability to form dynamic membranes on partially cured asymmetric cellulose acetate. Chemically modified porous polypropylene (Celgard) was also used as a support for poly(acrylic acid). Salt rejections, water fluxes, and streaming potentials of membranes were tested under hyperfiltration conditions. Sorption of the polyelectrolytes by the cellulose acetate supports was studied using spectrophotometric, ^{22}Na tracer, and electron microscopy techniques. The dynamic membrane formation was noted only for poly(acrylic acid) and for its 1:4:1 block copolymer with poly(styrenesulfonic acid). The ineffectiveness of other polyelectrolytes was discussed in terms of a negative zeta potential of cellulose acetate. The increase in salt rejection (R) due to the polyelectrolyte is strongly dependent on the initial R_i of the support. Sharp maxima in the ΔR -versus- R_i curves have been noted for R_i in the range of 40–55%. The most significant improvement in the hyperfiltration characteristics of cellulose acetate was attained with the 1:4:1 block copolymer. Flux of 17 gfd at 350 psi and $R = 93\%$ was obtained in short-term tests for a 0.1*N* feed solution. Long-term tests did not reveal any flux or salt rejection decline for membranes in which poly(acrylic acid) was complexed with phosphoramidic groups grafted onto Celgard.

INTRODUCTION

In an earlier publication,¹ the dynamic formation of ionically charged membranes on asymmetric cellulose acetate supports was described. Charged membranes, consisting of quaternized polyamines, were formed by pressure filtering a dilute polyelectrolyte solution through partially annealed cellulose acetate membranes which already displayed some salt rejection.

It was suggested¹ that the important criteria in membrane formation were (i) a binding interaction between the polyelectrolyte and the support which is aided by multiple contacts within a tortuous pore, and (ii) matching of the support pore size with some molecular dimension of the polyelectrolyte in solution.

In the present study of negatively charged polyelectrolytes, these criteria were investigated in greater detail through the comparison of weak and strong polyacids of various molecular weights, as well as block copolymers of mixed weak and strong polyacids. To examine the supposition that long-term stability of the membrane is governed by the strength and number of interactions with the polyelectrolyte, a noncellulosic support was grafted with groups which strongly complexed the charged macromolecule.

Knowledge of the electrical transport characteristics of ionically charged systems is obviously of great interest. Recently,^{2,3} measurements of the hy-

perfiltration streaming potentials have been used to determine the *in situ* electro-osmotic coefficients and transport numbers in "homogeneous" polyelectrolyte membranes. The electro-osmotic coefficient is directly related to important membrane properties such as the volume fractional water content and the Donnan effective charge density. In addition, the transport number reflects the ionic selectivity of the membrane and is thereby indicative of the mechanism of salt rejection. To aid in the elucidation of these aspects of dynamic membrane systems, the hyperfiltration streaming potentials were measured.

EXPERIMENTAL

Polyelectrolytes

Poly(acrylic Acid) (PAA). Poly(acrylic acids) of $\bar{M}_w \simeq 5 \times 10^4$ (Acrysol A-1, Rohm and Haas), $\bar{M}_w \simeq 1.5 \times 10^5$ (K-102, Goodrich Chemicals), and $\bar{M}_w \simeq 1.3 \times 10^5$ (Borden Chemicals) were used in the experiments.

Poly(styrenesulfonic Acid) (PSSA) and Poly(vinylsulfonic Acid) (PVSA). Poly(styrenesulfonic acid), sample #T-407, obtained from the Dow Chemical Corp. had a $\bar{M}_w \simeq 1.5 \times 10^4$ (from viscosity measurements in 0.5N NaCl). Poly(vinylsulfonic acid) was obtained from Dr. Y. Sinnreich of this laboratory; its \bar{M}_w derived from ultracentrifuge measurements was found to be 1.4×10^4 .

Block Copolymers (PAA/PSSA/PAA). Anionic polymerization was used in the preparation of block copolymers of styrene and ethyl acrylate.⁴ The latter monomer was purified by repeated distillation over α -methylstyrene dianion in order to remove impurities responsible for premature termination of the polyacrylate blocks.

A solution of dry styrene (0.2 mol in 250 cc THF) was added slowly *in vacuo* to the vigorously stirred solution of the initiator (2.5×10^{-3} mol of α -methylstyrene dianion in THF). The course of polymerization can be followed spectrophotometrically.⁵ After 1 hr at room temperature, the UV spectra taken on samples of the reaction mixture indicated that practically all styrene monomer was converted into a bifunctional "living" polystyrene, while the concentration of the "living" ends remained constant.

The reaction mixture was then cooled to -90°C , and freshly purified ethyl acrylate was added. Upon the addition of the second monomer, the characteristic yellow color due to the styryl carbanions vanished immediately. After 6 hr at -90°C , a block copolymer was precipitated by the addition of methanol. For the anionically prepared block copolymers having "living" polymers as intermediates, it is customary to determine their composition from the known amounts of monomers added.⁶ However, in the case of acrylic monomers, some spontaneous terminations do take place even at -90°C . A compositional analysis was, therefore, based on NMR data. The phenyl proton peaks at τ 2.95 and 3.4 and peaks of methylene protons next to oxygen at τ 5.88 (*q*) were taken as a measure for the amount of polystyrene and poly(ethyl acrylate), respectively, present in the copolymer. A triplet at τ 8.75 due to the methyl protons could also be clearly seen in the spectra of the copolymers; however, it was sitting on a very broad signal owing to the methylene and methine protons of the backbone chain and its integration could be misleading.

The molecular weights of thus obtained copolymers derived from their intrinsic viscosity in THF were in good agreement with values derived on the basis of the initial ratio of styrene to initiator and of the polystyrene to poly(ethyl acrylate) ratios derived from the compositional NMR analysis.

The copolymer was hydrolyzed by refluxing in 0.5*N* KOH in methanol and sulfonated at 0°C with a solution of 1% Ag₂SO₄ in 100% H₂SO₄. After 15 min, the reaction mixture was poured into ice water, filtered, and dialyzed in the absence of light to remove traces of Ag⁺. In some cases, traces of colloidal silver were found in the dialyzate. Such solutions were subjected to several hours of ultracentrifugation, and the copolymer was freeze dried. Potentiometric titrations of the thus obtained polyacids indicated that both the ratios between the SO₃H and —COOH groups and their overall concentrations were within 10% of the stoichiometric values.

Membrane Preparation

Asymmetric cellulose acetate supports were prepared as previously described.¹ The standard procedure for the preparation and testing of dynamic membranes was to filter, at 200 psi, a pH 4, 0.1% solution of polyelectrolyte in 0.1*N* KCl. This operation was carried out on at least five different supports of known flux and salt rejection, whose initial salt rejections covered the range of 20–80%. At approximately 30-min intervals, the salt rejection was measured until it was observed to have stabilized. The rejection of copolymers of PAA/PSSA and of PSSA was followed by UV absorption at 262 μ . The rejection was always found to be within 97–100%.

Porous, phosphorylated polypropylene films were obtained by chlorosulfonating Celgard (Celanese Plastics Corp.) and reacting the film with a 2% solution of *N*-tetramethyleneimine-*N'*,*N''*-bis(dimethyl)phosphoramidate in acetone for 24 hr at room temperature. The membranes were then washed with water and immersed for 24 hr in a 2% aqueous solution of PAA.

Membrane Adsorption Experiments

Cellulose acetate membranes (215 \pm 15 mg, wt. fraction H₂O = 0.62 \pm 0.02) were placed in separate sealed tubes, with 25 cc of a 0.1% polyelectrolyte solution of pH 4 and 3.5 for PAA and PSSA, respectively. After shaking for eight days, the membranes were washed with \sim 10 cc water, placed in 4 liters deionized water for 24 hr, and equilibrated for 10 min with 25 cc 0.1*N* NaCl solution whose ²²Na⁺ activity was 2.5 \times 10⁵ counts/ml-min. The membranes were rinsed with \sim 10 cc water and given two 15-min washings in 500 cc distilled water. The remaining radioactivity was counted for 2 min in a Packard Scintillation Counter. Blank trials performed on all the membranes prior to the adsorption experiments showed that the average total count declined to 50–70 counts/min (\sim twice the background) after two 15-min washes, and was indistinguishable from the background after a further 48-hr wash.

To test the effect of the diffusion of the polyelectrolyte into membrane on its salt rejection, a membrane whose initial salt rejection was 40% was allowed to equilibrate with a 0.1% solution of 1:4:1 copolymer in 0.1*N* KCl at 25°C. At various times the membrane was removed, rinsed with a few cm³ of distilled water, and tested for salt rejection with 0.1*N* KCl.

Adsorption Experiments on Powdered Cellulose Acetate

One-gram samples of Eastman 298-10 cellulose acetate powder (identical to that used in the membrane preparation) were placed in stoppered 100-cc Erlenmeyer flasks with 40 cc 0.1% copolymer in 0.1*N* KCl at pH 4. After shaking for the required number of hours, the powder was centrifuged down and the UV adsorption at 262 μ of a sample of supernatant was measured, using 0.1*N* KCl at pH 4 as a reference.

Hyperfiltration Testing and Streaming Potential Measurements

With the exception of long-term tests, the hyperfiltration and streaming potential measurements were carried out in mechanically stirred cells described previously.⁷ The long-term tests were carried out on a loop with a circulating feed in which the Manton-Gaulin pump provided an estimated linear velocity of 60 cm/sec.

Streaming potential measurements were made with Ag/AgCl electrodes and a Fluke 845-R high-impedance voltmeter whose output was fed into a 0–10 mV recorder. After pressurizing the system at 350 psi for approximately 40 min to allow the potential, flux, and salt rejection to stabilize, the pressure was lowered to 200 psi in 25-psi intervals, remaining at each pressure for approximately 2 min, which was more than sufficient time for the potential to stabilize. The pressure was then returned to 350 psi and the process repeated.

In several early experiments, it was found that when one Ag/AgCl electrode of a previously matched set was exposed to a cationic polyelectrolyte in solution, large asymmetry potentials were developed which were quite stable. With the electrode of the feed compartment chosen as the positive electrode, the streaming potential for a cation exchange membrane was negative as required by eq. (3) (see later). The sign of the asymmetry potential, with the feed solution electrode exposed to polyelectrolyte, was positive, so that the absolute potential was shifted to less negative values. However, measurements with electrodes which had been deliberately exposed to polyelectrolyte showed that the slope of E versus ΔP (i.e., the electro-osmotic coefficient) was unchanged. For this reason, the Ag/AgCl electrodes were only mounted in the hyperfiltration cell after the dynamic membrane had been formed and the cell thoroughly rinsed (with the dynamic membrane left in place). However, even this procedure could not absolutely assure that the electrode in the feed was not affected by small amounts of polyelectrolyte washed from the membrane back into the fresh feed solution. It is because of this element of uncertainty that the calculation of the apparent transport number during hyperfiltration, τ_+ , has been left out.

All salt rejections quoted have been calculated according to the usual definition:

$$R = 1 - (c''/c') \quad (1)$$

where c'' is the product concentration and c' is that of the feed. Chloride analyses were made by means of an automated chloride titrimeter (American Inst. Corp., Silver Springs, Md., U.S.A.).

Electron Microscopy

The dynamic membrane of the 1:4:1 PAA/PSA/PAA copolymer was first stained with uranyl acetate solution in order to clearly identify the position of

the polyelectrolyte. The membrane was then taken through a series of five ethanol/water baths until the water had been exchanged for pure ethanol with no visible damage to the membrane. This process was then followed by several Epon epoxy/carbon tetrachloride mixtures until the membrane was in pure Epon 812. In spite of the attempt to preserve the membrane structure, considerable shrinkage could be observed, and this is undoubtedly due to the fragile nature of the partially cured structure.

After curing at 45°C for 48 hr, the membrane was repotted in Epon and sectioned. The micrographs were obtained with a Phillips 300 electron microscope. Although the central region of the sample had been obviously collapsed by the potting operation, the salient feature of interest, i.e., the disposition of the polyelectrolyte in terms of depth of penetration, could be quite readily observed. An unusual feature of the micrograph is the porous nature of the "skin," and it is likely that this is an artifact of the preparation, perhaps due to the ethanol/water exchange. Observations on the structure of partially cured membranes have never, to our knowledge, been reported, although a number of studies⁸⁻¹⁰ have been made on the fully cured entities. This is probably due to the difficulties involved in preserving an artifact-free structure of the partially cured membrane.

RESULTS AND DISCUSSION

Poly(acrylic acid) (PAA), poly(styrenesulfonic acid) (PSSA), poly(vinylsulfonic acid) (PVSA), PAA/PSSA copolymers, and PAA/PSSA/PAA block copolymers were tested for their ability to form dynamic membranes on partially cured cellulose acetate (CA) supports. Previous work¹ indicated that the formation of a dynamic membrane may strongly depend on the initial salt rejection of the support. Hence, supports characterized by the initial limiting salt rejections (R_i) ranging from 10% to 80% were used in experiments with the polyelectrolytes summarized in Table I. (Salt rejection is defined as $R = 1 - (c''/c')$, where c'' is the concentration of the product solution and c' the concentration of the feed.) The limiting salt rejections (R_f) of the membranes after treatment with the polyelectrolyte solution were measured. It was assumed that the dynamic membrane formation is indicated by $\Delta R = R_f - R_i \gg 0$.

TABLE I
Polyelectrolytes Tested for Dynamic Membrane Formation

Polyelectrolyte	Molecular weight \bar{M}_w	Dynamic membrane formation
Poly(acrylic acid) (PAA)	150,000	+
Poly(acrylic acid)	50,000	+
Block copolymer of PAA/PSSA/PAA (1:4:1)	63,000	+
Block copolymer of PAA/PSSA/PAA (1:10:1)	150,000	—
Random copolymer of PAA/PSSA (2:1)	25,000	±
Poly(styrenesulfonic acid) (PSSA)	15,000	—
Poly(vinylsulfonic acid) (PVSA)	14,000	—

TABLE II
Partitioning of Poly(acrylic Acid) and Poly(styrenesulfonic Acid)
Within Partially Cured Cellulose Acetate Supports

Initial membrane salt rejection, %	Adsorbing polyelectrolyte	Counts remaining after final wash $\times 10^{-2}$
10.6	PAA	26.0
15.0	PSSA	2.8
30.0	PSSA	4.7
33.4	PAA	6.2
54.3	PAA	7.4
58.3	PSSA	2.8
90.0	PSSA	2.3
92.3	PAA	16.1

Changes 20–50% in respect to the original flux take place as a result of formation of a dynamic membrane. Usually higher values of ΔR were accompanied by a larger decline in flux. Membranes display, however, some flux decline (with no change in salt rejection) also in experiments prior to exposure to the polyelectrolyte solutions. Therefore, plots of ΔJ_v versus $(J_v)_0$ were not considered to be very significant.

The treatment with the strong acid polyelectrolytes, PSSA and PVSA, did not yield any significant increase in salt rejections, and $\Delta R < 3\%$ were obtained for any R_i . This was also the case for the random PSSA/PAA copolymer and for the 1:10:1 PAA/PSSA/PAA block copolymer. On the other hand, both the poly(acrylic acids) and the 1:4:1 PAA/PSSA/PAA block copolymer displayed dynamic membrane formation. The effect was even more pronounced for the 1:4:1 copolymer than for the poly(acrylic acid) homopolymer.

This phenomenon may be understood in terms of the interaction between the polyelectrolyte and the wall of the pore into which the polyelectrolyte must diffuse in order to form a dynamic membrane. Cellulose acetate is a weak cation exchanger¹¹ and possesses a negative zeta potential. Hence, the repulsion between the field of the double layer of the strongly dissociated negative poly-

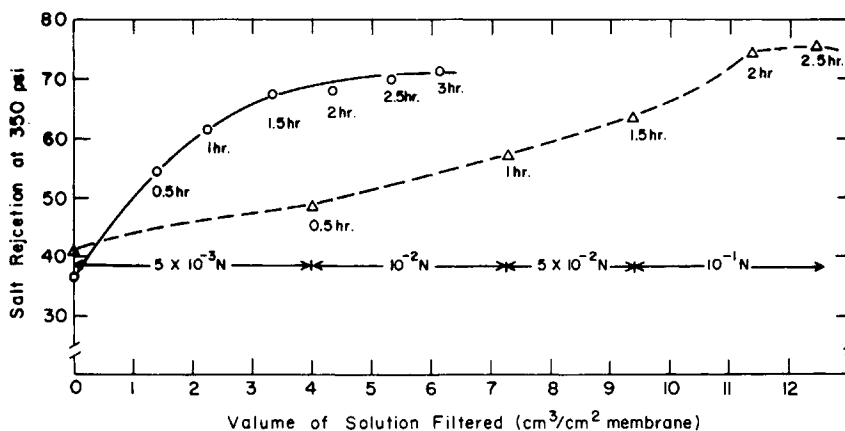


Fig. 1. Effect of time and concentration of KCl on dynamic membrane formation: (O) 1:4:1 copolymer dynamic membrane formed at 0.1N KCl; (Δ) 1:4:1 copolymer membrane formed at different concentrations of KCl.

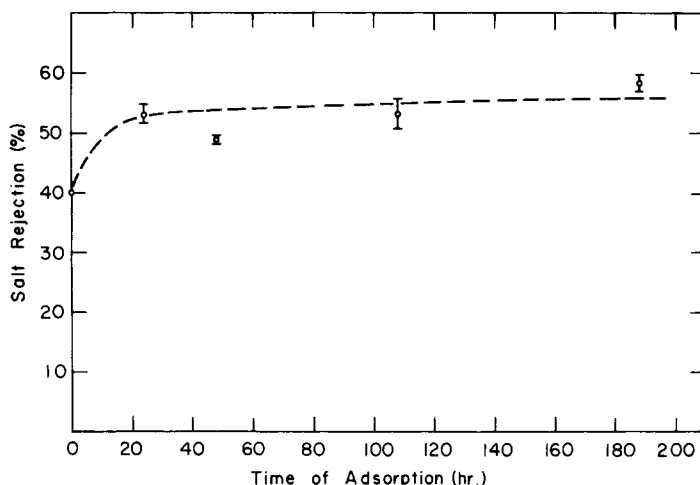


Fig. 2. Effect of diffusive partitioning on membrane salt rejection as a function of time. The polyelectrolyte solution contained 0.1% of the 1:4:1 copolymer in 0.1*N* KCl, 25°C.

electrolyte and that of the pore wall prevents the polyelectrolyte from entering all but the largest pores. On the other hand, PAA is only partially dissociated at pH 4 and can also interact favorably with the support wall by hydrogen bonding. This is confirmed by equilibrium partitioning experiments with PAA and PSSA with CA supports of different initial salt rejection (Table II). Without entering at this time into details with regard to the effect of the membrane cure state on the partitioning of PAA, it is clear that considerably more PAA can penetrate into the membrane than PSSA.

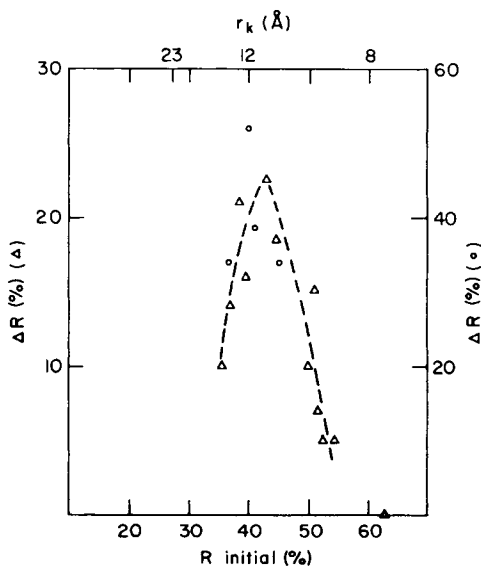


Fig. 3. Increment in salt rejection due to dynamic membrane formation with 1:4:1 copolymer vs. initial salt rejection of the CA microporous support. Feed concentration, 10^{-1} *N* NaCl; pressure, 350 psi; (Δ) results after 0.5 hr of standard treatment (left-hand ordinate); (O) results at the plateau (cf. Fig. 1) (right-hand ordinate).

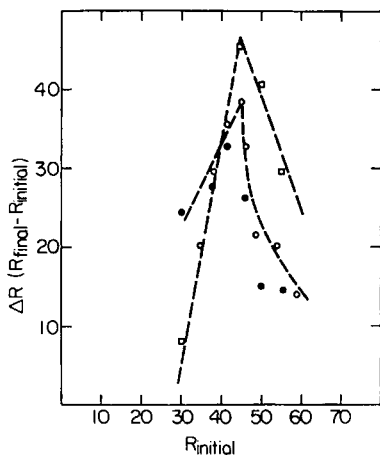


Fig. 4. Increment in salt rejection due to dynamic membrane formation vs. initial salt rejection of the CA microporous support. Feed concentration, $10^{-2}N$ NaCl; pressure, 350 psi; (\square) PAA/PSSA/PAA (1:4:1) block copolymer, $\bar{M}_w \approx 6 \times 10^4$; (\circ) PAA, $\bar{M}_w = 5 \times 10^4$; (\bullet) PAA, $\bar{M}_w = 1.5 \times 10^5$.

The effect of the double layer is also felt with the 1:4:1 block copolymer which did form a dynamic membrane. In Figure 1, the effect of different ionic strengths of KCl electrolyte on dynamic membrane formation is shown. One should also note that in the absence of supporting electrolyte in the polyelectrolyte solution, no dynamic membrane formation could be detected. Thus, even with the block copolymer, some contraction of the double layer about the PSSA section is necessary before the PAA block can drag the PSSA into the pore.

The effect of the drag exerted on the polyelectrolyte by the water flow can also be demonstrated. A comparison of the salt rejection as a function of the volume of polyelectrolyte solution which passed through the membrane (Fig. 1) with the equilibrium diffusion of polyelectrolyte (Fig. 2) clearly indicates that the water flow drives the polyelectrolyte into the membrane.

In displaying the results of dynamic membrane formation on CA supports, we have found it useful to plot ΔR versus R_i . Sarbolouki and Miller¹² have shown

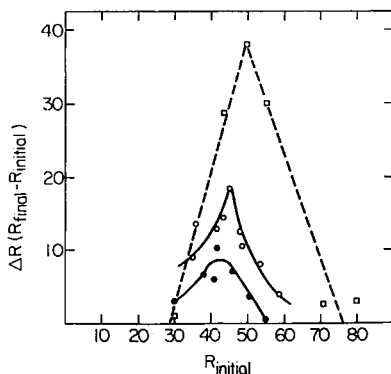


Fig. 5. Increment in salt rejection due to dynamic membrane formation vs. initial salt rejection of the CA microporous support. Feed concentration, $10^{-1}N$ NaCl; pressure, 350 psi; (\square) PAA/PSSA/PAA (1:4:1) block copolymer, $\bar{M}_w \approx 6 \times 10^4$; (\circ) PAA, $\bar{M}_w = 5 \times 10^4$; (\bullet) PAA, $\bar{M}_w = 1.5 \times 10^5$.

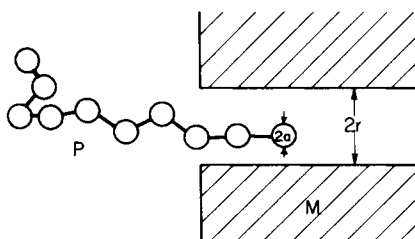


Fig. 6. Schematic representation of a polyelectrolyte molecule diffusing into a pore. The balls represent the volumes of rotation of the monomer units. P = Polyelectrolyte molecule; M = pore wall.

that the initial salt rejection can be correlated to an average equivalent pore size in the asymmetric skin. Thus, a plot of ΔR versus R_i shows the change in salt rejection as a function of the average pore size; and in Figure 3, results are shown for the 1:4:1 copolymer. We may note that the pronounced maximum obtained is independent of the formation time (or volume of polyelectrolyte solution), which indicates that the same phenomenon (which we have identified as diffusion into surface pores) is responsible throughout for the increase in salt rejection. Fairly sharp maxima were also obtained for plots of ΔR versus R_i for PAA (Figs. 4 and 5) and in the previous study of polycations.¹ Drioli et al.¹³ also found a similar effect for aluminum chloride dynamic membranes on partially cured cellulose acetate, which indicates the generality of the phenomenon.

If one accepts the values for the pore radii determined by Sarbolouki and Miller,¹² then all the dynamic systems studied to date display a maximum effect for membranes whose average pore radius is between 10 and 14 Å. Considering the range of molecular weights covered by the various polyelectrolytes tested, such a pore radius can only be interpreted in terms of the basic polyelectrolyte monomer segment, rather than a molecular radius of gyration or a mean end-to-end distance. The concept of a polyelectrolyte entering a pore and diffusing into it in a worm-like fashion (Fig. 6) may seem to contradict the prevailing concepts of the hydrodynamics of polymer molecules in solution which tend to regard some geometric characteristic of the entire molecule as the diffusing entity. However, additional evidence that it is the individual monomer segment which is important has also been found in the study of the partitioning and diffusion of polystyrene into porous glass.¹⁴

The following experiment also reinforces our conclusions: A solution of 1:4:1 copolymer (1 mg/cc) was filtered through a membrane with an initial salt rejection of 39.5% until the salt rejection had risen to 73%, during which time 48 cm³ of solution passed the membrane. The membrane was then reversed and 0.5 liter H₂O was used to backwash polyelectrolyte which had entered the support. Upon retesting the membrane, the salt rejection had dropped back to 34%, indicating that all the polyelectrolyte had been removed. UV spectrophotometric determination of the copolymer in the backwashings (concentrated to a volume of 5 cc) indicated that 0.9 mg of 1:4:1 PAA/PSA/PAA copolymer had been taken up per cm² of membrane. A parallel experiment with PSSA neither indicated dynamic membrane formation (in agreement with previous trials) nor could any PSSA be detected in the backwashings. It should also be noted that adsorption experiments with 1:4:1 PAA/PSSA block copolymer on powdered CA do not

TABLE III
Adsorption of 1:4:1 PAA/PSSA/PAA Block Copolymer on Cellulose Acetate Powder

Concentration, g/100 cc $\times 10^4$	Optical density of stock solution at 262 m μ	Optical density of solution in contact with CA	
		70 hr	153 hr
0.5	0.34	0.38	0.38
2.5	0.72	0.77	0.77
4.0	0.99	1.00	1.00
5.0	1.19	1.23	1.23
7.5	1.50	1.58	1.58

reveal any indication of surface adsorption phenomena (Table III) so that the partitioning effect is due solely to the pore geometry. This was also true of experiments conducted with polycations.¹

Defining a partition coefficient K_p such that

$$K_p = \frac{\text{mass of polyelectrolyte entering membrane}}{\text{mass of polyelectrolyte brought up to membrane surface}} \quad (2)$$

we obtain a value of 0.188.

Assuming a statistical partitioning¹⁵ of rigid spheres of radius r_s by cylindrical pores of radius r_p (we may regard each monomer segment as a bead or sphere), we obtain

$$K_p = 2 \left(1 - \frac{r_s}{r_p}\right)^2 - \left(1 - \frac{r_s}{r_p}\right)^4 \quad (3)$$

This, of course, assumes that the hydrodynamic drag due to the water flow does not change the "flexibility" of the sphere. If r_s for the polyelectrolyte also includes a few water molecules usually considered to be strongly bound to the charge site, a value between 7 and 12 Å may be considered reasonable for a molecule containing both PAA and PSSA units. Thus, r_p is found from eq. (3) to be 10–20 Å, which is in good agreement with the values suggested for the average pore size in the range of initial salt rejection in which the maximum is observed.

It should be noted that an alternate model of dynamic membrane formation by polyelectrolytes has been previously proposed by Blatt et al.,¹⁶ which predicts the formation of a polyelectrolyte gel layer at the membrane feed interface as the result of concentration polarization.

In such a case, the contribution of the gel layer to the salt rejection of the membrane will depend on the relative salt selectivities of the support and gel. If one supposes that the support has a lower salt permeability than the gel, then the gel will effectively govern the salt rejection and an increase in salt rejection will be observed subsequent to the formation of a dynamic membrane. The contribution of the salt rejection of the gel to the overall salt rejection of the membrane will decrease with the increase in the salt rejection of the support. However, its absolute value would not be expected to *decrease* when the gel layer is deposited on a more tight support. Thus, the existence of sharp maxima in the ΔR -versus- R_i plots is strong evidence against such a mechanism playing a significant role in the systems under discussion.

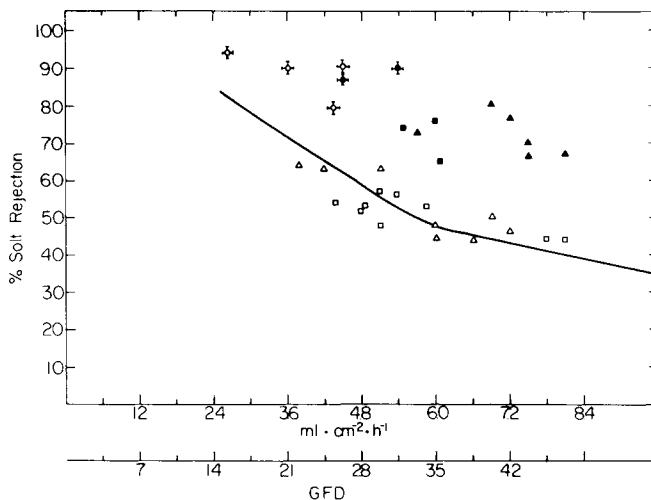


Fig. 7. Rejection vs. flux at 350 psi: (●, ○) PAA/PSSA/PAA (1:4:1) block copolymer; (■, □) PAA, $\bar{M}_w = 1.5 \times 10^5$; (▲, △) PAA, $\bar{M}_w = 5 \times 10^4$. Closed symbols are for $10^{-2}N$ NaCl; open symbols for $10^{-1}N$ NaCl feed. Solid line represents untreated, partially cured CA.

Membrane Performance and Characterization

The salt rejection-versus-flux characteristics of the dynamic systems for 0.01 and 0.1N NaCl feed solutions at 350 psi are shown in Figure 7. For comparison, the average behavior of 65 partially cured cellulose acetate (CA) membranes has been drawn as a solid line. The standard mean deviation of the salt rejections from this line is $\pm 2.7\%$.

For the $10^{-2}N$ NaCl feed, the copolymer and the poly(acrylic acid) dynamic membranes of either molecular weight are significantly improved in comparison with the untreated CA. However, for the 0.1N NaCl feed, the PAA rejection has dropped to the point that, in terms of overall membrane performance, there is no significant difference between the dynamic membrane and untreated CA.

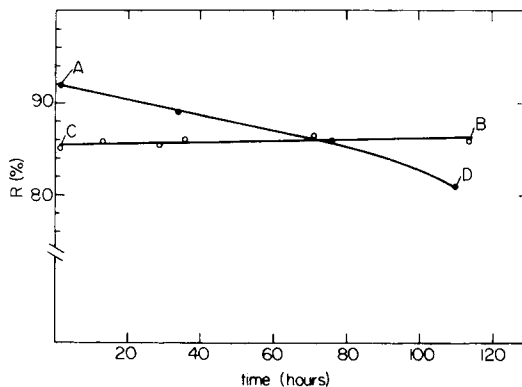
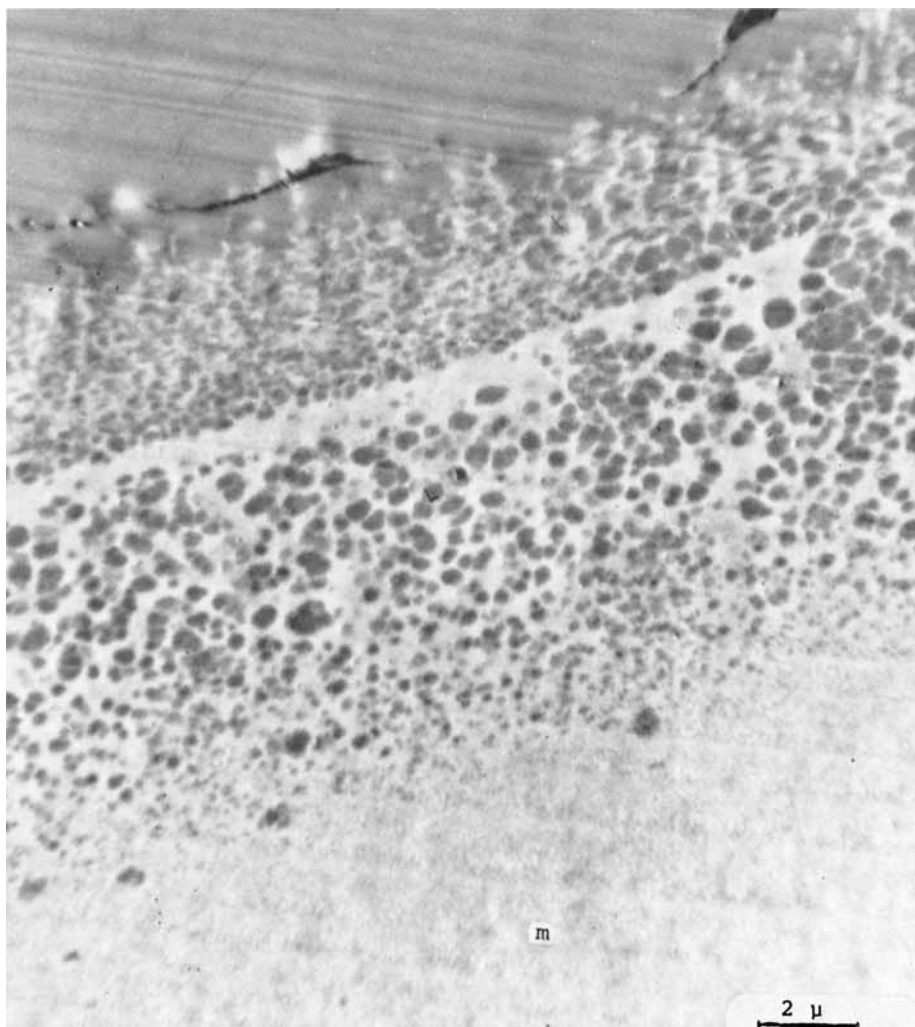


Fig. 8. Stability of dynamically formed membranes as a function of time. Hyperfiltration experiments at 1000 psi: (●) PAA/PSSA/PAA block copolymer on CA support; flux at A, 20 GFD; flux at D, 22.5 GFD; (○) PAA, $\bar{M}_w = 5 \times 10^4$ adsorbed and complexed to a phosphorylated Celgard support; flux at C, 19 GFD; flux at B, 20 GFD.

This is in marked contrast to the copolymer salt rejection which retains its advantage over untreated CA even at the 0.1N NaCl feed concentration.

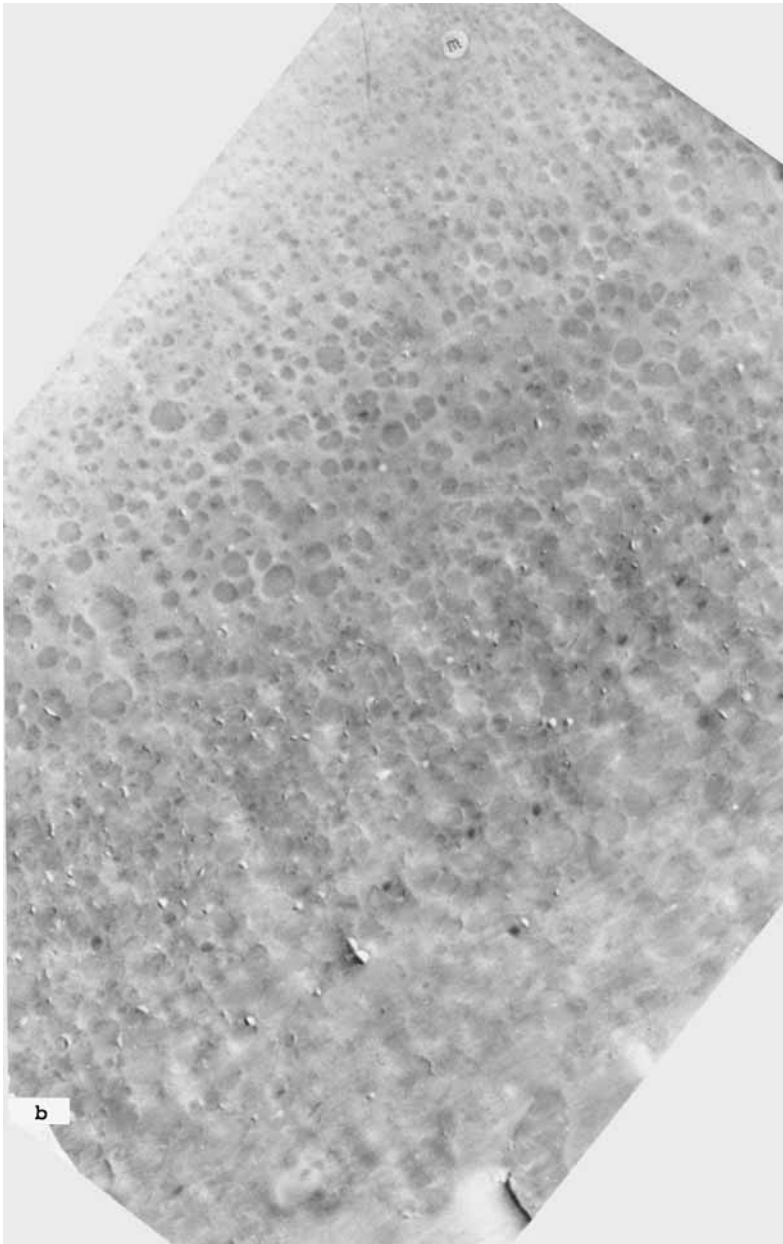
The improvement of the salt rejection through the replacement of PAA by the block copolymer may be partially due to the fact that in the latter, the concentration of free ions is probably higher than in the former due to the presence of the strong acid regions. On the other hand, the interaction with the pore interface facilitating the penetration of the polyelectrolyte molecule into the pore is provided by the poly(acrylic acid) blocks.

Although the initial properties of the copolymer dynamic membranes tested appeared quite promising for brackish water desalination, the long-term tests were less so (Fig. 8). Within 100 hr, the rejection decreases considerably with a corresponding increase in the flux. Electron micrographs of a copolymer dynamic membrane reveal that the polyelectrolyte slowly diffuses past the "skin"



(a)

Fig. 9 (continued)



(b)

Fig. 9. (a) Electron micrograph of sectioned CA dynamic membrane, upper layer. (b) Electron micrograph of sectioned CA dynamic membrane, bottom layer. m = Fragment of the middle layer.

and penetrates well into the larger pores in the substructure (Fig. 9). It is this movement which shows up as a small but significant polyelectrolyte leak in the formation step (see Membrane Formation) and leads to a time dependence in its properties.

TABLE IV
Hyperfiltration Performance of Some Dynamic PAA Membranes
Formed on Treated Celgard Support

Chloro- sulfonation reaction time, min	Polyelectrolyte adsorbed	Water flux, GFD		0.01 <i>N</i> Salt rejection, %
		400 psi	1000 psi	
5	PAA, 150	32	59	57
10	PAA, 150	—	170	44
10	PAA, 50	—	20	85.5
20	PAA, 50	—	35.5	72

The problem of the stability of the dynamic polyelectrolyte membrane also appeared in the previous work on positively charged membranes¹ and is probably the most serious obstacle to the practical application of the systems discussed here. Ideally, it seems that the forces holding the polyelectrolyte on the surface of the pore wall should be in the nature of a covalent bond or at least involve strong complexation. Recent investigations have shown that poly(acrylic acid) forms strong, water-insoluble complexes with phosphoramides.⁴ To test their effectiveness in dynamic membranes, the surface of a microporous polypropylene support, Celgard, was chemically modified to include phosphoramidate groups

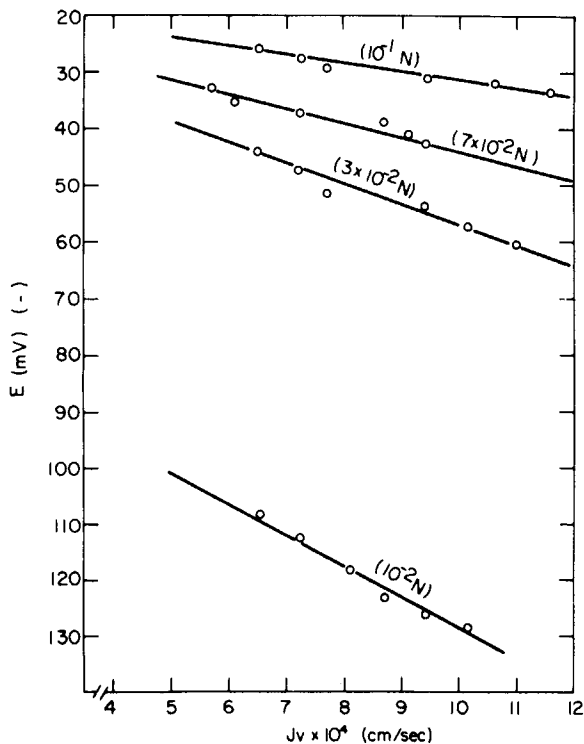


Fig. 10. Streaming potential vs. flow rate for PAA dynamic membranes. Feed solutions, 10^{-2} - $10^{-1} N$ KCl.

TABLE V
Salt Rejection and Electro-osmotic Coefficients
of Polyacid Dynamic Membranes on Cellulose Acetate Supports

Polyelectrolyte adsorbed	Membrane no.	Initial membrane salt rejection, %	Feed concentration, (moles/liter) $\times 10^2$	Salt rejection, %	Electro-osmotic coefficient, $\beta F, 1/F$
PAA/PSSA/PAA copolymer (1:4:1)	1	43	1.9	86	2.80
			20.8	76	2.35
			1.2	92	2.90
	2	55	3.3	88	1.45
			7.8	84	0.96
			14.5	74	0.67
			1.4	94	3.80
	3	40	3.2	94	1.80
			6.9	93	1.50
1.1			77	4.90	
PAA-50,000	4	40	3.2	65	1.85
			7.0	57	1.35
			8.9	51	1.00
PAA-150,000	5	42	1.2	74	2.44
			3.1	62	1.32
			6.7	62	0.86
			10.2	53	0.74

(see Experimental section) and immersed in a 2.0% solutions of PAA. Membranes were thoroughly washed and tested under hyperfiltration conditions.

As one might have expected, the salt rejection was not as large as in membranes formed on CA supports (Table IV) since in the microporous support used in this experiment the pores are slits $\sim 1000 \text{ \AA}$ long¹⁷ which vary between ~ 150 and 300 \AA in width. Therefore, the polyelectrolyte geometry within the pore bore no resemblance to the case of cellulose acetate. However, the flux and rejection stability seemed to be very satisfactory (Fig. 8).

Additional information regarding the dynamic membrane can in principle be obtained from the hyperfiltration streaming potential, which is related phe-

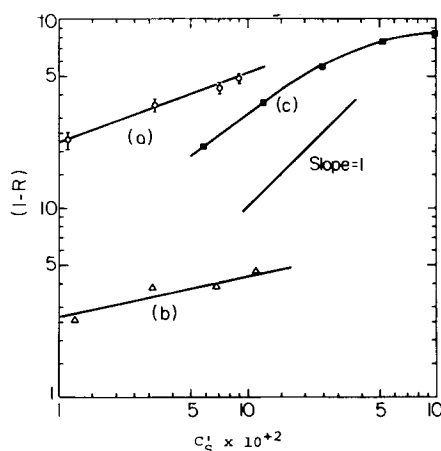


Fig. 11. Log-log plots of $(1 - R)$ vs. C_s' for the "dynamic" and for the "homogeneous" polyelectrolyte membranes. Concentration range, 10^{-2} – $10^{-1}N$ KCl. (a) Dynamic membrane with PAA; $\bar{M}_w = 5 \times 10^4$ at R_i max. (b) Dynamic membrane with PAA; $\bar{M}_w = 1.5 \times 10^4$ at R_i max. (c) Polylysine/collodion "homogeneous" membrane from ref. 24 (the concentration scale shifted one decade to the right).

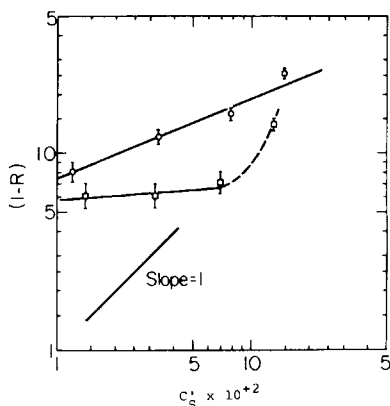


Fig. 12. Log-log plots of $(1 - R)$ vs. C_s' for the PAA/PSSA/PAA block copolymer dynamic membranes. Concentration range, 10^{-2} – $10^{-1}N$ KCl; (O) initial salt rejection of CA, 50%; (□) initial salt rejection of CA, 55%.

nomenologically^{2,3} to the electro-osmotic coefficient β and the transport number of the positive ion τ_+ . For Ag/AgCl measuring electrodes,

$$E = \frac{-\beta}{L_p} J_v - \frac{2RT}{F} \tau_+ \ln \gamma'_\pm c' / \gamma''_\pm c'' \quad (4a)$$

or

$$E = -\beta(\Delta P - \sigma \Delta \pi_s) - \frac{2RT}{F} \tau_+ \ln \gamma'_\pm c' / \gamma''_\pm c'' \quad (4b)$$

Some typical plots of E versus J_v are shown in Figure 10, and the values obtained for electro-osmotic coefficients for different dynamic membranes at several feed concentrations are shown in Table V. The coefficients display a regular decrease with increasing feed concentration as one expects for an increase in the coion concentration in the membrane.^{2,3} However, the absolute values of βF in Table V are much larger than the 0.3–0.5 $1/F$ found for dense ion exchange membranes¹⁷ of similar salt rejection. While accurate determinations of τ_+ could not be obtained in the present study (see Experimental section), they appear

TABLE VI
Salt Rejection and Flux for Dynamic Membranes
Formed from 1:4:1 PAA/PSSA/PAA Copolymer^a

Membrane no.	0.1N NaCl		0.05N MgCl ₂		0.1N MgCl ₂	
	Salt rejection, %	Flux, GFD	Salt rejection, %	Flux, GFD	Salt rejection, %	Flux, GFD
1 ^b	93.0	17 ± 1	97.6	16 ± 1	97.1	15 ± 0.5
2 ^c	78.0	14 ± 1	84.7	16 ± 1	83.6	15 ± 0.5

^a Feed solutions, NaCl and MgCl₂; pressure, 350 psi.

^b Before treatment: R_i for 0.1N NaCl, 39%; flux, 30 ± 3 GFD.

^c Before treatment: R_i for 0.1N NaCl, 46%; flux, 27 ± 3 GFD.

to be as low as 0.4–0.7, in contrast to values very close to unity for dense ion exchangers.

A reasonable explanation for the electro-osmotic coefficient and transport number behavior is to regard the dynamic membrane as a composite polyelectrolyte structure, with a dense selective layer located within the fine pores of the "skin" followed by a loose polyelectrolyte gel trapped within the larger pores in the substructure, as Figure 9 suggests. For membranes which are in series,¹⁸ the overall electro-osmotic coefficient is a weighted average of the coefficients in addition to a nonlinear additive term which can in some circumstances be the leading term. Since we have no objective basis on which to assign individual values to all the necessary transport coefficients in our postulated layers, a detailed calculation is not warranted. However, previously obtained values for electro-osmotic coefficients in loose polyelectrolyte membranes³ were $\sim 2/F$, which is the correct order of magnitude even without nonlinear additive effects. In addition, the similarity of the electro-osmotic coefficients for dynamic membranes possessing different salt rejections reinforces the conclusion that these coefficients characterize a secondary gel-like layer common to all. Hence, the electrokinetic data seem to be consistent with the two-layer picture for the dynamic membrane which was suggested by Figure 9.

The estimates of the cation transport number are between those expected for a neutral membrane and a cation exchanger. Indeed, the behavior of the salt rejection in these membranes does not fit the pattern expected of the mechanism of either a charged or neutral membrane. Although the salt rejection does decline as the concentration is increased, the decline is less than expected due to Donnan exclusion. The slopes of plots of $\log(1 - R)$ versus the log of the feed concentration are substantially less than unity (Figs. 11 and 12) which was also the case for PAA dynamic membranes formed on hydrous zirconium oxide.^{19,20}

The ambivalence of the copolymer dynamic membrane between a neutral and charged salt rejection mechanism is demonstrated by the behavior toward divalent cations such as Mg^{2+} . For a cation exchange membrane, the rejection of divalent cation is usually substantially less than that of a monovalent, while for a neutral membrane the situation is reversed. In Table VI, it may be seen that the rejection of a divalent cation such as Mg^{2+} is just slightly greater than that of NaCl.

In the past, several workers^{21–23} have suggested that charged membranes with low water contents display salt exclusion much higher than predicted by a classical Donnan mechanism. The dynamic membranes investigated to date behave as members of this group in which this, as yet undefined, mechanism is very much in evidence. The development of a predictive model for such systems must remain a future challenge.

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