Mosaic Membranes for Desalination

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Mosaic Membranes for Desalination

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FOREWORD

This is one of a continuing series of reports designed to present accounts of progress in saline water conversion and the economics of its application. Such data are expected to contribute to the long-range development of economical processes applicable to low-cost demineralization of sea and other saline water.

Except for minor editing, the data herein are as contained in a report submitted by the contractor. The data and conclusions given in the report are essentially those of the contractor and are not necessarily endorsed by the Department of the Interior.

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I. Abstract

Charge mosaic membranes are amphoteric membranes of composite structure, i.e., these membranes consist of small regions of anion selective material interspersed with small regions of cation selective material. In order to be useful in piezodialysis, each ionic region has to extend substantially uniformly from one surface of the membrane to the other one. For practical application the membranes must possess sufficient mechanical strength to withstand pressures up to 1600 psi.

Three different approaches were investigated in the preparation of charge mosaic membranes, all of them being based on the incompatibility of different polymers. In the first approach phase separation in block copolymer films composed of styrene and vinyl pyridine was utilized. Films with regularly arranged phases were obtained which could be chemically transformed into cationic and anionic domains. The smallness of the domains (average domain width of the order of several hundred Angstroms) prevented them to extend undisturbed through the film thickness. Piezodialysis effects were not observed with these membranes in their amphoteric state, very likely for two reasons, improper film morphology and formation of extended regions of poly-poly salts on the boundaries between the anionic and cationic domains.

In a second approach phase separation was utilized in films prepared from blends of random copolymers containing cross-linkable butadiene sequences. Films with very regularly arranged phases were obtained. The individual domains extended undisturbed through the film thickness because of their large sizes (average domain width of the order of several hundred microns). In spite of proper film morphology, this preparation technique remained unsuccessful because of insufficient cross-linking across the phase boundaries. Upon swelling of the anionic films in water, the films ruptured at the phase boundaries or at least pinholes formed.

Films possessing sufficient mechanical strength in their amphoteric form were obtained only after reducing the average domain dimensions to the order of several microns by blending copolymers of higher butadiene contents. One of these films composed of sulfonated polystyrene and quaternized polyvinyl pyridine exhibited a very weak piezodialysis effect with an enrichment factor in the range of 1.03 to 1.05 at a feed concentration of 1.2 wt.-% NaCl (at 1000 psi). The low value of the enrichment factor was very likely a consequence of incomplete separation of both polyelectrolyte precursors due to their relatively high butadiene contents.

In a third approach blending of block copolymers with homopolymers was investigated. This method seems to be the most promising approach for the preparation of charge mosaic membranes. By blending styrene-vinyl pyridine block copolymers

with homopolystyrene, films were obtained with block copolymer domains of several hundred microns diameter, regularly arranged in the polystyrene matrix. After quaternization these domains swelled in water to spherical shapes, protruding on both sides of the film, without the development of cracks or pinholes on the phase boundaries. Indeed, under reverse osmosis conditions, these composite films exhibited salt rejections identical to those as obtained from films of the same block copolymer. Unfortunately, block copolymers of proper molecular weight for supplying the anionic centers in such a composite membrane were not available, and therefore, this promising preparation of charge mosaic membranes still lacks its ultimate test.

II. Introduction and Scope of Work

Reverse osmosis and piezodialysis are both membrane processes for water desalination which are practically identical from an engineering point of view. The processes differ in the relative transport of water and salt through the membrane, and therefore, depend on the structure of the latter. For reverse osmosis membranes with very low salt transport have to be selected, whereas for piezodialysis the membranes have to exhibit strong coupling between ion and water transport. Ideal membranes for piezodialysis are charge mosaic membranes. Such kind of membranes are composed of discrete, uniform domains of cationic and anionic nature which have to extend continuously from one surface of the membrane to the other. Although ideal structures of charge mosaic membranes with optimum effectiveness in piezodialysis can be derived from theoretical considerations, actual membrane synthesis meets considerable difficulties.

A simple way to prepare charge mosaic membranes consists of manually arranging the individual domains, such as cation and anion exchange beads, in a checkerboard fashion, and fixing these beads in a common matrix.[1] In an alternative approach, cation and anion exchange membranes are alternatingly stacked and glued or fused together.[2] After slicing the stack, charge mosaic membranes are obtained composed of stripes of anionic and cationic domains. Both methods do not allow the preparation of large sized membranes.

Charge mosaic membranes of unlimited size could be obtained by utilizing the general incompatibility of polymers. Films composed of two different polymers will exhibit phase separation in nearly all cases provided the polymers exceed a limiting molecular weight. In order to obtain membranes composed of oppositely charged polyelectrolytes, separated into discrete domains, salt formation between the oppositely charged polymer chains has to be prevented. By selecting two polymers in such way that one of them can be transformed into a polycation and the other one into a polyanion, each chemical transformation of one polymer not affecting the other polymer, a charge mosaic membrane will result from the phase separated film. The main problem of this method concerns the necessary cross-linking of the membrane, because of both kinds of domains being water soluble in their ionic forms.

A. Membranes from Block Copolymers

The first approach toward the preparation of charge mosaic membranes utilized the phase separation as it occurs in block copolymer films. The best method for the preparation of block copolymers being free of homopolymers is by means of an anionic polymerization mechanism. The monomers selected were styrene (S) and 2-vinyl pyridine (2VP) both polymerizing well under anionic conditions although the sequence of monomer addition being restricted because of the nucleophilic attack of the styryl carbanions on the P2VP chains. In order to make block copolymers which contain a P2VP sequence sandwiched between two PS blocks coupling reactions with terminal diiodo or dibromo compounds were applied.

Selection of the polymer combination PS and P2VP had the advantage that both polymers are strongly incompatible and that both of them can be chemically transformed relatively easily into strong polyelectrolytes. The P2VP can be quaternized by treating the film in the gas phase with methyl bromide, and the PS can be sulfonated with sulfur trioxide complexes in chlorinated hydrocarbons. The P2VP, especially in its quaternized formed, is not attacked by this sulfonation method. The normal sulfonation procedure for PS employing concentrated sulfuric acid together with a silver catalyst is not applicable with these composite films because they dissolve under this condition.

The block copolymers were cast either from benzene or tetrahydofuran and yielded clear films with good phase separation as shown by electron microscopy. The anion exchange membranes obtained by quaternization of the P2VP domains possessed good mechanical strength, the hydrophobic PS domains serving as physical cross-links. Investigation of flux and rejection properties of these anion exchange membranes indicated the existence of a general relationship between both properties. These investigations were then extended to include other types of cationic as well as anionic membranes which were obtained either by grafting of polyethylene films or from vulcanized, butadiene containing copolymers. It could be shown that for all kinds of ionic membranes, irrespective of charge, chemical nature of the polymer, and film morphology, the salt rejection, R_S, and the water permeability, K_1, are uniquely related by an equation of the form

$$K_1 = A \exp(-BR_S)$$

where A and B are constants. This equation could be interpreted by a simple model based on the difference between the transport volumes for mobile coions and water.

The electric repulsive forces between a fixed ion and a mobile coion decreases the transport volume of the latter, thus creating a transport depletion of salt flux relative to the water transport. This relationship, generalizing the behavior of ionic membranes in reverse osmosis, is of importance in the preparation of charge mosaic membranes. Matching the cationic and anionic domains in a composite film with respect to their salt rejecting properties automatically matches the domains with respect to their water permeabilities.

The preparation of charge mosaic membranes from block copolymer films composed of PS and P2VP domains was successful as far as the amphoteric nature of the films is concerned. In these membranes both polymeric blocks are water soluble and the membranes are held together only by salt formation between the sulfonic acid groups and the quaternized pyridinium ions in the phase boundaries where an intimate blending of PS and P2VP occurs to a limited extent. Dynamic-mechanical measurements on block copolymer films usually indicate the presence of a third phase with an onset of chain mobility different from both homopolymer domains. This third phase can be assigned to an intimate mixture of both components in the phase boundaries. The absence of chemical cross-links in the quaternized and sulfonated S-2VP block copolymer films was indicated by their solubility in concentrated acids.

Under reverse osmosis conditions, the sulfonated and quaternized S-2VP block copolymer films showed high flux due to their high degree of hydration, and very low salt rejection. Salt enrichment in the effluent, indicative for a piezodialysis effect, was not observed with these membranes. In their behavior under reverse osmosis conditions the membranes strongly resembled poly-poly-salt membranes.

The absence of a piezodialysis effect seems to be caused by an improper morphology of the block copolymer films. Although such films possess distinct and regularly separated phases, the phase separation is restricted and phase dimensions cannot exceed limiting values given by the molecular weights of the individual blocks. With a layer arrangement of the phases, the average thickness of a layer remains in the range of several hundreds of Angstroms and corresponds to the average coil dimension of the polymer block. In extremely thin films of only a few hundred Angstroms thickness phase separation takes place in form of narrow ribbons each ribbon apparently extending undisturbed through the film thickness as indicated by electron microscopy. Electron micrographs of such ultrathin films reveal a morphology resembling an intricate two dimensional maze. Unfortunately, such thin films do not survive the necessary chemical treatments without damage.

In thicker films (10 microns and thicker) which can be easily handled, the two dimensional maze changes into a three dimensional one, i.e., such films resemble in their morphology a stack of a great number of ultrathin films. Although each phase still proceeds continuously through the thickness of the film, the domains are now strongly entwined and interlocked. This morphology does not comply with the one demanded for piezodialysis membranes.

One might now consider to approach the demanded morphology by increasing the phase dimensions in the block copolymer films. It seems reasonable to assume that overlapping of different phases can be avoided if the average phase dimensions become comparable with the film thickness. This assumption was shown to be true by the good resolution in the electron micrographs of ultrathin films of only several hundred Angstroms thickness. Immediately it can be seen that film thickness can be increased this way only by a factor of ten with respect to the ultrathin films. A film with a thickness of a few tenths of a micron would already demand molecular weights of several millions for the individual blocks of the copolymer. With such large domain sizes an additional complication arises. One has to consider that each polymeric block inside a domain is anchored only by its ends at the phase boundaries. For a molecular weight of one million this would correspond to a cross-link density of only 0.02%. Films with such low cross-link densities swell extremely and possess hardly any mechanical strength.

A further complication arises with respect to film hydration in the case of charge mosaic membranes derived from block copolymers of the A-B type. As long as only the P2VP domains are quaternized film strength is supplied by the hydrophobic PS domains. Swelling can proceed only until the swelling pressure equals the stress generated in the PS network. In charge mosaic membranes derived from PS and P2VP (A-B type) this limitation does not exist. As pointed out previously, the sulfonated and quaternized PS-P2VP membranes are held together only by ionic bonds between the sulfonic acid groups and the pyridinium ions in the phase boundaries. This ionic cross-linking is a dynamic one, and its degree depends on the salt concentration the membrane is equilibrated with. Imbibed salt ions exert a shielding effect on the polyions in the phase boundaries thereby decreasing the number of interfacial cross-links. In addition the change of the hydrophobic PS network into a hydrophilic one increases the swelling capability of the P2VP domains, and as a consequence decreases the salt rejecting properties of the latter.

In order to overcome this difficulty the domains were chemically cross-linked. Unfortunately, both polymers PS and P2VP cannot be easily cross-linked. Peroxide curing and gamma-irradiation were not successful and resulted in polymer degradation. Cross-linking of the P2VP domains was accomplished by partial quaternization with 1,5-dibromopentane. The PS phase could be partially cross-linked by treating the film, swollen in dichloroethane, with a solution of aluminum trichloride in ether. The resulting charge mosaic membrane showed lower flux than a non-cross-linked one, but still piezodialysis was not observed.

Although there are strong indications that the smallness of the domains in block copolymer membranes is responsible for the absence of a piezodialysis effect, these membranes possess an additional structural feature detrimental to the desired effect. The cationic and anionic domains in films of A-B type block copolymers are separated by a thin layer of poly-poly-salt of high salt permeability. A better membrane structure would be one where this layer were replaced by a phase of a hydrophobic polymer. Such membrane morphology demands the synthesis of block copolymers composed of three different blocks, two blocks representing the anionic and cationic precursors, respectively, both separated by a block representing a matrix polymer. The matrix polymer must be inert in all chemical reactions by which the ionic centers are introduced. This condition is easily met by the quaternization reaction but not by the sulfonation. Furthermore, in anionic polymerization the basicities of all three carbanions involved have to be such that the desired block sequence is feasible, e.g., a combination of S, 2VP, and methyl methacrylate (MMA) can be obtained only in the following sequences S-2VP-MMA or MMA-2VP-S-2VP-MMA depending whether mono or dianionic initiators are used. Regardless whether the PS or the PMMA block is used as the anionic precursor, anionic and cationic domains will always remain adjacent in the phase separated film.

In an attempt to make films from ternary block copolymers the combination S, 2VP, and isoprene (IP) was used in the arrangement 2VP-S-IP. It was intended to use the PS as the matrix, and to selectively sulfonate the PIP with an ether complex of chlorosulfonic acid. This attempt failed because of the films being soluble in ether.

Even with the use of proper ternary block copolymers one might doubt whether useful charge mosaic membranes can be obtained. A priori there exists no argument why cationic and anionic precursors should not form adjacent phases in the films even if properly separated by a third polymer block in the copolymer chain.

B. Membranes from Blends of Random Copolymers

With block copolymers the domain size in the phase separated films has to remain in the molecular range due to the covalent bonds between the polymer components. With both polymer components being present as homopolymers the average domain size in the phase separated films increases approximately by a factor of ten thousand. Blends of homopolymers dissolved in a common solvent yield films with very regularly arranged phases of the size of several hundred microns. These domains are much larger than the film thickness, and therefore, extend undisturbed from one side of the membrane to the other. Films from polymer blends are ideal for charge mosaic membranes with respect to their structure but they lack the necessary cross-links to make them water insoluble after introduction of the ionic centers. Such films have to be chemically cross-linked after phase separation has taken place. This means that both polymers which are blended have to contain groups which can be cross-linked under mild conditions.

In the second approach to prepare charge mosaic membranes with sufficiently large domain sizes blends of random copolymers were applied, each of the copolymers containing a low percentage of butadiene units.

The preparation of phase separated films from copolymer blends provides a broader selection of useable polymers than film preparation from block copolymers. There remains only the obvious restriction that at least one of the components must be non-ionic. A considerable number of random copolymers, all of them containing varying amounts of butadiene, were prepared and tested (S, 2VP, MMA, methacrylic acid, 2-chloroethyl methacrylate, 2-bromoethyl methacrylate). Cross-linking was mainly performed by vulcanization with sulfur monochloride, since peroxide curing yielded relatively weak films.

Unblended films, composed of a single copolymer, yielded relatively good films with salt rejections in the range of 40-80%. The corresponding flux properties of these films were in agreement with the predicted values derived from the general relationship between salt rejection and flux for ionic membranes. Complications arose with phase separated films from copolymer blends. Very good and regular phase separations were obtained but these composite films possessed very low mechanical strength after being transformed into charge mosaic membranes. When swollen in water the films developed numerous cracks and pinholes at the phase boundaries. This seems to be caused by the difference in the rates of swelling for both kinds of domains.

The disastrous effect of uneven swelling of composite films could be observed best on a film where both copolymer components were cast side by side in form of stripes. The film was composed of a methacrylic acid (MA) and a 2VP copolymer. Upon placing the quaternized and vulcanized film into dilute sodium hydroxide solution, the P2VP stripes swelled much faster than the PMA stripes. The film expanded evenly in the direction perpendicular to the stripes but after a short time the P2VP stripes started to wrinkle along the phase boundaries and then to break off locally.

Blending of S and 2VP random copolymers of higher butadiene contents resulted in films with smaller domain dimensions in the range of 10-20 microns. These films, after vulcanization, possessed sufficient mechanical strength for being tested in their amphoteric form. One of these films exhibited a very weak piezodialysis effect with a salt enrichment factor in the range of 1.03-1.05 at a feed concentration of 1.2 wt.-% NaCl. The low degree of salt enrichment in the permeate was very likely a consequence of incomplete separation of both polyelectrolyte precursors due to their relatively high butadiene contents which increased their miscibility. This explanation was supported by staining experiments with universal indicator.

C. Membranes from Blends Containing Block Copolymers

From the observations made on blends from random copolymers one might conclude that composite films with large domain sizes cannot be prepared because of the faster or more highly swelling phase breaking lose from the less swelling one. Although supported by the negative results obtained with chemically cross-linked films from copolymer blends this conclusion cannot be generalized. It is possible to prepare films where a strongly swelling polyelectrolyte forms discrete, large domains in a completely hydrophobic matrix polymer without the occurrence of cracks at the phase boundaries. Such films can be obtained from blends of block copolymers with homopolymers.

Already with the first block copolymers prepared from S and 2VP it was observed that films exhibited regular macroscopic phase separation if the block copolymer contained some homopolymer, usually PS, as resulting from impure polymerization conditions. Generally, these films were of low mechanical strength, and therefore, blends of block copolymers with homopolymers were not further investigated until chemical cross-linking of random copolymer blends proved unsuccessful. When the investigation of such blends was resumed it was speculated that the mechanical weakness of films of these involuntarily obtained homopolymer-block copolymer blends was caused by the low molecular weight of the homopolymer and not by the phase separation. It is obvious that under these conditions the molecular weight of the homopolymer cannot exceed its corresponding block length in the block copolymer. Indeed, blending a S-2VP block copolymer with a PS homopolymer of high molecular weight yielded a strong film with circular block copolymer domains (average diameter of about 0.3 mm) arranged in a very regular fashion. After quaternization, these domains swelled considerably in water thereby protruding in semispherical shape from both membrane surfaces. Under reverse osmosis conditions, this composite film proved to be free of pinholes, exhibiting a salt rejection equal to one of a film made solely from the same block copolymer. It seems that physical cross-links, as formed between the homopolymer and its corresponding polymer block in the copolymer, allow relaxation of stresses generated by swelling differences at the phase boundaries, thus preventing the formation of cracks.

D. Conclusions

Summarizing one can conclude from the performed investigations that composite membranes as obtained from polymer blends are most promising for the preparation of charge mosaic membranes. Such films possess an ideal morphology with respect to size and arrangement of the domains but present some problems concerning the necessary cross-linking of the membrane. The latter problem can be solved best by blending of two block copolymers with or without a common homopolymer serving as film matrix. Utilization of phase separation in films derived from one block copolymer does not seem promising because of the smallness of the domains.

III. Membranes from Block Copolymers

A. Anionic Polymerization

Block copolymers can be prepared best by anionic polymerization methods.[3-7] Under stringent experimental conditions termination reactions remain absent and the system consists of living polymer chains. Chain propagation is usually very fast and proceeds until complete consumption of the monomer at least for all practical purpose. The living chain ends of the first polymer initiate the polymerization of a second monomer with formation of block copolymers. Provided chain terminating impurities were not introduced in the system with the second monomer the resulting block copolymer is completely free of homopolymer. By sequentially feeding different monomers copolymers of corresponding block sequence result. The molecular weight distributions of anionically prepared polymers are usually very narrow provided both the initiation step is considerably faster than the propagation step, and the monomer addition is performed in such way that each living chain end has access to the same number of monomer units at any time. The narrow molecular weight distribution of the individual blocks is greatly enhancing the formation of well defined domains in the phase separated films.

One main problem in the anionic preparation of block copolymers for use as charge mosaic membranes is given by the restrictions in the choice of monomers and the possible arrangements of blocks. Monomers possessing groups attackable by carbanions cannot be polymerized at all or only with low yields of poorly defined products. The great differences in the basicities of the polymeric carbanions derived from different monomers severely restricts the possible arrangements of different blocks. Carbanions of high basicity, e.g., as derived from S or α-methyl styrene (MeS) will initiate the polymerization of all other monomers whereas the carbanion of MMA has no initiating capabilities. The high basicity of some carbanions also causes some other restrictions in block sequencing. A living P2VP chain initiates the polymerization of S but the resulting poly tyryl carbanions attack the P2VP chains with the result of cross-link formation. chain branching, and chain degradation.

For the preparation of charge mosaic membranes from block copolymers a combination of two monomers has to be selected where both of them are easily convertible into polyelectrolytes by means of compatible reactions. A strong base polyelectrolyte can be obtained in the simplest way from P2VP by quaternization with gaseous methyl bromide. This reaction is a very mild one whereas all other chemical means for generating cationic centers in a membrane demand repeated swelling and deswelling of the latter (e.g., chloromethylation of PS and subsequent amination). A strong acid polyelectrolyte can be obtained only by sulfonation of PS. Since it was intended to combine a strong acid with a strong base in the charge mosaic membrane, the combination of S and 2VP was selected. Although P4VP quaternizes faster than P2VP (detrimental effect of alkyl substitution in 2-position), the latter monomer had to be chosen because of P4VP becoming insoluble in tetrahydrofuran (THF) already at relatively low molecular weights. The sensitivity of P2VP toward nucleophilic attack by strongly basic carbanions demanded the use of coupling reaction for the preparation of block copolymers of sequence S-2VP-S.

In the present investigation anionic polymerization procedures were only considered as preparative means for the synthesis of block copolymers. Therefore, experimental techniques were developed which allowed to carry out the polymerizations without involving unduly complicated glassware. The first version of the polymerization equipment is shown in Fig. 1. Fused glassware with break seals was not used. As demanded, the polymerization vessel could be connected by a narrow stainless steel tube through selfsealing serum caps with the storage vessels containing solvent, catalyst, monomers, and coupling agent. During these transfer procedures a small positive nitrogen pressure was maintained in all vessels. Two separate nitrogen supply lines were used, one connected with the polymerization vessel, the other one with the storage vessels. In each line the nitrogen was purified by being passed through a heated column of BTS catalyst (Badische Anilin und Soda Fabriken) followed by a column of silica gel. The pressure could be adjusted by means of mercury filled bubblers.

The polymerization vessel was a round bottom flask of 500 ml volume with an O-ring joint on the main neck and possessing a narrow side neck which was closed by a selfsealing serum cap. The flask was connected over the O-ring joint to a Lew-type magnetic stirrer assembly which also allowed to connect the flask either with the vacuum line or with the nitrogen supply. Monomers and catalyst solutions

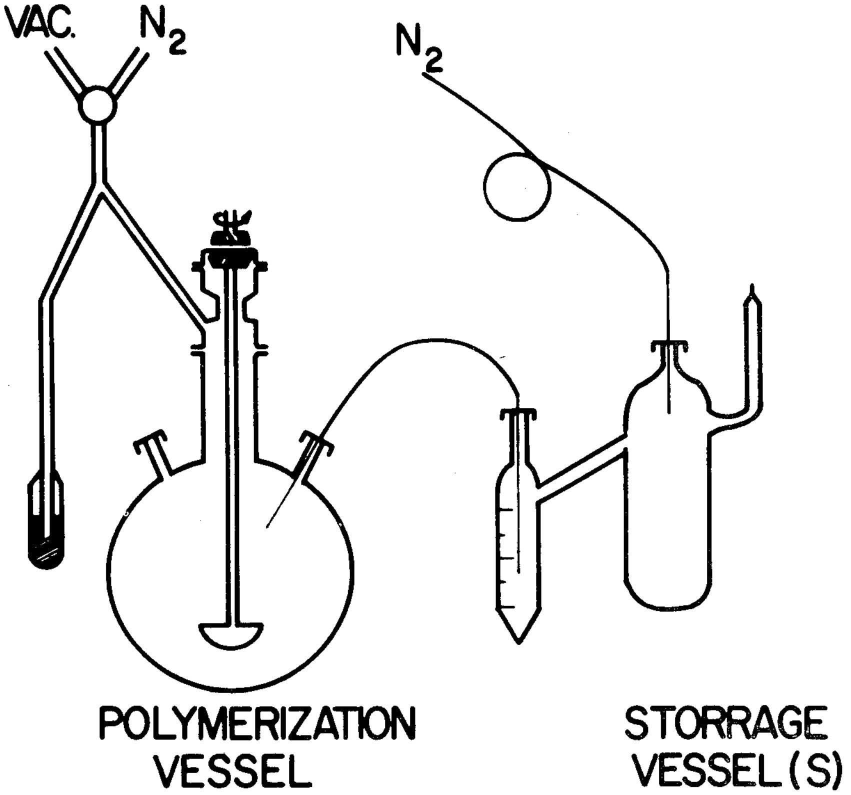


Figure 1 - Schematic drawing of anionic polymerization equipment.

were stored in similar vessels consisting of a storage bulb and a calibrated tube connected by a side arm. For the catalyst solutions the bridging side arm contained a coarse fritted disc. Storage bulb and calibrated tube had narrow necks at their tops closed with serum caps. An additional side arm of the storage bulb was initially connected with a small round bottom flask and served for distilling the monomers into the storage bulb under high vacuum. After distillation this side arm was fused off and the storage bulb was connected with the nitrogen line by pushing a syringe needle on the end of a Teflon tubing through the serum cap on the storage bulb. Previous to the final high vacuum distillation of the monomers the latter were treated with sodium and benzophenone until the blue color of the ketyl prevailed. This treatment did not initiate the polymerization of S but with 2VP some polymerization took place. The storage vessel for the THF was a simple round bottom flask without a calibrated tube, the amount of solvent being determined by weighing. The THF was distilled into the storage vessel under high vacuum after treatment either with sodium ketyl or naphthalene sodium. The latter purification treatment was preferred since the slightest trace of benzophenone in the solvent deactivates the growing chains.

The catalyst used were Na or K naphthalene, Na or K α-methylstyrene tetramere, and butyllithium. The sodium compounds were prepared by reacting sodium mirrors with THF solutions of naphthalene or MeS. For the potassium compounds a liquid Na-K-alloy was used. The reactions were carried out under nitrogen in the large bulb of the storage vessel. The fritted disc in the side arm allowed filtration of the catalyst solution from metal particles. For the butyllithium catalyst a commercial solution was diluted with purified benzene. All catalyst solutions were titrated immediately before use.

At the start of a polymerization, the polymerization vessel was connected to the stirrer assembly, flamed under vacuum, and filled with nitrogen. The solvent vessel with freshly distilled THF was connected to the nitrogen line over a Teflon tubing and a needle through the serum cap. A long stainless steel needle was then inserted through the serum cap and rinsed with a few milliliters THF pressured through. The other end of the needle was then pushed through the serum cap on the side neck of the polymerization vessel, and the latter was filled with solvent. The catalyst solution was introduced in a similar way. The flexible nitrogen connection allowed filling of the calibrated tube by tilting the storage vessel. The stainless steel feed tube was first rinsed with catalyst solution before being connected with the polymerization vessel through the serum cap of the side neck. The flow of the catalyst solution was started by a small pressure difference which was then equalized, and further flow regulation was accomplished by raising or lowering the storage vessel. With the use of narrow gauge stainless steel tubes this arrangement proved to be very sensitive for the regulation of the flow rates. The feeding of the monomers and the coupling solution was accomplished in the same way.

The first part of the catalyst solution was used to remove impurities from the solvent. Colored catalyst solutions were added dropwise until the first barely discernible color tint prevailed. In the case of butyllithium a small amount of 1,1-diphenylethyelene or styrene was used as an "indicator." In most of the experiments the polymerization vessel was first rinsed with dilute catalyst solution before the final filling with solvent. The spent rinsing solution could be removed with a needle through the side neck. In the same way polymer samples could be taken during different stages of the polymerization.

During the later stage of the investigations block copolymers of butadiene and isoprene were prepared. These very volatile monomers necessitated some change in the experimental design since serum caps did not provide a sufficiently tight seal. The second version of the polymerization equipment is shown in Fig. 2. The main changes in the new design consisted of placing stopcocks behind each serum cap and by connecting all vessels with O-ring joints to a common manifold for vacuum and nitrogen. This new arrangement was not as versatile as the old one but it allowed to work under high vacuum conditions.

The storage vessels for catalyst, monomers and coupling agent were of similar design as previously but possessed a three-way stopcock at the top of the calibrated tube. The storage bulb was without neck and was filled under high vacuum over a side arm which later was fused off. After filling purified nitrogen was admitted. For storage the contents were completely transferred into the storage bulb which was kept in dry ice. Under this condition the stopcock grease was not attacked by solvent vapors and storage time could be extended to several weeks of intermittend use.

At the start of the polymerization solvent was distilled through the manifold into the polymerization vessel under high vacuum. The solvents were predried with calcium hydride and finally treated with a metalorganic compound (potassium naphthalene for THF and potassium ketyl for benzene). After distillation nitrogen was admitted. The storage vessels were connected to the manifold and the space under the serum cap as evacuated and then filled with nitrogen. The transfer from the storage vessels to the polymerization flask was again performed with a narrow stainless steel tube leading through the three-way stopcock. After rinsing the tube it was introduced through the side arm of the polymerization vessel. The

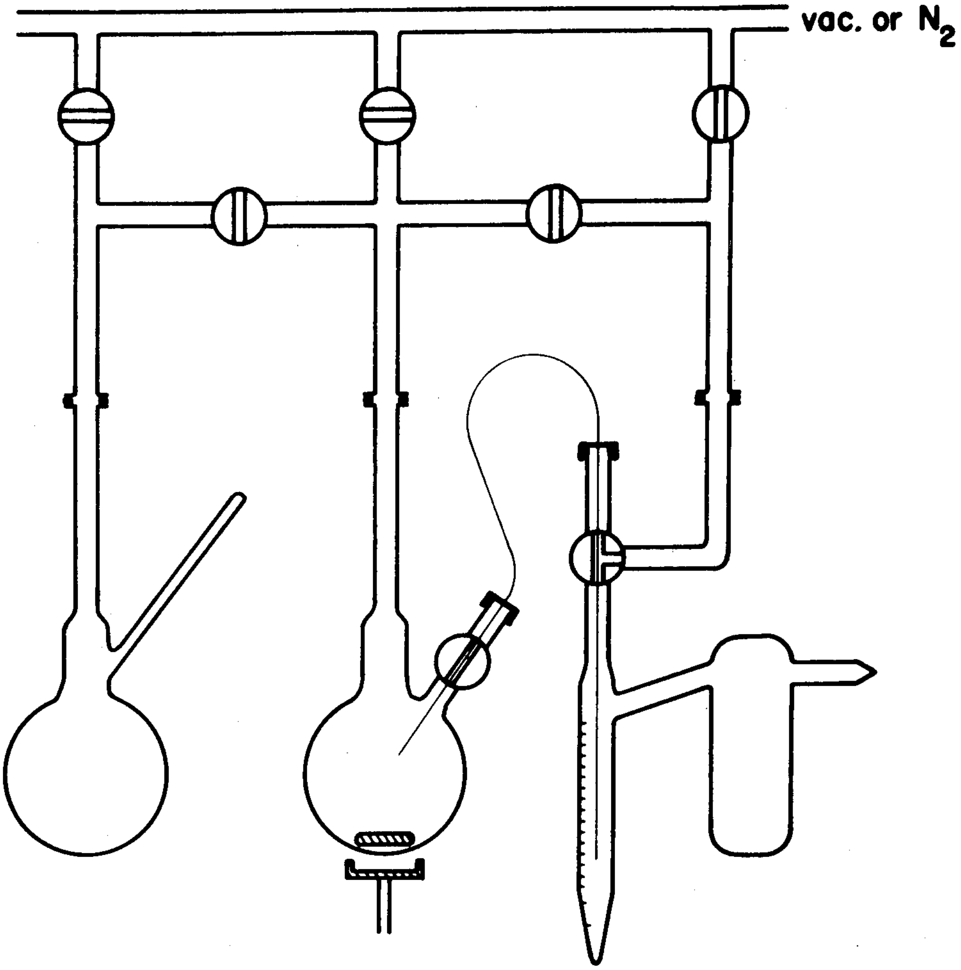


Figure 2 - Schematic drawing of polymerization equipment used in high vacuum work.

flow was started and maintained by a small driving pressure which could be adjusted by proper manipulation of the different stopcocks of the manifold.

As an illustrative example the preparation of an alternating block copolymer (R-117) is described in detail. The polymerization equipment was assembled and flamed in vacuum. After cooling under purified nitrogen about 50 ml of dry THF were introduced in the flask followed by 5 ml of sodium naphthalene solution. The stirrer was set at high speed to splash the solution vigorously over the walls of the polymerization vessel. The spent catalyst solution was then removed with a stainless steel tubing under nitrogen pressure.

After the polymerization vessel was freed from adsorbed impurities, a weighed amount of THF was added under nitrogen followed by dropwise addition of sodium naphthalene solution under stirring. The addition of sodium naphthalene was continued until the very first indication of a faint green color prevailed and did not fade for at least half an hour. At this point the final amount of catalyst solution was added, corresponding in the present case to 2 ml (0.58mmoles sodium naphthalene as determined by titration). The polymerization vessel was cooled to 0°C and the styrene was added very slowly by proper adjustment of the driving nitrogen pressure. With the first drops the green color of the sodium naphthalene changed immediately to orange. A total of 15 ml styrene corresponding to 13.6 g was added very slowly.

About 15 min after all of the styrene was added a sample of the polymerization solution was taken. The PS was precipitated, filtered, and dried. Complete consumption of the styrene was found. The intrinsic viscosity of the PS in benzene was 0.260 dl/g corresponding to a molecular weight of 47,000 which was identical with the molecular calculated from the amounts of catalyst and monomer used.

After taking the PS sample the polymerization flask was cooled to -40°C and the 2VP (a total of 15 ml corresponding to 14.7 g) was added in the same way as the styrene. The orange color of the styryl carbanions changed with the first drops to the dark red color of the vinyl pyridyl carbanions. Again 20 min were allowed for the polymerization to reach completion and then a sample was taken. The polymer was precipitated in heptane filtered, and dried. Complete monomer conversion had occurred. The intrinsic viscosity of the block copolymer in benzene was 0.321 dl/g.

To the solution of living polymer in the polymerization flask a dilute solution (0.077mmoles/ml) of diiodopentane was added dropwise in three portions of 1.14 ml each. After each portion samples were taken, the polymer later isolated and its solution viscosity in benzene determined. The intrinsic viscosity values of the three samples were found to be 0.541, 0.640, and 0.645, respectively. These values indicate a rather efficient coupling reaction.

All of the anionically prepared homo and block copolymers are compiled in Tables I and II. The abbreviations used in both tables are explained in Table III. The polymerization experiments reported in Table I were carried out with the equipment shown in Fig. 1. The solvent was THF in all experiments except for some of the polymerizations involving methacrylonitrile. In the column showing polymer compositions the kinds of monomers and their arrangement in the block copolymer are indicated. In parenthesis the relative block lengths are shown. Polymerization experiments summarized in Table II were carried out with the equipment shown in Fig. 2. In the last column of this table number average degrees of polymerization are given as calculated from the amounts of catalyst and monomers used. In Table III the abbreviations used in both of the previous tables are compiled in order of appearance.

B. Block Copolymers Exclusive of the Combination S-2VP

Practically for all work on block copolymer membranes polymers composed of S and 2VP were used. In addition to their preparation a considerable number of other kinds of block copolymers were prepared which were not investigated beyond preliminary tests. These block copolymers will be shortly discussed.

1. Block Copolymers Containing 4VP

Poly(4-vinyl pyridine) is insoluble in THF if its molecular weight exceeds a rather low limiting value.[9] In all polymerization experiments heterogeneous systems formed except for one case, R-18. In this polymerization a very high molecular weight block copolymer resulted which remained soluble in the THF solution at -50°. The isolated polymer was soluble only in a THF-alcohol mixture and exhibited very good phase separation. Because P4VP being considerably more reactive in quaternization than P2VP it was of interest to prepare block copolymers containing 4VP. All further trials were not successful in obtaining a homogeneous polymerization system and the one exceptional case cannot be explained.

2. Block Copolymers Containing MAN

These block copolymers were prepared with the intention to obtain composite films possessing an unreactive matrix polymer. The polymerizations were not successful, colored polymers were obtained, especially in combination with 2VP. The film forming properties of all polymers were not promising.

3. Polymers of p-ClS

p-Chloro and p-bromo styrene can be polymerized anionically.[10] With p-fluoro styrene polymerization did not take place. The homo PpClS was prepared for use as a polyfunctional initiator. The polymer can be very easily metalated with sodium naphthalene in THF yielding polycarbanions which are reactive in subsequent anionic polymerizations.[11,12] It was intended to use these polycarbanions for the prepara-

TABLE I

Compilation of Anionically Prepared Homo and Block Copolymers

Sample No.	Catalyst	Polymer Composition	Molecular Weights and Remarks
R-1	BuLi	S-2VP (1:1)	
R-2	BuLi	S	
R-3	BuLi	2VP	27,000
R-4	BuLi	S-2VP (1:1)	
R-7	BuLi	S-2VP (1:1)	170,000
R-9	BuLi	S-2VP (1:1)	
R-11	BuLi	S-2VP-S (1:1:1)	260,000
R-13	BuLi	S-2VP-S (1:2:1)	150,000
R-14	BuLi	S-2VP-S (1:2:1)	300,000
R-16	BuLi	S-4VP (5:1)	heterogeneous
R-17	BuLi	S-4VP(10:8)	"
R-18	BuLi	S-4VP (1:1)	homogeneous
R-19	BuLi	S-4VP (1:1)	heterogeneous
R-20	BuLi	S-2VP (1:1)	
R-21	BuLi	S-2VP/4VP	heterogeneous
R-23	BuLi	S	48,000
R-24	Na-MeS	$(-S-2VP-)_n$ (1:1)	
R-26	Na-MeS	$(-S-2VP-)_n$ (1:1)	
R-27	Na-Naphth	$(-S-2VP-)_n$ (1:1)	
R-28	Na-Naphth	S	
R-29	Na-Naphth	$(-S-2VP-)_n$ (1:1)	
R-31	Na-Naphth	$(-S-4VP-)_n$ (1:1)	
R-32	K-Naphth	$(-S-2VP-)_n$ (1:1)	
R-33	K-Naphth	$(-S-2VP-)_n$ (1:1)	
R-34	K-Naphth	S-4VP (5:1)	Heterogeneous
R-35	BuLi	S-MAN (1:1)	
R-36	BuLi	S-MAN (1:1)	
R-37	BuLi	S-MAN (1:1)	
R-38	BuLi	S-MAN (1:1)	
R-39	BuLi	S-MAN (1:1)	
R-40	BuLi (Tol)	S-MAN (1:1)	
R-41	BuLi (Tol)	S-MAN (1:1)	
R-42	BuLi (Tol)	2VP-Man (1:1)	
R-45	BuLi	S	42,000

TABLE I (continued)

Sample No.	Catalyst	Polymer Composition	Molecular Weights and Remarks
R-46	BuLi	S	65,000
R-47	K-Naphth	S	
R-48	K-Naphth	S	690,000
R-49	Na-Naphth	S-MA	
R-50	BuLi	MeS-2VP (1:1)	
R-55	K-Naphth	MeS	
R-56	K-Naphth	2VP	
R-57	K-Naphth	MeS	
R-58	K-MeS	MeS	
R-59	BuLi	MeS-2VP (1:1)	
R-60	BuLi	2VP	
R-61	BuLi	MeS-2VP (1:1)	
R-62	K-MeS	MeS-2VP (1:1)	
R-62	K-MeS	MeS	
R-63	K-MeS	2VP-MeS-2VP (1:3:1)	
R-64	BuLi	MeS-2VP (1:1)	
R-65	K-MeS	2VP-MeS-2VP (1:4:1)	
R-67	K-MeS	S	580,000
R-103	BuLi	TDI	
R-104	BuLi	S-TDI	
R-105	BuLi	S-TDI	
R-106	BuLi	pClS	
R-107	BuLi	S-pClS (1:6)	
R-108	BuLi	S-pClS (1:1)	
R-109	K-Naphth	pClS	
G-110	K-Naphth	pClS	
R-111	K-Naphth	2VP-S-pClS-S-2VP (1:1:5:1:1)	
R-112	K-Naphth	2VP-S-pClS-S-2VP (2:1:3:1:2)	
R-113	K-Naphth	2VP-S-pClS-S-2VP (5:2:2:2:5)	
R-114	K-Naphth	$(\text{-S-2VP-})_n$ (1:1)	36,000 (PS only)
R-115	K-Naphth	$(\text{-S-2VP-})_n$ (5:2)	23,000 (PS only)
R-116	K-Naphth	$(\text{-S-2VP-})_n$ (3:2)	46,000 (PS only)
R-117	K-Naphth	$(\text{-S-2VP-})_n$ (1:1)	47,000 (PS only)
R-118	K-Naphth	$(\text{-S-2VP-})_n$ (1:1)	7,000 (PS only)
R-119	K-Naphth	2VP	110,000

TABLE I (continued)

Sample No.	Catalyst	Polymer Composition	Molecular Weights and Remarks
R-120	K-Naphth	$(\text{-S-2VP-})_n$ (1:1)	
R-121	Na-PpClS	2VP-MAN	
R-122	Na-PpClS	S	
R-123	Na-PpClS	2VP	
R-124	Na-Naphth	2VP	
R-125	Na-PpClS	S-MAN	
R-126	Na-PpClS	S-MAN	
R-127	BuLi	MAN	
R-128	Na-PpClS	S-MAN	
R-129	Na-PpClS	S-AN	
R-130	Na-PpClS	S-AN	
R-131	Na-PpClS	S-AN	
R-132	Na-PpClS	2VP	
R-133	Na-PpClS	2VP-TDI	
R-134	Na-Naphth	S	living chains reacted with p-ClBPO
R-135	Na-Naphth	TRI-S-TDI (1:10:1)	reacted with t-BuHPO
R-136	Na-Naphth	p-FS	no polymerization
R-137	BuLi	p-FS	no polymerization
R-138	BuLi	TDI	

TABLE II

Isoprene Containing Block Copolymers Prepared Anionically

Polymer No.	Catalyst	Polymer Composition	Degree of Polymerization (Calculated from Catalyst)
I-1	Li-I	I	330
IS-1	BuLi	I-S-I (1:5:1)	360
IS-2	BuLi	I-S-I (1:2:1)	1,800
IS-3	Na-Naphth	$(\text{-S-I-})_n$ (1:1)	8,000 (before coupling)
IS-4	Li_2-Cat	$(\text{-S-I-})_n$ (2:1)	1,200 (" ")
IS-5	Na-Naphth	$(\text{-S-I-})_n$ (1:1)	2,800 (" ")
IS-6	Na-Naphth	$(\text{-S-I-})_n$ (2:1)	150 (" ")
IV-1	BuLi	I-2VP-I (1:2:1)	400
IV-2	BuLi	I-2VP-I (1:2:1)	1,800
IV-3	BuLi	I-2VP (2:1)	900
IV-4	Na-S	$(\text{-I-2VP-})_n$ (1:1)	6,600 (before coupling)
IV-5	Na-S	I-2VP-I (1:2:1)	13,000
IV-6	Na-S	$(\text{-I-2VP-})_n$ (1:2)	insoluble gel
ISV-1	Li-I	I-S-2VP-S-I (1:2:1:2:1)	400
ISV-2	Li-I	I-S-2VP-S-I (1:2:1:2:1)	500
ISV-3	BuLi	I-S-2VP-S-I (2:14:2:14:2)	900
ISV-4	Li_2-Cat	$(\text{2VP-I-S-I-2VP})_n$ (1:1:2:1:1)	80,000 (before coupling)

TABLE III

Abbreviations used in Tables I and II in Order of Appearance

Catalyst Column:	BuLi	Butyllithium
	Na-MeS	α-Methylstyryl sodium
	Na-Naphth	Sodium Naphthalene
	K-Naphth	Potassium Naphthalene
	Tol	Toluene used as solvent, all other polymerizations were carried out in tetrahydrofuran
	Na-PpClS	Poly(p-chlorostyrl) sodium
	Li-I	Isoprenyl lithium
	Li_2-Cat	L,1-Dilithio-1,1,4,4-tetraphenyl butane (8)
	Na-S	Styryl sodium
Polymer Composition Column:		
	S	Styrene
	2VP	2-Vinyl Pyridine
	4VP	4-Vinyl Pyridine
	MAN	Methacrylonitrile
	MA	Methylacrylate
	MeS	α-Methyl styrene
	TDI	2,4-Toluene diisocyanate
	pClS	p-Clorostyrene
	AN	Acrylonitrile
	p-FS	p-Fluorostyrene
	I	Isoprene
Remarks Column:	p-ClPBO	p-Clorobenzoyl peroxide
	t-BuHPO	tert-Butyl hydroperoxide

tion of grafted block copolymers. Even with relatively short block lengths large domains will result in the phase separated films. Impurities, introduced with the monomer feed are of minor importance with polycarbanions and short chain homopolymers cannot form. For the preparation of charge mosaic membranes, the first block directly attached to the PpClS back bone has to be a polyelectrolyte precursor followed by a polymer block serving as inert matrix in the composite film. By blending two of these grafted block copolymers, each with a different polyelectrolyte precursor but a common matrix polymer, a film with large domain sizes should be obtained.

This work was discontinued because of a suitable matrix polymer not being found. Polymerization of MAN was not successful, and preliminary experiments with polymer blends composed of PS, P2VP, and PMMA indicated unsatisfactory phase separation in the ternary polymer mixture. Blending of solutions of PS and P2VP in THF resulted in a turbid mixture which yielded a film with large, well defined domains of both polymers. With addition of a solution of PMMA to the turbid mixture of PS and P2VP the ternary blend became completely clear and phase separation did not take place upon standing. A film cast from this clear solution yielded a phase separated film of extremely small domain sizes.

These experiments were repeated with all three polymers being now random copolymers containing small amounts of butadiene. The results obtained on blending the solutions were identical to those obtained with the homopolymers. The film from the ternary blend was cross-linked by vulcanization with sulfur monochloride to allow sulfonation of the PS and quaternization of the P2VP. In reverse osmosis tests the ionic films were practically impermeable. Obviously the ionic domains were completely surrounded by PMMA. It seems that this polymer combination is not a suitable one for obtaining useful phase separation in the films.

4. Combined Anionic and Free Radical Polymerization

Free radical polymerization provides a much wider choice in the selection of matrix polymers than anionic polymerization. It was therefore tried to introduce terminal peroxide groups in anionically prepared polymer chains. In the first attempt, R-134, it was hoped that carbanions might react faster with the chlorine than with the peroxide group of p-chlorobezoyl peroxide. In order to have always a deficiency of carbanions during the reaction, the carbanion solution (living PS) was syphoned into a dilute solution of p-chlorobenzoyl peroxide. Nevertheless, the carbanions seemed to have reacted preferentially with the peroxide groups, and the polymer was inactive in a subsequent polymerization of vinyl chloride.

In a second experiment a block copolymer was prepared, R-135, in which the PS block was sandwiched between two short blocks of poly(2,4-toluene diisocyanate).

The remaining isocyanate groups were reacted with tert-butyl hydroperoxide without isolating the polymer. This polymer proved to be an active catalyst in vinyl chloride polymerization. Vinyl chloride does not polymerize thermally and demands free radical initiation. The resulting polymer is not a true block copolymer but a combination of a block and a graft copolymer which contains considerable amounts of homo PVC. The film forming property of this polymer were not promising.

5. Isoprene Containing Block Copolymers

These polymers were prepared for two reasons. Firstly, for cross-linking studies, and secondly, because with these polymers it should be possible to obtain a block sequence in which the cationic and anionic blocks are separated by a block of neutral polymer. Polymer for the latter purpose were prepared by starting the polymerization with isoprene in benzene (1,4-placement) and then changing to the other monomers after addition of THF. Polyisoprene can be sulfonated with an ether complex of chlorosulfonic acid[13] which is too weak to attack the PS. Quaternization of the 2VP and selective sulfonation of the isoprene should result in charge mosaic membranes in which both domains are isolated by PS. The film forming properties of the block copolymers were very good but unfortunately all of the films either dissolved or swelled so strongly in ether that the sulfonation reaction could not be carried out.

The cross-linking studies with these films will be reported in connection with work on films derived from polymer blends.

C. Characterization of S-2VP Block Copolymers

A considerable number of block copolymers were prepared from the monomer combination S and 2VP. Butyllithium initiation yielded either S-2VP or S-2VP-S block copolymers, the latter one being obtained by coupling of the living 2VP carbanions. Dianionic catalysts were used with coupling for the preparation of alternating block copolymers of structure $(\text{-S-2VP-})_n$. By employing coupling reactions the molecular weight distribution of the coupled copolymer is narrowed in the case of monocarbanions but strongly broadened in the case of living dicarbanions. The coupling reaction is a statistically occurring process which yields a most probable distribution with the polymeric $(\text{2VP-S-2VP})^{-2}$ dianionions representing the "monomeric" units. During the coupling reaction of monoanions (S-2VP) some of them remain uncoupled and the molecular weight distribution of the final polymer can be expected to be bimodal with a low content of S-2VP polymer possessing half the molecular weight of the main portion of the product. Both kinds of block copolymers obtained by coupling were analyzed by gel permeation chromatography (GPC).

The GPC analyses were made by Waters Associates with their GPC Model 300, using a set of four Styragel columns with porosities of 10^3, 10^4, 10^5, and 10^6Å. Dual detectors were arranged in tandem. The one detector was a low volume differential refractometer, the other one a UV photometer set at 2540Å wave length. Sample loads were of 5 mg. (0.25 wt./vol.-% for 120 sec.) and the flow rate in the columns was 1 ml/min. The solvent was THF.

The polymer R-20 was initiated by BuLi, the polymer R-29 was initiated by sodium naphthalene. Both polymers were coupled with 1,5-diiodopentane after depletion of the 2VP feed. The GPC curves of both polymers are shown in Fig. 3 and 4. The molecular weight distribution of R-20 shows a relatively narrow peak without indication of a bimodal distribution, although some low molecular weight tailing of the distribution is indicated. The molecular weight distribution of R-29 shows the presence of several maxima and a distinct low molecular weight tailing. Except for the low molecular weight tailing both GPC curves are of the anticipated shapes.

Evaluation of both GPC curves for average molecular weight values is not possible without further calibrations. The refractive index increment for P2VP as well as its hydrodynamic volume in THF are not known. The hydrodynamic volume of a polymer in a given solvent is decisive for the retardation of this polymer in a GPC column of given pore size. The hydrodynamic volume of a polymer of intrinsic viscosity $[\eta]$ and molecular weight M is proportional to the product $[\eta]$ M. Indeed, by plotting values of this product for different polymers in the same solvent versus the corresponding elution volumes in GPC a universal calibration curve is obtained.[14]

The molecular weight-viscosity relationships for PS and P2VP is benzene

$$\text{PS (benzene)}: [\eta] = 9.2\text{x}10^{-5}M^{0.74} \qquad (15)$$

$$\text{P2VP (benzene)}: [\eta] = 1.7\text{x}10^{-4}M^{0.64} \qquad (16)$$

show that the hydrodynamic volumes of both polymers differ considerably. For two polymer chains of a molecular weight of 10^5 the hydrodynamic volume in benzene for PS is 1.7 times the value of P2VP. The retention of the latter polymer in GPC is therefore much higher than of PS.

During further fractionation studies it was found that inherent difficulties exist in GPC of 2VP containing polymers. In Fig. 5 and 6 GPC curves in THF are shown of a PS sample (R-117/1) and a 2VP-S-2VP block copolymer sample (R-117/2) of overall composition 1:1. The polymers were obtained by dianionic growth and sampling the reaction solution before and after addition of the 2VP. The molecular weight of the PS in both samples is therefore the same, and the molecular weight of each P2VP block in the second sample is half the molecular weight of the PS block. The intrinsic viscosities of samples R-117/1 and R-117/2 in benzene were 0.260 and 0.32o dl/g, respectively. The small viscosity increase resulting from

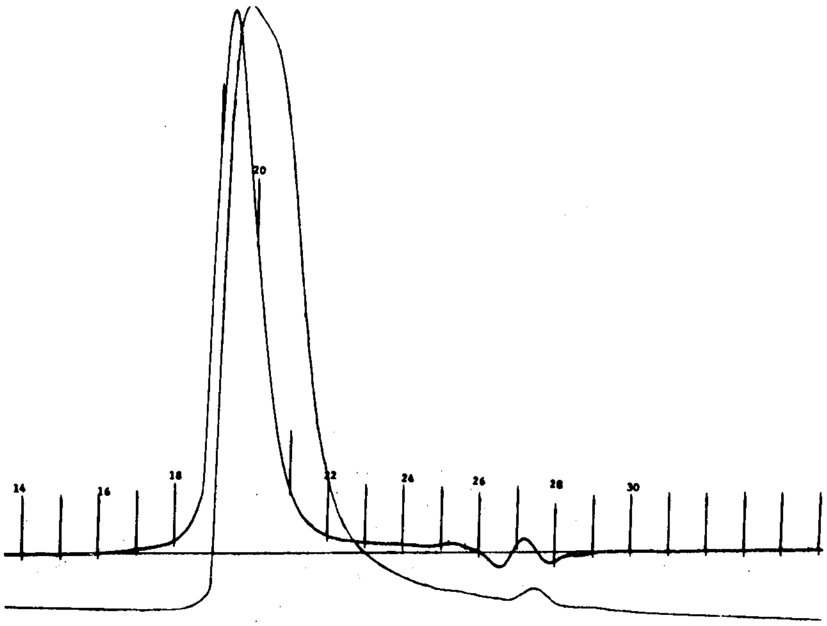


Figure 3 - Gel permeation chromatography trace of a styrene-2-vinyl pyridine block copolymer (R-20) prepared by coupling of the vinyl pyridine monocarbanions with diiodopentane. Solvent: THF.

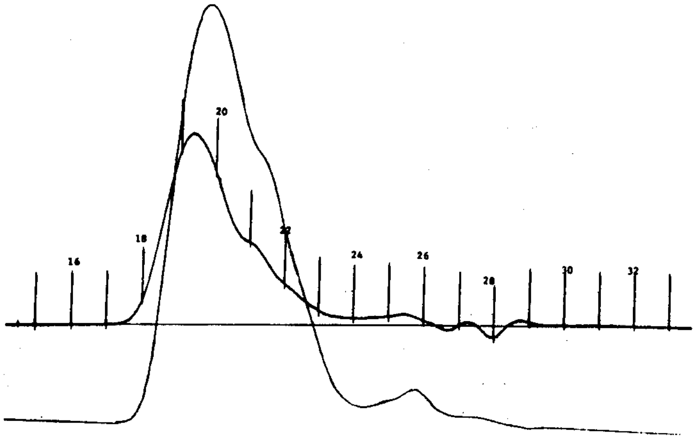


Figure 4 - Gel permeation chromatography trace of an alternating styrene-2-vinyl pyridine block copolymer (R-29) prepared by coupling of the vinyl pyridine dicarbanions with diiodopentane. Solvent: THF.

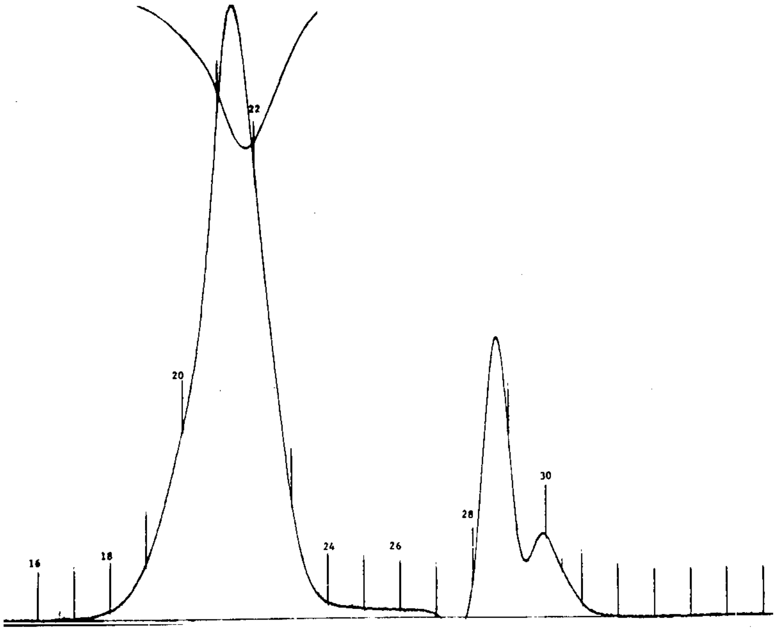


Figure 5 - Gel permeation chromatography trace of a dianionically prepared homopolystyrene (R-117/1). Solvent: THF.

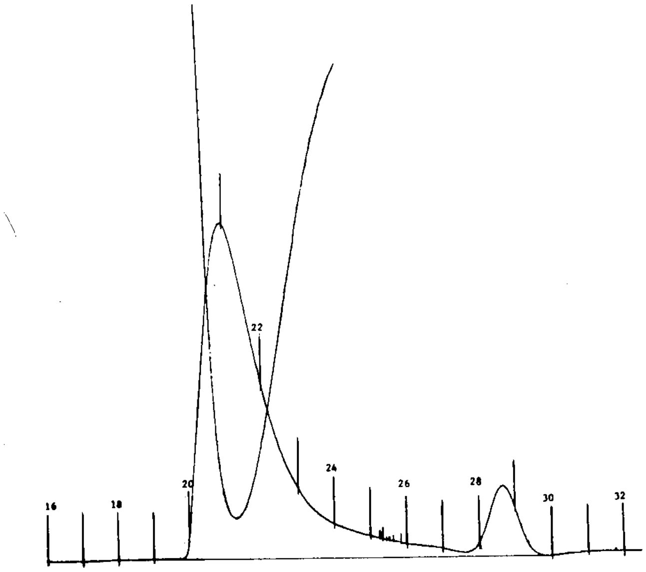
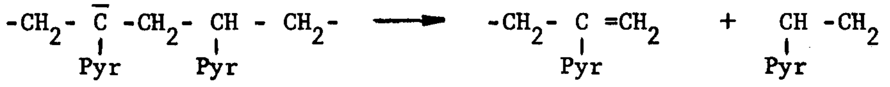


Figure 6 - Gel permeation chromatography trace of a 2-vinyl pyridine-styrene-2-vinyl pyridine block copolymer (R117/2) derived from dianionically grown polystyrene of Fig. 5. Solvent: THF.

the addition of the two P2VP blocks to the center PS block indicates the smallness of the P2VP contribution to the hydrodynamic volume of the copolymer. A homo PS with a molecular weight corresponding to the block copolymer would possess an intrinsic viscosity of 0.440 dl/g.

The GPC curve of the PS, Fig. 5, is relatively narrow and almost symmetrical except for a very weak high molecular weight tailing. In comparison the GPC curve of the block copolymer, Fig. 6, is asymmetric with the high molecular weight tailing completely missing but with a pronounced low molecular weight tailing. Because of the great difference in the hydrodynamic volumes of PS and P2VP average molecular weights cannot be calculated but for comparison one might calculate number average values for the coil dimensions from both chromatograms. Such a calculation still represents only a first approximation since it is based on the assumption that each fraction of the polymer has the same chemical composition, an assumption which is not completely correct. Deviations in the chemical composition of the block copolymer fractions will affect the optical sensors and consequently two polymer chains of the same coil dimension but different composition will contribute differently to the ordinate of the GPC curve. Neglecting this complication, the number average value of the contour length of the PS sample is 792Å whereas a value of only 493Å is obtained for the block copolymer. The considerably lower value for the block copolymer is caused by the pronounced low molecular weight tailing of its GPC curve.

The difference in the GPC curves of the PS and the block copolymer sample is rather puzzling and demands some speculations on its cause. The tailing of the GPC curve of the block copolymer toward higher elution volumes indicates the presence of low molecular weight material being absent in the PS sample. This would mean that this material cannot contain PS blocks, and therefore, can have resulted only from a transfer reaction during 2VP polymerization. Transfer reactions are usually absent in anionic polymerization mechanisms although they cannot be excluded a priori in the polymerization of 2VP. The latter polymer is susceptible to nucleophilic attack by carbanions of high basicity.[17-19] The center of attack is the ring carbon adjacent to the nitrogen. Thereby the nitrogen acquires a negative charge and subsequently reacts with a hydrogen of a tertiary chain carbon. The further fate of the pyridine ring is at present of minor importance but the tertiary carbanion of the chain can induce chain scission.



$$-CH_2-\underset{\text{Pyr}}{\underset{|}{\bar{C}}}-CH_2-\underset{\text{Pyr}}{\underset{|}{CH}}-CH_2- \longrightarrow -CH_2-\underset{\text{Pyr}}{\underset{|}{C}}=CH_2 + \underset{\text{Pyr}}{\underset{|}{CH}}-CH_2 \qquad (1)$$

Depending on which side the PS block is initially attached, there will result either a terminated block copolymer and a living P2VP chain or a terminated homo P2VP chain and a living block copolymer chain. In either way low molecular weight homo P2VP can be formed.

Nucleophilic attack of the P2VP blocks by 2VP carbanions is also indicated by gel formation during the coupling reaction of dianionically growing block copolymers. Upon addition of the coupling agent to the solution of living $^{-}$(2VP-S-2VP)$^{-}$ chains the viscosity of the solution increases as anticipated but also a faint turbidity develops. The intensity of the latter increases with increasing concentration of dicarbanions, thus at very high concentrations of the latter even complete gelation can take place. It was first thought that the formation of microgels is a consequence of cross-linking by quaternization with difunctional halogen compounds. A test with a solution of terminated P2VP revealed that cross-linking by quaternization with dihalogen compounds does not take place under the conditions of the coupling reaction. Therefore, gel formation during coupling of a living P2VP system can be caused only by polymer chains possessing more than two carbanions per chain. In systems with high dicarbanion concentrations gelation can occur even in the living polymer system.

The above findings can be explained by the nucleophilic attack of 2VP carbanions on P2VP segments. At low concentrations of dicarbanions it is very unlikely that both carbanions of the same chain will attack pyridine rings of P2VP segments thereby forming cross-links. But this possibility increases with the concentration of dicarbanions in the system. Thus at low dicarbanion concentrations branched P2VP blocks will result possessing several living ends which provide cross-links upon coupling only.

Although the low molecular weight tailing of the GPC curve of the block copolymer could be explained by the formation of low molecular weight homo P2VP during polymerization it is not possible to explain from the polymerization mechanism the absence of the high molecular weight content previously present in the PS sample. The only explanation would be based on the assumption that the hydrodynamic volume of the PS is decreased by attaching P2VP blocks on each of its ends. This assumption were justified if the interaction energy between PS and P2VP segments is greater than between segments of the same kind. Because this would also mean that PS and P2VP are compatible, contrarily to the experimental findings, the above explanation is not acceptable.

The change from a nearly symmetrical GPC curve of the PS to a strongly asymmetric one of the block copolymer indicates weak interactions between the latter and the Styragel of the columns. One has to consider that P2VP is a weak base and the smallest amount of acidic groups on the Styragel would exert a strong retentive effect on the polymer. Acidic groups in the Styragel could result from free vinyl groups of the cross-linking agent (divinyl benzene) which become oxidized during the use of the column. It was found in other laboratories that homo P2VP in either THF or chloroform does not leave the GPC columns in a detectable way. It could not be decided whether the polymer remained permanently in the columns or whether it was smeared out over such a range that its concentration in the eluate never exceeded the detection level of the sensors. With dimethylacetamide or dimethylformamide completely normal GPC curves resulted from homo P2VP. These findings could also be explained by P2VP retention through acidic groups on the Styragel. Dialkylamides usually contain very small quantities of free alkylamines as impurities. These amines are stronger bases than P2VP and will neutralize the acidic groups of the column thus preventing polymer-gel interaction.

Because of the yet unclarified complications in GPC of 2VP containing polymers further use of this method was discontinued. Unfortunately, the information concerning the apparent improvement of GPC with the use of dialkylamides as solvent was received after termination of work.

In general the block copolymers were characterized by calculating the molecular weights of the individual blocks from polymerization data. With the known amounts of catalyst in moles, [Cat], and monomer in grams, [M], the molecular weight is given by

$$\text{monoanionic growth:}\quad \overline{M}_n = [M]/[Cat] \qquad (2)$$

$$\text{dianionic growth:}\quad \overline{M}_n = 2[M]/[Cat] \qquad (3)$$

These values are subject to some error due to the uncertainty in the effective catalyst concentration. Changes in membrane performance demand considerable changes in the block lengths of the copolymers and it could be safely assumed that these changes were larger than the error involved in their calculation.

Solution viscosities of block copolymers are not very meaningful especially if the hydrodynamic volumes of both polymeric blocks differ so strongly as in the case of PS and P2VP. Therefore, such measurements were used only to check on the effectiveness of the coupling reaction although final molecular weights cannot be derived from these data.

D. Morphology of S-2VP Block Copolymer Films

Films from block copolymers composed of S and 2VP were cast either from THF or benzene solutions of 10-20 wt./vol.-% concentrations. The films were cast in the usual way on glass plates with the use of a doctor knife (Boston Bradley Applicator), and were dried either on air or inside a polyethylene container. In general no significant difference in membrane performance was observed between films dried in both ways. The films were floated by submerging the glass plates for a very short time in methanol. When the film edges started to wrinkle, the plate was placed into water. In this way completely smooth films were obtained whereas floating in methanol resulted in strongly wrinkled films. Alcohols are very good solvents for P2VP whereas the water uptake is considerably lower, about 10-15%.

The first block copolymers made contained some homo PS due to impure polymerization conditions. Films from these polymers were slightly opaque and in some cases exhibited even some macroscopic phase separation in form of a fine regular network of less light transmissive material. Such films usually possessed low mechanical strength. With improvement of the polymerization procedures pure block copolymers were obtained which yielded completely clear films without macroscopic phase separations. The occurrence of phase separation in molecular dimensions was indicated in these films by their dichroism in solvents selective for one phase. Films swollen in methanol were clear and yellow in transmission but bright blue in the scattered light. The same dichroism was observed on quaternized films in water. If a quaternized film was dried and then placed into toluene again weak dichroism was observed. The dichroism is caused by the optical anisotropy of the films which results from selective swelling of only one kind of phase. It demands a rather regular arrangement of phases of similar dimensions. A very faint bluish tint was also observed during selective swelling of random copolymers films of S and 4VP, but in this case the effect was only of short duration and vanished when swelling equilibrium was reached. With block copolymer films the dichroism persists indefinitely provided morphological changes are not taking place.

The evenness of the interference color of selectively swollen block copolymer films is a good indication of their structural homogeneity. Film inhomogeneities occur most likely if solvent mixtures are used as casting solutions. With solvent mixtures dichroism also occurs in block copolymer solutions especially if they are concentrated. This effect was most pronounced with a S-4VP block copolymer (R-18) which was dissolved in a mixture of THF and methanol, the amount of the latter solvent being adjusted to result in a clear solution. Phase separation was indicated by the presence of bright blue schlieren which represent macroscopic regions in the solution where phase separation on a molecular level, very likely in form of a layer structure, has taken place. The intensity of schlieren formation diminishes with dilution. A film cast from a dilute solution turned evenly blue upon swelling in methanol but a film from a concentrated solution developed bright blue streaks in the draw direction of the casting blade. Although in the latter case, the swollen film possessed good strength in the draw direction it split easily in the direction normal to the draw direction.

It seems surprising that films derived from A-B type block copolymers (S-2VP and S-4VP) are insoluble in methanol and dilute acids. This property indicates that the PS forms a three dimensional network in which the soluble PVP blocks are imbedded. Obviously, by casting from a concentrated solution of the S-4VP polymer the layer structure existing in large regions of the solution is partially preserved during casting and is smeared out over an extended region in the draw direction of the casting knife. In this region the film retains the layer structure with respect to both phases with very little three dimensional bridging by PS domains. As a consequence the mechanical strength of the swollen film differs considerably in both directions. In dilute block copolymer solutions phase separation does not exist to a great extent, and if, these regions are completely destroyed by the shear forces during casting. Upon drying such films the PS domains arrange in a three dimensional network which provides even film strength in all directions.

The phase separation occurring on a molecular level were investigated by electron microscopy. In the first investigation a surface replica of block copolymer film (R-29) was used. The electron micrograph is shown in Fig. 7. Surface replication is not a promising method for the investigation of phase separation as occurring in block copolymer films but nevertheless the micrograph of Fig. 7 shows some structural features of the film surface which are caused by phase separation. On some parts of the film surface irregular patterns can be observed which are composed of strongly entwined narrow ribs slightly protruding from the film surface. One might assume that these ribs represent those polymeric domains which swell more strongly during film preparation or subsequent film treatment. During swelling these domains are partially squeezed out of the rigid PS matrix and do not shrink back completely during drying of the film. The average width of the protruding ribs is about 300-400Å which is too wide if they solely represent P2VP domains. Very likely these ribs represent larger regions of higher swelling capability. One can only conclude from the surface replica that block copolymer films show anisotropic swelling behavior in molecular regions.

The best method for the elucidation of the morphology of block copolymer films is by transmission electron microscopy. This method has been extensively applied in morphological investigations of S-B-S block copolymers.[20-23] With these block copolymers the electron densities of both polymer blocks do not differ sufficiently and a staining method has to be applied. The double bonds of the PB are reacted with osmium tetroxide thus increasing the electron density of this phase. With

Figure 7 - Electron micrograph of a surface replica of an alternating styrene-2-vinyl pyridine block copolymer film (R-29).

block copolymers derived from S and 2VP staining was found to be unnecessary and electron micrographs with good contrast were obtained from untreated ultrathin films. Unfortunately, without a staining procedure an unambiguous assignment of the phases in the electron micrographs was not possible.

Transmission electron microscopy for morphological studies is carried out best on ultramicrotome slices of relatively thick films. This approach allows to compare phase separations in different film direction. In addition thicker films dry much more slowly than ultrathin ones thus providing more time for the phases to arrange. The lack of an ultramicrotome did not allow us to take this approach, and therefore, ultrathin films of only several hundred Å thickness had to be prepared by casting from dilute solutions of less than 2% polymer content.

It was found after several trials that these thin films adhered too strongly on the glass surface and could not be floated. For this reason polymer coated microscopy slides were used for casting. Coating polymers were selected which did not swell in the casting solvent of the block copolymer but dissolved either in water or methanol. The supporting polymers were poly(N-vinyl pyrrolidone) for THF solutions and hydroxyethyl cellulose for benzene solutions. The experimental procedure for film formation was as follows.

Cleaned microscopy slides were dipped in 2% solutions of either poly(N-vinyl pyrrolidone) in chloroform or hydroxyethyl cellulose in water. The solutions were freed of dust by pressing them through Millipor filters. The coated slides were placed in Petri dishes together with a few drops of the casting solvent to provide a saturated vapor atmosphere. The latter condition is important to prevent the thin films from drying too fast thus impairing the phase separation. The casting solutions were in the range of 0.2 to 2.0%, the highest concentration already yielding films too thick for good observations in transmission. With an eye dropper a few drops of the polymer solution was placed on the slide and the Petri dish was immediately covered. By tilting the dish the polymer solution was spread over the slide surface and any excess was run off. The covered dishes were kept over night to allow a slow evaporation of the solvent. The dried films were cut into small pieces with a razor blade and usually floated in methanol. Ultimately, the film samples were always spread on water, picked up with the supporting copper grid, and dried in vacuum.

It was rather surprising that the films gave good contrast in transmission without staining of one phase. The difference in the electron densities of both phases is very likely a consequence of the sample preparation. The P2VP is slightly hydrophilic and swells in water to a small extent. Upon drying on the grids the P2VP domains retain their swollen, and therefore, less dense structure. This density difference suffices for the contrast in the electron micrographs. Accordingly, the denser PS domains are represented in the micrographs as dark areas, the light areas representing the P2VP domains. It was hoped that by quaternizing the P2VP domains heavy atoms such as bromine could be introduced thus making these domains the electron denser ones. This approach failed due to the increased swelling of the quaternized P2VP which more than compensated the effect of the bromine.

The polymers investigated were R-20, a block copolymer of structure S-2VP of composition 1:1, and an alternating block copolymer, R-29, also fo composition 1:1. In Fig. 8 to 11 the transmission electron micrographs are shown of polymer R-20 with films cast from THF solutions of 0.2, 0.5, 1.0, and 2.0%, respectively. The film obtained from the lowest concentration (0.2%) was of very uneven thickness as indicated by the large white areas in Fig. 8. The white circular areas surrounded by dark circles are very likely holes. At this lowest casting concentration the PS domains form rather regularly arranged circular dots of about 180Å diameter. These PS dots are still present at higher casting concentration (0.5%), Fig. 9, but in this slightly thicker film the circular PS domains already start to unite into short ribbons. A still thicker film of the same polymer (1.0%), Fig. 10, shows mainly short PS ribbons with very few circular dots remaining. During the change of the shape of the PS domains the dimensions of the circular domains remains constant. In all three micrographs the average diameter is about 180Å and this is also the value of the average with the PS ribbons. At a casting concentration of 2.0%, Fig. 11, the overlapping of phases is so strong that a clear resolution cannot be obtained. Because of the strained P2VP phase dimensions cannot be given in this case.

The micrographs of the S-2VP block copolymer films gave the impression that isolated PS domains are imbedded in a continuous P2VP phase. Since with this block copolymer one polymer chain can only participate in two phases one might wonder why the films did not dissolve in methanol. This should be the case if the phases were really two-dimensionally arranged, meaning that in a cross-section of the film each phase would extend vertically from one surface to the other. A closer observation of the micrographs reveals that this is not the case. The area between the dark PS domains shows a very diffuse background structure resulting from PS domains situated at greater depth. The short depth of focus of the electron microscope will provide a sharp image only from the top layer of the film. Actually, the PS domains are much more interconnected than shown on the micrographs thus providing the necessary cross-links to make the film insoluble.

In Fig. 12 and 13 phase separations in an alternating blockcopolymer film are shown. The polymer, R-29, had a structure $(\text{-S-2VP-})_n$ with each block possessing a

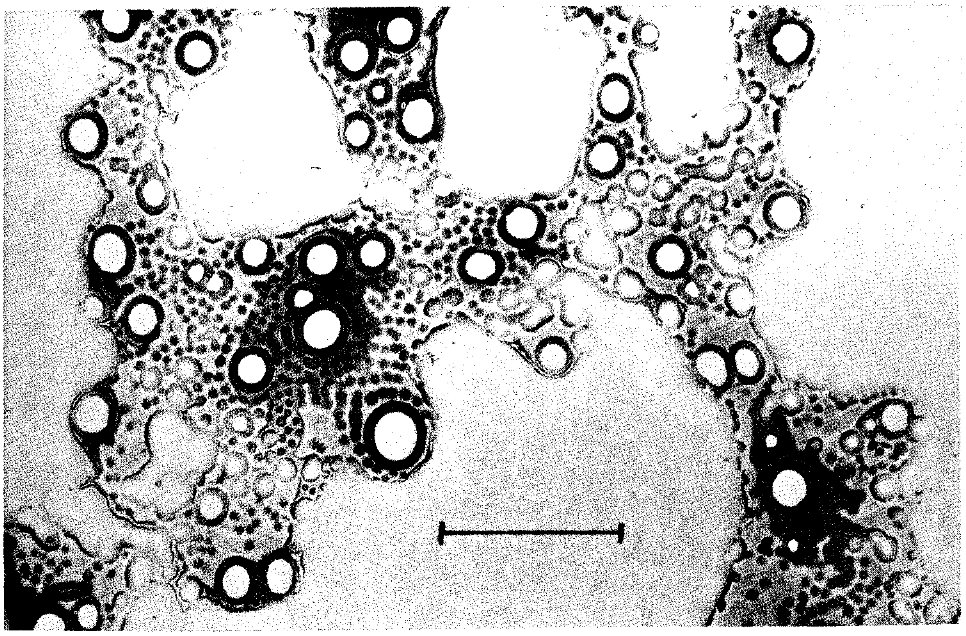


Figure 8 - Transmission electron micrograph of a styrene-2-vinyl pyridine block copolymer film (R-20) cast from THF at 0.2% concentration.

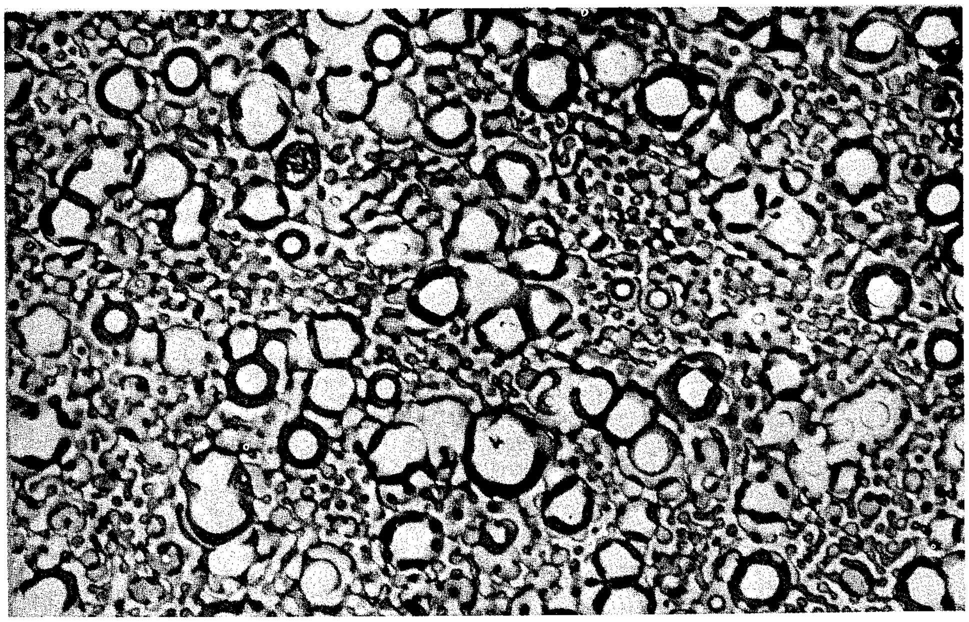


Figure 9 - Transmission electron micrograph of polymer R-20 cast from THF at a concentration of 0.5%.

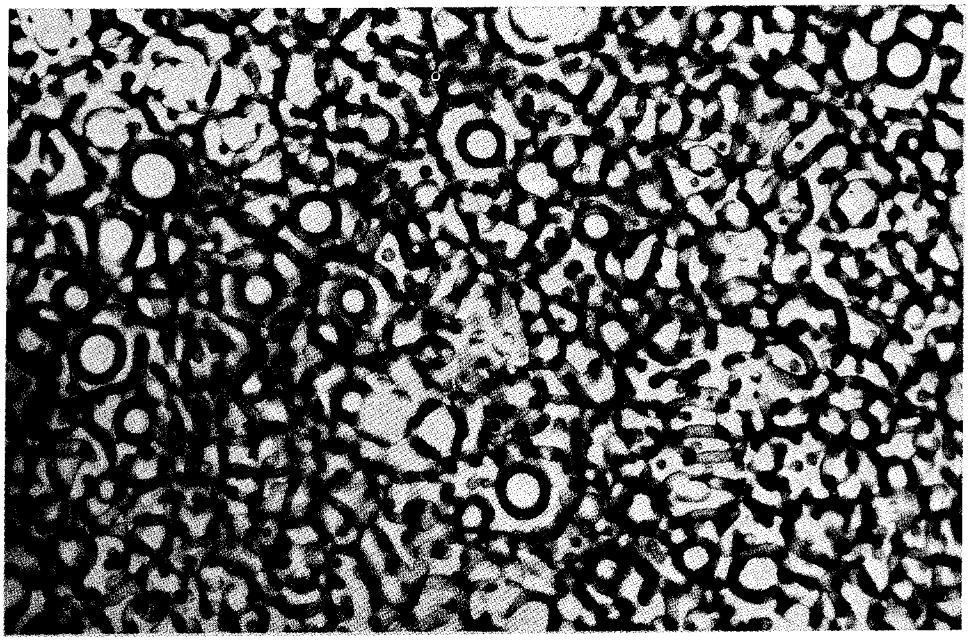


Figure 10 - Transmission electron micrograph of polymer R-20 cast from THF at a concentration of 1.0%.

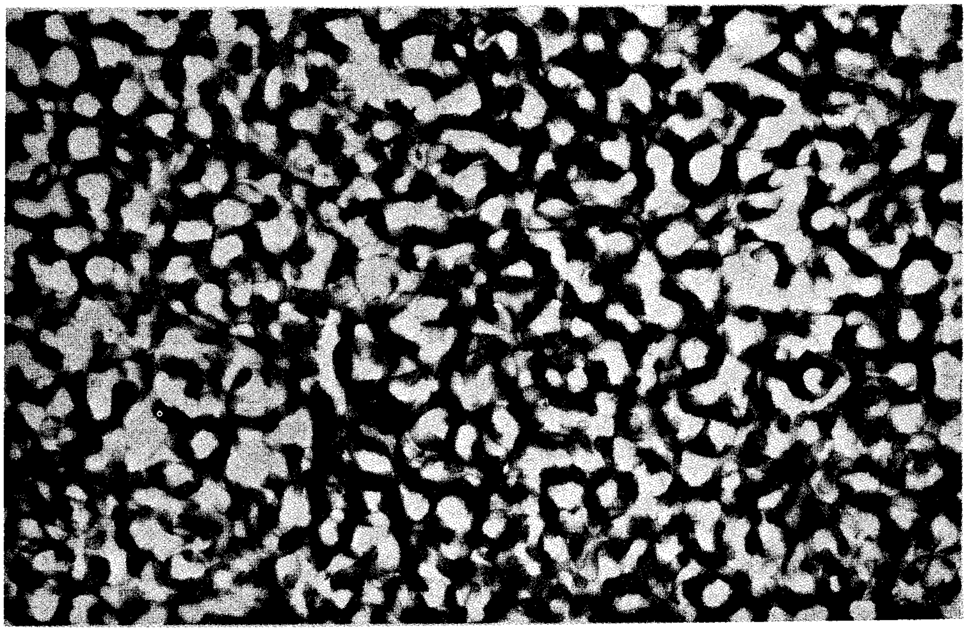


Figure 11 - Transmission electron micrograph of polymer R-20 cast from THF at a concentration of 2.0%.

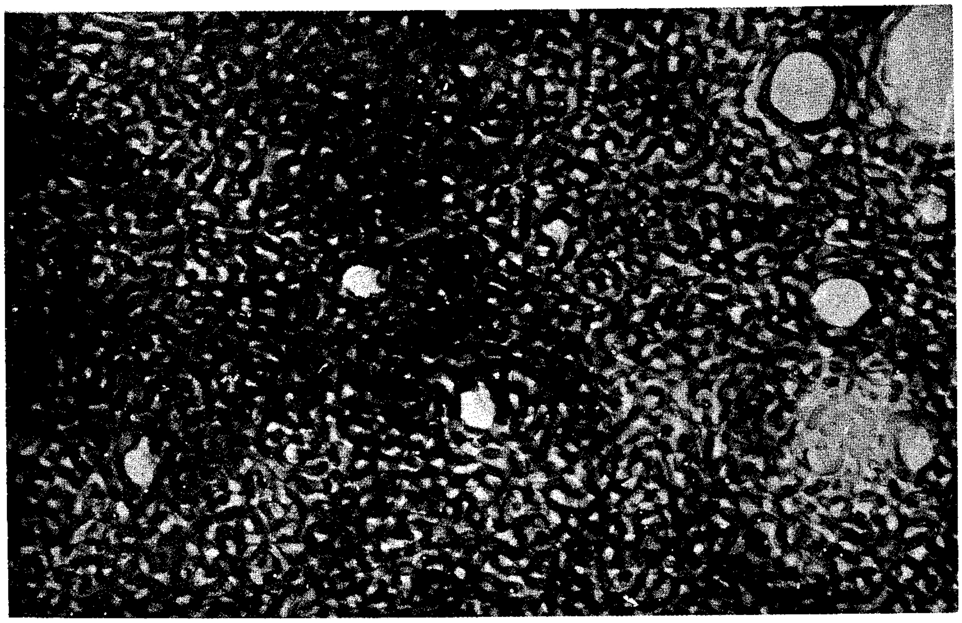


Figure 12 - Transmission electron micrograph of an alternating styrene-2-vinyl pyridine block copolymer film (R-29) cast from THF at a concentration of 0.5%.

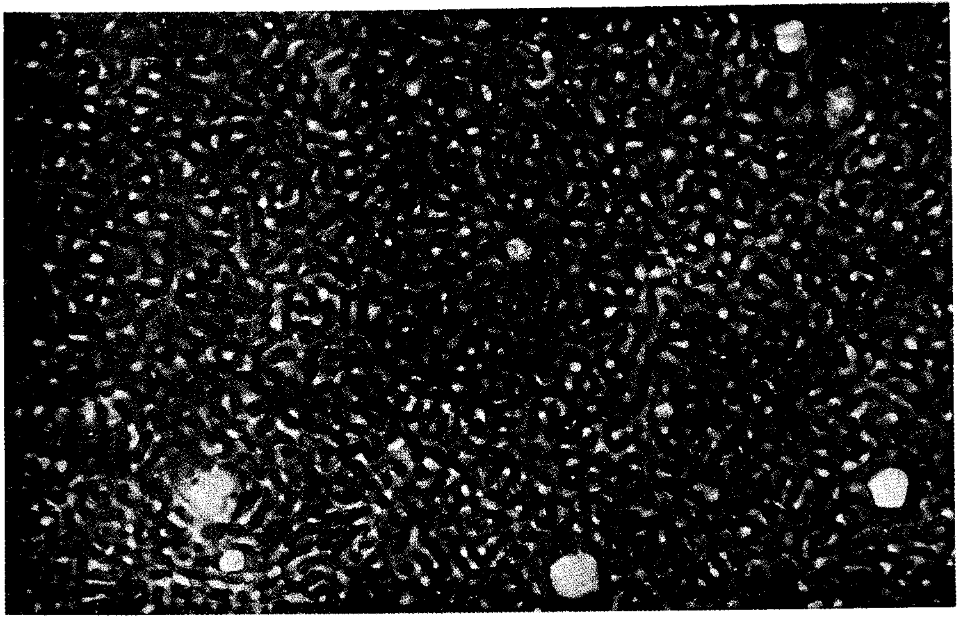


Figure 13 - Transmission electron micrograph of polymer R-29 cast from THF at a concentration of 1.0%.

molecular weight of about 10,000. The films were cast from THF at concentrations of 0.5 and 1.0%, respectively. The film morphology of the alternating block copolymer closely resembles the morphology of the S-2VP block copolymer film. The PS domains form short ribbons of an average width of about 120Å which strongly overlap already at the lower casting concentration.

Cast from THF solution both structurally different block copolymers produce films of nearly identical morphologies. A difference in the film morphologies was observed between both polymers if films were cast from benzene. On Fig. 14 and 15 electron micrographs are shown of films from polymers R-20 and R-29, respectively, cast from benzene. There exists a distinct difference in morphologies as compared with THF cast films. The polymer R-20 exhibits a micrograph with rather badly defined phase separation. The circular areas have an average diameter of about 200Å. With polymer R-29 a very regular phase separation has taken place in a film cast from benzene solution at 0.6% concentration. The P2VP phase in this film forms long and narrow ribbons which are highly branched thereby surrounding the PS domains. The phase arrangement closely resembles a very intricate maze.

The difference in film morphologies of alternating block copolymers cast from THF and benzene is also shown to some extent by differences in the tensile properties of the films. Table IV summarizes tensile measurements on films of one mil thickness which were in swelling equilibrium with water. This condition was selected because dry films are very brittle and yield very erratic results. The reported values are average of groups of three samples which were cut from the film in draw direction of the casting blade and normal to it. The data of benzene cast films show less influence of the draw direction on the tensile properties as compared with THF cast films. From the electron micrographs this difference, even if only small, is unexpected. One might speculate that casting from THF is affected by the water miscibility of THF. It cannot be avoided that a small amount of water condenses on the surface of the casting solution due to its fast evaporation. The condensed water dissolves and changes the solubility parameter in the surface layer. Most likely, due to the small hydrophilicity of the P2VP phase separation in the surface layer becomes enhanced and the draw direction is thereby impressed on the film morphology. Similar observations were made with respect to the solvent effect in the macroscopic phase separation of films prepared from blends of homo PS and homo P2VP.

Tensile measurements on quaternized films were not made. Quaternized films derived from the polymers included in Table IV were rather strong and could be handled easily. Upon prolonged storage in water the mechanical strength of the quaternized films decreased. The loss in strength was most pronounced with the film possessing the highest P2VP content, R-115. The freshly prepared film was

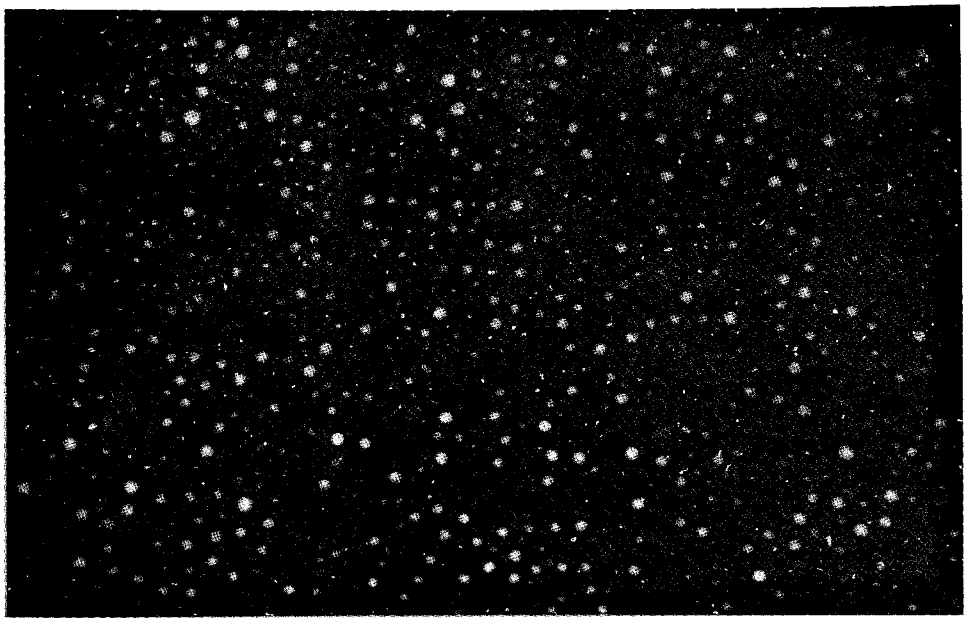


Figure 14 - Transmission electron micrograph of polymer R-20 cast from benzene at a concentration of 0.5%.

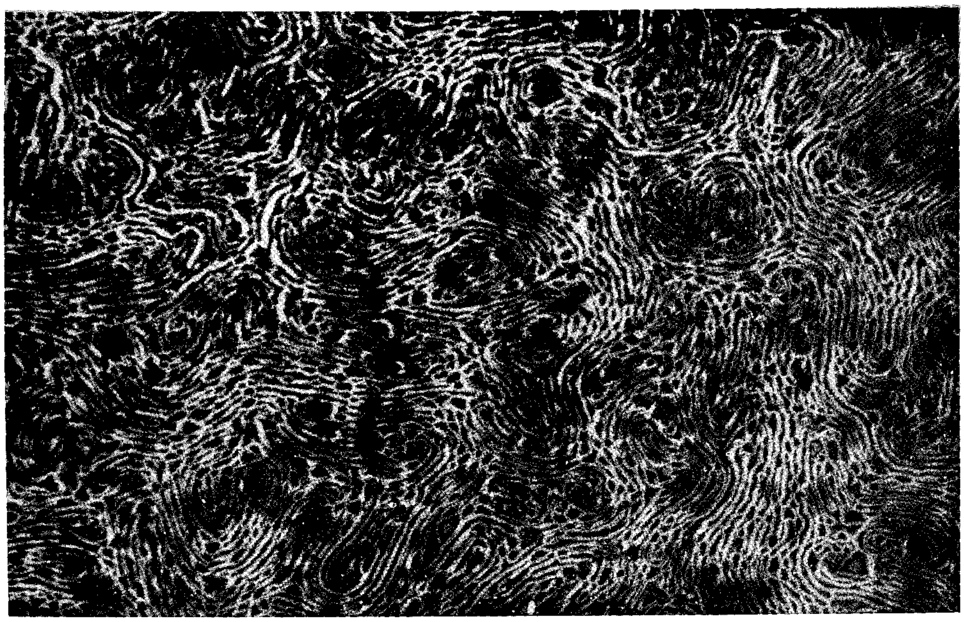


Figure 15 - Transmission electron micrograph of polymer R-29 cast from benzene at a concentration of 0.6%.

TABLE IV

Tensile Properties of Alternating S-2VP Block Copolymers in Swelling Equilibrium with Water. (Values (kg/cm^2) Measured Parallel and Normal to Casting Direction.)

	Film Cast from THF			Film Cast from Benzene		
	Modulus	% Elongation at Break	Tensile Strength	Modulus	% Elongation at Break	Strength
R-116 (Molecular Weight Ratio: PS : P2VP = 46,000 : 34,000)						
parallel	4,800	56	190	8,000	40	180
normal	5,700	54	195	7,600	30	200
R-114 (Molecular Weight Ratio: PS : P2VP = 36,000 : 40,000)						
parallel	9,000	50	340	2,800	90	148
normal	2,500	50	124	2,900	80	140
R-115 (Molecular Weight Ratio: PS : P2VP = 23,000 : 60,000)						
parallel	600	180	62	1,300	96	96
normal	600	200	92	1,100	70	82

completely clear, slightly bluish due to the phase separation, and of good strength. After about two months in water the film exhibited iridescent spots on the surface and disintegrated upon lifting. This change in mechanical strength must have been caused by morphological changes taking place at very low rates. One has to consider that the PS network in quaternized films is under a rather high stress, the swelling of the films proceeding until the swelling pressure equals the generated stress in the PS network. This situation leads to stress-cracking of some of the PS domains with subsequent loss in mechanical properties. The partially broken PS network then allows rearrangement of the domains with further stress release. The iridescent colors occurring on the film surface are very likely caused by protruding ribs similar to the surface structure shown in the electron micrograph of Fig. 7.

The effect of a solvent mixture on film morphology is shown by the electron micrographs of Fig. 16 and 17 which were derived from polymer R-20 cast from a 1.0% THF solution containing 15 vol.-% methanol. The film sample was of rather uneven thickness but it still shows as a characteristic feature the formation of large narrow PS ribbons with an average width of about 200Å. Compared with the electron micrographs of Fig. 8 to 11, the film morphology was considerably changed by the addition of methanol. The larger magnification in Fig. 17, about 2.7 times

Figure 16 - Transmission electron micrograph of polymer R-20 cast from THF-methanol mixture (5:1) at a polymer concentration of 10.%.

Figure 17 - Transmission electron micrograph as of Fig. 16 but at 2.7 times the magnification.

the magnification of the micrograph of Fig. 16, reveals that actually two layers with different morphologies exist in the film. Whether the PS ribbons are imbedded in the film or are situated on one of the film surfaces cannot be decided. Regardless of the actual situation of the PS ribbons, the electron micrographs clearly indicate the coagulating effect of the methanol on the PS part of the block copolymer.

It is interesting to note that block copolymer films cast from THF-methanol mixtures swell considerably more in selective P2VP solvents (methanol or dilute acids) than films of the same polymer cast from pure THF. These highly swelling quaternized films exhibit very low salt rejection and high flux. The same result is obtained with block copolymers which were quaternized before casting. These polymers are soluble in THF-water mixtures and yield films which swell more strongly than corresponding ones quaternized after casting. Again under reverse osmosis conditions these films possess very low salt rejection and high flux. In both cases the solvent mixture has the effect of strongly solubilizing the P2VP and precipitating the PS. Film morphologies result in which the PS domains form a very open network which allows increased swelling of the P2VP domains. These results can be considered to indicate a limitation in the size of the P2VP domains for membranes with good reverse osmosis properties.

Films cast from blends of homo PS and a block copolymer exhibited macroscopic phase separation and were extremely weak. Already during spreading on water of the methanol floated ultrathin films rupture occurred. Generally, low mechanical strength was observed with films containing some homo PS as a result of impure polymerization conditions. This observation unfaborably affected further work with polymer blends since it was believed that blends of homo and block polymers will always result in weak films. This seems to be the case only if the homo polymer is of a molecular weight comparable with the molecular weight of its corresponding block in the copolymer. Blending of a block copolymer with a homopolymer of high molecular weight yields films with regular and well defined macroscopic phase separations. These films are surprisingly strong and free of pinholes at the phase boundaries. Such films will be discussed in a later section of the report.

In Fig. 18 and 19 electron micrographs of films are shown which were obtained by blending THF solutions of a block copolymer (R-20) and of a homo PS (R-23) of molecular weight of 48,000. The films were macroscopically inhomogeneous and consisted of large homo PS and block copolymer areas. It was of interest to see how the latter areas were affected in their morphology by the homo PS. The film of Fig. 18 containing 10 wt.-% of PS shows that a considerable amount of the PS has been dissolved in the PS domains of the block compolymer. The PS domains are

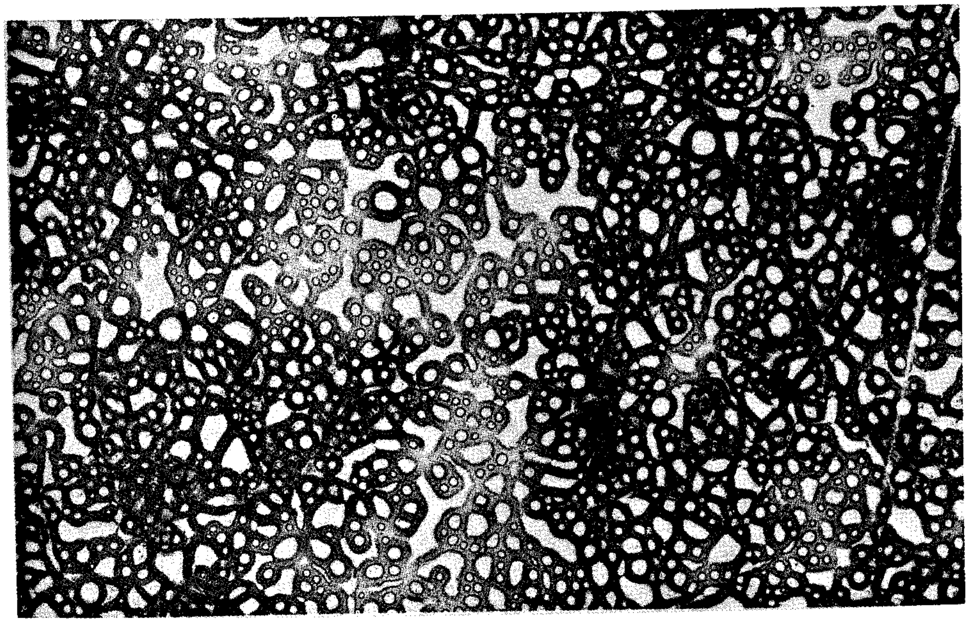


Figure 18 - Transmission electron micrograph of a styrene-2-vinyl pyridine-styrene block copolymer film (R-20) containing 10 wt.-% of homopolystyrene (R-23). Film cast from a 1.0% solution in THF.

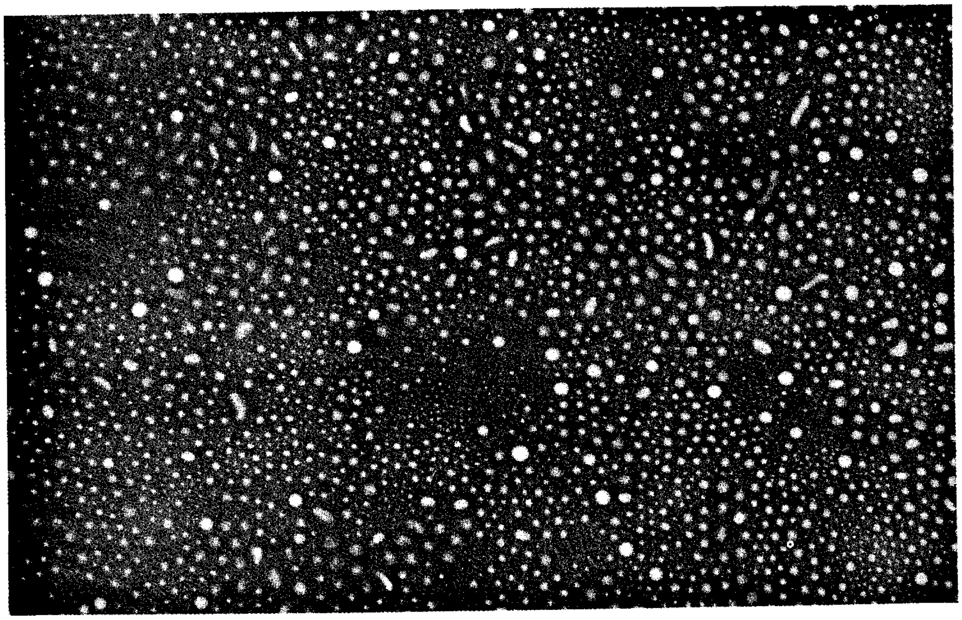


Figure 19 - Transmission electron micrograph of block copolymer R-20 blended with 20 wt.-% of homopolystyrene R-23. Film cast from a 1.0% solution in THF.

now continuous but still form a rather regular patter. Without the addition of PS the PS domains formed short ribbons as shown in Fig. 3. With a higher concentration of PS in the blend, 20 wt.-% in Fig. 19, the PS forms a completely continuous matrix with the P2VP being imbedded in form of very small circular domains of irregular size. In many of these domains the P2VP film was ruptured due to the rigidity of the extended PS matrix.

The high regularity of macroscopic phase separation in polymer blends is illustrated by the optical micrograph of Fig. 20. Impure polymerization conditions during the preparation of a MeS-2VP block copolymer (R-61) resulted in the formation of a considerable amount of homo PMeS. The film cast from this blend exhibited an extremely regular structure. The dark ribbons in Fig. 20 arranged in starlike fashion and the circular areas inbetween consist mainly of homopolymer. The remaining areas turned brightly blue upon swelling in methanol which indicates that they represent phase separated block copolymer areas. The film was extremely weak. If a solution of this polymer blend was cast without application of a doctor knife (no shear forces during casting) the regular arrangement of the phases was not observed although phase separation did take place but in a completely irregular pattern.

Regular macroscopic phase separation in films from polyblends depends on many variables, such as the solubility parameters of the polymers, relative viscosities of both polymers, and casting conditions etc. All films resulting from involuntarily obtained polymer blends indicated that the individual phases extended undisturbed through the films. This latter property complies with the most important condition in the structure of charge mosaic membranes. It was therefore hoped that by overcoming the low mechanical strength of these films the latter would represent the most promising candidates for the preparation of charge mosaic membranes. This approach was started immediately after the preparation of charge mosaic membranes from block copolymers yielded negative results and will be discussed in a later section.

E. Anion Exchange Films From S-2VP Block Copolymers

The use of block polymers in the preparation of ion exchange membranes has the advantage over other methods that films can be cast from solution and can be used without further chemical treatment except for the one by which the ionic groups are introduced. Other means of preparation demand either film curing or polymerization in situ in order to introduce the necessary cross-links in the film. Block copolymers for the preparation of ionic membranes have to be composed of a polyelectrolyte precursor and a hydrophobic polymer which remains uneffected during the chemical transformation of the former. During film formation both polymeric blocks separate into distinct domains of which the hydrophobic ones provide the physical cross-links.

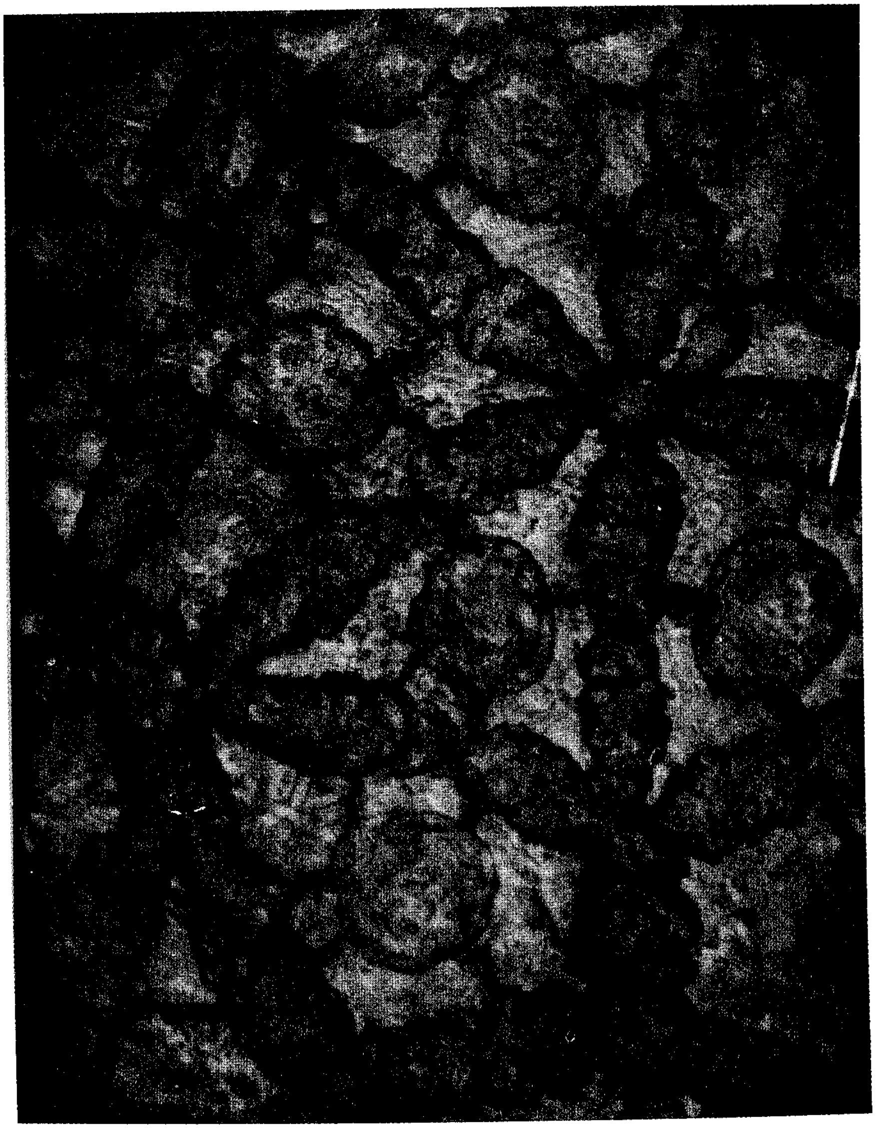


Figure 20 - Optical micrograph of an α-methyl styrene-2-vinyl pyridine block copolymer (R-61) containing substantial amounts of homopoly(α-methyl styrene).

With block copolymer films there exists also the possibility to avoid the chemical transformation of the polyelectrolyte precursor after film formation, i.e., one can cast films from copolymers composed of hydrophobic and polyelectrolyte blocks. The disadvantage of this kind of film preparation is connected with an unfavorable film morphology. Polyelectrolytes are usually not soluble in pure organic solvents and solvent mixtures containing water have to be used. During phase separation in the film the polyelectrolyte domains are formed in a very highly swollen state and the hydrophobic domains arrange accordingly. This means that such films can always accommodate a very high water uptake. If the same polymer is cast with the polyelectrolyte in its precursory form, the hydrophobic network is much tighter since the difference in the swelling properties of both phases will be very small. After transformation of the precursor into its ionic form swelling in water can proceed only until the swelling pressure equals the stress generated in the hydrophobic matrix. Under this condition of preparation the polyelectrolyte domains swell considerably less than under the former one.

The same condition applies if the film is cast from a solvent mixture with one component being a good solvent for the polyelectrolyte precursor but a poor one for the hydrophobic component. If in addition this solvent component evaporates more slowly than the other one, the precursor blocks are still in a highly swollen state when the hydrophobic network already becomes rigid. Again the polyelectrolyte has more space available before its swelling becomes restricted by the generated stress in the matrix.

Films from PS and P2VP containing block copolymers possess no useful reverse osmosis properties if they are cast either from benzene or THF solutions containing alcohols or from THF-water mixtures with the P2VP blocks being already quaternized. In both cases highly swollen films are obtained which exhibit extremely high flux and negligible salt rejection.

The combination of S and 2VP in the block copolymers allows a facile preparation of anion exchange membranes. The P2VP part of the films can be easily quaternized with gaseous methyl bromide without any change in the PS part. Quaternization with other bromine or iodine compounds meets some difficulties due to the high solubility of the PS in alkylhalides. Partial quaternization with 1,5-dibromopentane was accomplished either by adding a very small amount (less than 5% of the polymer weight) to the casting solution and subsequent heating of the film or by treating the film in a dibromide atmosphere at elevated temperature. In both cases the films had to remain on the glass plate otherwise they became strongly distorted and ruptured under reverse osmosis conditions. Quaternization with dibromides introduces chemical cross-links in the P2VP domains thereby reducing their swelling properties.

For quaternization with methyl bromide in the gas phase the films were removed from the glass plate, dried in vacuum, and then treated at 70°C and 1 atm. gas pressure for at least 25 hrs. If films remained on the glass plate and were treated with methyl bromide for different lengths of time graded films were obtained. Such films which exhibited directional properties in reverse osmosis, will be discussed separately.

The first block copolymers prepared from S and 2VP contained some homo PS due to improper polymerization conditions. Anion exchange films prepared from these polymers gave unreproducible salt rejections in reverse osmosis unless extremely thick films (thicker than 10 mils) were used. As mentioned earlier, block copolymers containing small amounts of homo PS show weak macroscopic phase separations. During film formation the PS and P2VP separate by forming individual domains on a molecular scale. The size of the PS domains is restricted by the neighbouring P2VP domains and the former can accommodate additional homo PS only in a very limited amount. Excess homo PS is then exuded from the regions of molecular phase separation of the block copolymer and forms its own phase surrounding the latter. Obviously the phase boundaries between the homo PS regions and the regions of phase separated block copolymer are rather weak and allow pinhole formation under pressure.

With improved polymerization conditions block copolymers practically free of homopolymer were obtained. Films from these polymers were completely clear and did not reveal any structural features under the optical microscope. These films exhibited optimum salt rejection in reverse osmosis. Whether optimum salt rejection was obtained with one of the anion exchange films could be determined by comparing salt rejection with water permeability of the film.

When a considerable number of anion exchange films were tested in reverse osmosis it was found that all films which could be considered free of pinholes or other imperfections showed a unique relationship between salt rejection, R_s, and water permeability, K_1, of the form

$$K_1 = A \exp(-BR_s) \qquad (4)$$

where A and B are constants under constant reverse osmosis conditions (salt concentration and applied pressure). This relationship, shown in Fig. 21, applies over a range of salt rejections from 5 to 80%, and a range of water permeabilities from 0.3 to 250 gdt-mil. The actual data of the membranes represented in Fig. 21 and the compositions of the polymers are summarized in Tables V and I, respectively.

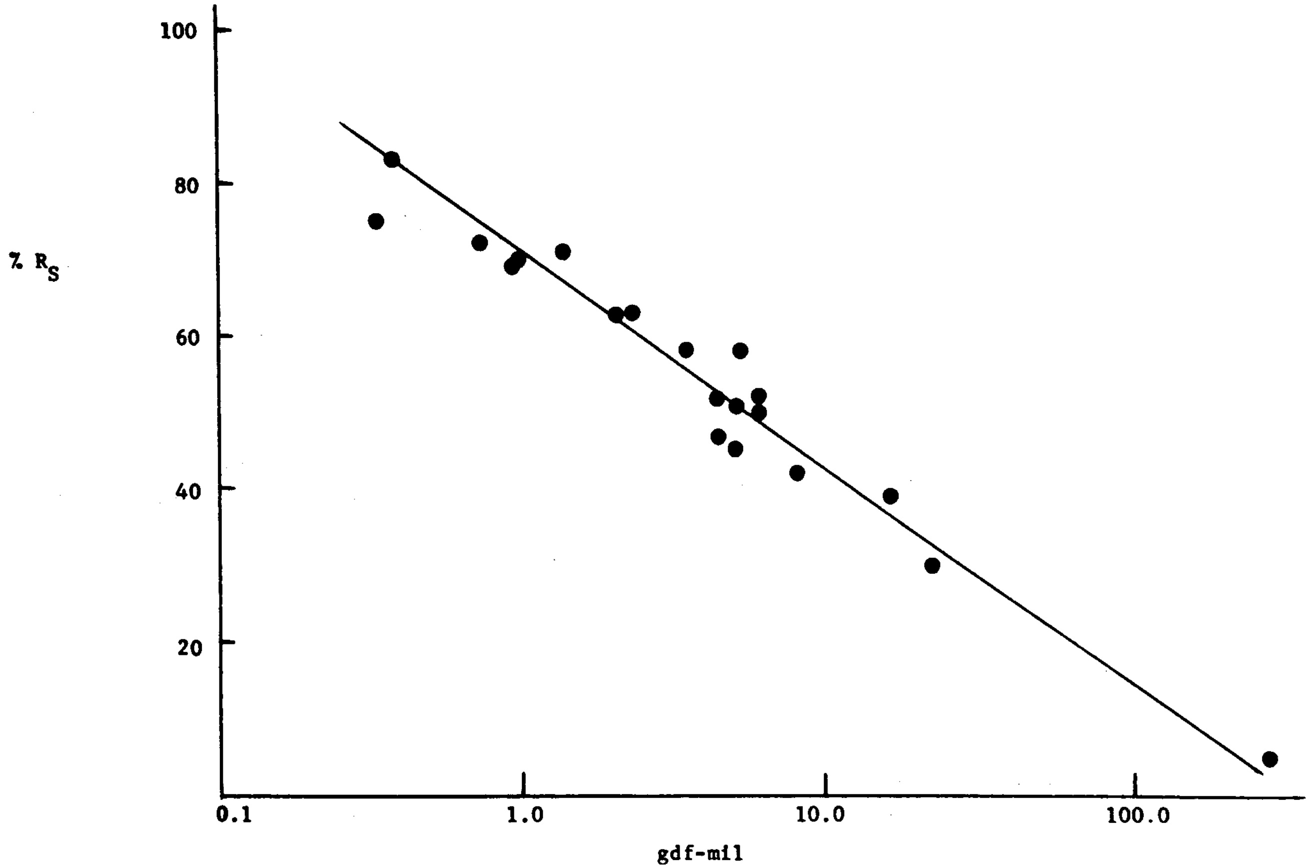


Figure 21 - Salt rejection versus water permeability of different styrene-2-vinyl pyridine block copolymer films in their cationic form. Reverse osmosis conditions: 0.6 N NaCl at 1600 psi.

TABLE V

Reverse Osmosis Properties of Different Block Copolymer Membranes Composed of Styrene and 2-Vinyl Pyridine. Films cast from Tetrahydrofuran except were Noted.

Reverse Osmosis Conditions: 0.6 N NaCl at 1600 psi.

Polymer No.	Quaternization	Film Thickness (mil)	Salt Rejection (%)	Flux (gdf-mil)	Hydration (%)
R-27	Dibromopentane + Methylbromide	1.8	82.9	0.38	31.1
R-27	Methylbromide	1.5	75.1	0.34	33.8
R-18	Methylbromide	2.2	71.6	0.85	48.5
R-18	HCl	1.4	69.0	0.96	--
R-116	Methylbromide	1.3	70.0	1.00	37.5
R-116	Methylbromide	1.4	71.1	1.4	30.9
R-116 Bz	Methylbromide	1.5	63.1	2.1	29.0
R-116 Bz	Methylbromide	1.8	62.7	2.4	37.5
R-132	Methylbromide	1.5	58.0	3.6	--
R-117	Methylbromide	1.5	58.3	5.5	--
R-29	Dibromopentane + Methylbromide	5.4	52.0	4.6	--
R-114	Methylbromide	1.9	51.2	5.3	48.5
R-9	HCl	30.0	52.1	6.3	60.8
R-114	H_3PO_4	1.5	50.1	6.2	--
R-29	Methylbromide	1.2	47.4	4.6	--
R-114 Bz	Methylbromide	1.7	44.9	5.2	50.3
R-117	Methylbromide	1.8	42.2	8.5	54.4
R-118 Bz	Methylbromide	2.1	39.4	17.0	71.4
R-26	Methylbromide	1.3	29.6	23.3	--
R-115	Methylbromide	2.6	5.1	270.0	85.8

There exists a relatively narrow scattering of experimental points in Fig. 21 which might be caused either by small imperfections of some of the membranes or, more likely, by incertainties in the determination of the water permeabilities. In order to compare the water permeabilities of the membranes water flux has to be standardized for unit membrane thickness. It is the thickness measurement which introduces some error in the values of the permeability constants. Although membrane thickness was always measured immediately after termination of a reverse osmosis experiment, the obtained value not necessarily will correspond with the effective thickness value under pressure.

The effect of changes in membrane thickness under pressure is shown in Fig. 22 which presents data obtained on different sulfonated block copolymer films reported by Shell Development Company.[24] The reverse osmosis conditions were the same as for the films presented in Fig. 21 and therefore, the line drawn in Fig. 22 corresponds with the line of the previous figure.

The polymers T-29, T-187, and T-199 closely obey the relationship between R_s and K_1 which was established from anion exchange films of S and 2VP block copolymers. The polymers W-6 and W-33 deviate considerably from this relationship if the reported values (full circles in Fig. 22) are used. Both films were highly hydrated and showed a high compressibility under the experimental pressure of 1500 psi. The pressure dependence of film compression was reported by Shell for both polymer films, W-6 and W-33, and at 1500 psi corresponded to 75 and 50%, respectively. With corresponding thickness corrections applied the values of both cation exchange films (open circles in Fig. 22) agree perfectly with the demanded relationship.

The good agreement of data obtained in different laboratories strongly supports the general validity of Eq. (4). Furthermore, the data show that the reverse osmosis properties of ion exchange membranes are independent of the kind of fixed ions in the membranes as well as membrane morphology. The latter statement is supported by the value for a sulfonated polyethylene film (polyethylene treated with a chloroform solution of chlorosulfonic acid) which is included in Fig. 22 (open triangle designated PE). The relationship, Eq. (4), was further tested and confirmed with a number of different anionic and cationic membranes which were evaluated for their use in the preparation of charge mosaic membranes from polymer blends. These values will be presented in a later section.

With all ionic membranes tested so far significant deviations from the linear relationship of Fig. 21 were observed only to occur toward lower salt rejection indicating membrane imperfections which could be proven by the presence of tiny rust specks on the supporting filter paper. It is not necessary for a film to

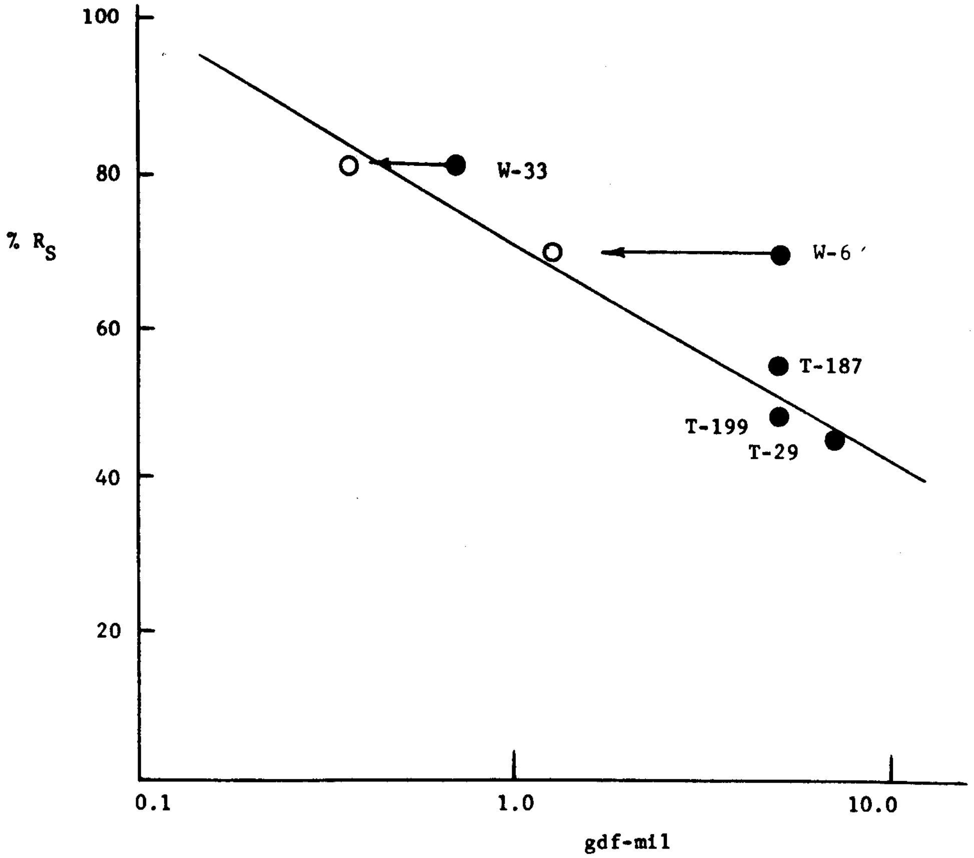


Figure 22 - Salt rejection versus water permeability for sulfonated block copolymer films reported in Ref. 24. Reverse osmosis conditions: 0.6 N NaCl at 1500 psi.

possess the maximum number of ionic centers in order to have reverse osmosis properties in agreement with Fig. 21 provided the concentration of ionic centers is evenly distributed through the film, i.e., the film does not have graded properties.

The block copolymer films from S and 2VP possessed rather stable reverse osmosis properties provided they were not too highly hydrated (less than 40%). With these films salt rejection and water flux remained constant for over a week, the maximum test period investigated. With more highly hydrated films the salt rejection dropped after a few days and in several cases the films ruptured. As already mentioned, these films also lost their mechanical strength during storage in water after several months. It could be that under high pressure conditions the morphological changes took place at an accelerated rate.

With decreasing salt concentration of the feed the salt rejection of ionic films increases. This is shown in Fig. 23 for some of the block copolymer films of Fig. 21. The data of these films are summarized in Table VI. The effect of feed concentration is greater for highly rejecting membranes of low hydration and becomes smaller for membranes of high hydration and low rejection. This dependence on film hydration could be anticipated since in highly hydrated membranes the feed solution passes through the membrane nearly unchanged. The relationship between salt rejection and water permeability at low feed concentration (0.2 N NaCl at 1000 psi) is again of general validity for all ionic membranes and was proven by the reverse osmosis properties of a number of anion and cation exchange membranes which will be reported later.

TABLE VI

Reverse Osmosis Properties of Different Block Copolymer Films Composed of Styrene and 2-Vinyl Pyridine Quaternized with Methyl Bromide. Reverse Osmosis Properties: 0.2 N NaCl at 1000 psi.

Polymer Number	Salt Rejection (%)	Flux (gdf-mil)
R-116	82.1	2.0
R-116	79.0	2.2
R-116	71.5	3.3
R-114	62.5	9.4
R-117	61.0	8.4
R-118	58.0	8.5
R-118	44.0	14.8

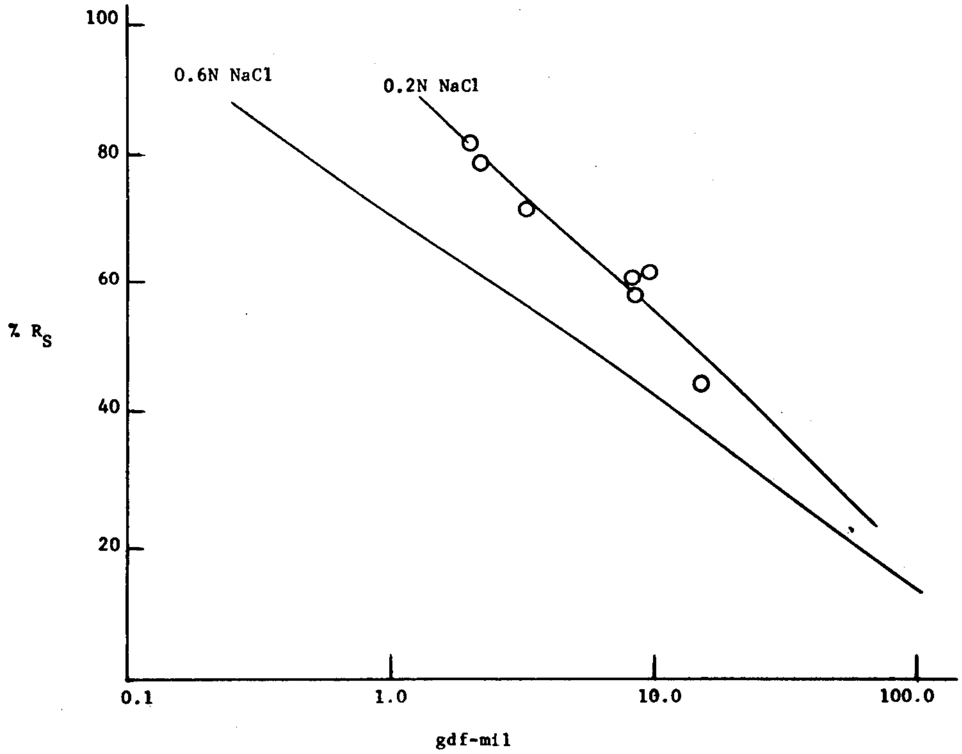


Figure 23 - Salt rejection versus water permeability of different styrene-2-vinyl pyridine block copolymer films in their cationic form. Reverse osmosis conditions: 0.2 N NaCl at 1000 psi.

Summarizing one can say block copolymers are especially suited for the study of ionic membranes in reverse osmosis because of the facile film preparation. The established general relationship between salt rejection and water permeability of ionic membranes is of importance for the preparation of charge mosaic membranes since it shows that matching of both ionic domains with respect to either one of the properties automatically matches the domains with respect to the other property. Furthermore, the relationship expressed by Eq. (4) shows that improved salt rejection of a membrane can be obtained only by sacrificing some of its water permeability. In order to obtain useful water flux extremely thin membranes have to be used whereas changing to more exotic membrane compositions will not result in improved membranes.

The importance of Eq. (4) in its general validity for the characterization of ionic membranes in reverse osmosis tempted us to speculate on the underlying basic principles. Salt exclusion from ionic membranes is usually treated by a Donnan equilibrium. The high concentration of counter ions in the membrane prevents further ions of this kind from entering the membrane. The demanded electrical neutrality in turn prevents the coions from the feed from entering. The quantitative relationship is then given by the Donnan equation which correlates salt concentration in the feed, c', salt concentration in the swollen membrane, c'', and concentration of fixed ions in the membrane, c*.

$$c'^2 = c''^2 + c''c^* \tag{5}$$

The above equation is already simplified for dilute solutions by ignoring the effect of ion activities and by considering only concentrations.

Application of Eq. (5) for reverse osmosis conditions, especially for correlating salt rejections with water permeabilities, meets several difficulties. Eq. (5) describes a membrane system in static equilibrium with a salt solution, and therefore, is not directly applicable for a system with a pressure gradient across the membrane generating a steady state flow. But even neglecting these objections for a moment there still remains the problem of correlating salt exclusion and permeability. The latter value describing a rate process cannot be derived from simple thermodynamic considerations. In this respect the Donnan equation becomes rather useless and a different approach was used which is based on a model describing differences in the transport volumes for mobile ions and water. This treatment is presented in the following section.

I. General Correlation Between Salt Rejection and Permeability of Ionic Membranes

The mode of water transport through water swollen polymer membranes under a hydraulic pressure gradient, i.e., molecular diffusion or bulk flow, could be shown to play the dominant role in salt rejection by nonionic membranes.[25] In nonionic polymer membranes, a diffusive water flux under a pressure gradient is the required condition for a good salt rejection. Such membranes lose their salt rejecting characteristic if water moves through the membrane by bulk flow as a consequence of excessive swelling or high water uptake.

From studies of water transport in polymer membranes,[25] it became clear that most ionic polymer membranes belong to the flow type with respect to the mode of water transport. Water flows through the highly swollen membrane phase of ionic polymers and, consequently, the principles based on the solution-diffusion mechanism cannot explain the salt rejection observed with these membranes. The mechanism of solution-diffusion may play a role only in very tight ionic membranes which can be classified as belonging to the diffusion type despite the fact that they are ionic in nature.

It is quite obvious that interaction of fixed charges and mobile coions of salts, often referred to as Donnan type exclusion, is largely responsible for the salt rejection of ionically charged polymer membranes.[26] However, the direct application of the Donnan equilibrium in reverse osmosis encounters inherent difficulties and ambiguities in the analysis. These are 1) An equilibrium between a two component system (solution phase) and a three component system (membrane phase) should be considered. Therefore, a rigorous treatment can be done only with an activity coefficient based on the molal concentration, particularly for membranes that have high polymer concentration. 2) The transport property of membranes (particularly water flux), however, is based upon the characteristic parameters per unit volume of the membrane. In other words, the transport property of membranes should be expressed in terms of molar concentration that can be considered nearly equal to molal concentration only in a dilute solution of two component systems. 3) A membrane under actual reverse osmosis condition is subjected to gradients of both pressure and concentration. Consequently, the activity coefficients involved in the Donnan equilibrium at the actual condition of reverse osmosis cannot explicitly be determined. It is necessary to use, therefore, reverse osmosis data to explain the change of activity coefficients rather than attempt to explain the reverse osmosis data by the changes of activity coefficients.

During the evaluation in reverse osmosis of block copolymer membranes composed of S and quaternized 2VP a relationship between water permeability, K_1, and salt rejection, R_S, was found to exist as given by Eq. (4). This relationship which is graphically shown in Fig. 21 and 23 is valid in the range of $0.1 < R_S < 0.9$. The data of Fig. 22, including sulfonated polymers, suggested that this relationship is a general one, encompassing all kinds of ionic membranes irrespective of their ionic charges. Indeed, the validity of this assumption can be supported by the data shown in Fig. 33 which includes ionic membranes of many different kinds.

The dependence of R_S on K_1 for ionic membranes, Eq. (4), differs considerably from the corresponding relationship for nonionic membranes. Especially for ionic membranes the decrease of R_S with increase in K_1 is much less pronounced than for nonionic membranes where R_S decreases abruptly as K_1 exceeds a limiting value. With respect to the water transport, highly hydrated membranes belong to the flow type in which salt flux and water flux are strongly coupled. Consequently, only very low salt rejection is expected in highly hydrated nonionic membranes. In ionic membranes salt rejection and water flux can be correlated best by a concept which assigns different transport volumes to salt and water.

The water up-take in the ionic domains will be governed by the number of fixed ions and by the film morphology since swelling will proceed until the swelling pressure equals the generated stress in the hydrophobic matrix. Because of Coulombic repulsion the fixed ions on the polyelectrolyte will arrange into a diffuse ionic lattice without long-range order in the immediate surrounds of each individual ion. Salt and water transport will proceed through this diffuse ionic lattice. For the water transport the total volume of the hydration water may be available, whereas for the salt transport the available water volume will be smaller because Coulombic repulsion between the fixed ions on the polymer and the coions of the salt will restrict their mutual approach to a minimum distance. Outside this salt excluding water shell surrounding each fixed ion, the salt solution will invade the membrane at feed concentration.

For the mathematical description of this model the following volumes have to be defined, all of them referring to one fixed ionic site.

V_o ... Total volume of the hydrated membrane per ionic site
V_1 ... Volume impermeable for water
V_2 ... Volume impermeable for salt

According to these definitions the volume $(V_2 - V_1)$ will be available for the transport of pure water only, whereas the volume $(V_o - V_2)$ will allow the transport of unchanged feed solution. If one assumes that the rates of volume flow in both volume elements are the same, the total water flux can be represented by

$$J_1 = \Phi_1 + \Phi_2 \tag{6}$$

where

$$\Phi_1 = \frac{(V_2 - V_1)}{(V_o - V_1)} J_1 \qquad (7)$$

$$\Phi_2 = \frac{(V_o - V_2)}{(V_o - V_1)} J_1 \qquad (8)$$

The salt flux, J_2, is then given by

$$J_2 = \Phi_2 C_2' \qquad (9)$$

where C_2' is the feed concentration of the salt. The effluent concentration, C_2'' is then given by

$$C_2'' = J_2/J_1 \qquad (10)$$

and for the salt rejection, R_S, follows

$$R_S = 1 - (J_2/J_1C_2') \qquad (11)$$

The salt rejection in then related to the volumes V_o, V_1, and V_2 by

$$R_S = (V_2 - V_1)/(V_o - V_1) \qquad (12)$$

With $(V_o - V_1)$ representing the total water volume assigned to one ionic center, the concentration of fixed ions, C*, in moles/kg water, is given by

$$C^* = 1/(V_o - V_1)N \qquad (13)$$

where N is Avogadro's number ($N = 6.02 \times 10^{23}$).

The volume given by the difference $(V_2 - V_1)$ corresponds to the volume of the salt excluding water shell surrounding each fixed ionic center. This volume, in Å^3, can be calculated from Eqs. (12) and (13) and is given by

$$V_2 - V_1 = 10^{27} R_S/C^*N \qquad (14)$$

Because the thickness of the salt excluding water shell represents the minimum approach distance of two similarly charged ions, the salt excluding shell volume has to be constant irrespective of the kind or the concentration of fixed ions in the membrane, at least in a first approximation, although this volume might depend somewhat on the feed concentration as will be discussed later.

In Table VII are listed $(V_2 - V_1)$ values for several S-2VP block copolymer films, quaternized with methylbromide, where C* was determined by conductometric titration with silver nitrate. It can be seen that the shell volumes are fairly constant. In the last comumn of Table VII the radii of equivalent spheres are shown which closely correspond to the minimum approach distance between a fixed ion of the polymer and the coion of the salt. For this calculation both ions were assumed as dimensionless point charges.

The volume fraction of water in a swollen membrane, H, is given in the present notation by

$$H = (V_o - V_1)/V_o \tag{15}$$

If it is assumed that $(V_2 - V_1)$ is constant, at least in a first approximation, Eq. (12) can be rewritten in the form

$$R_S = \frac{m}{V_o} (\frac{1}{H} - 1) \tag{16}$$

where $m = V_2 - V_1 = \text{const.}$

TABLE VII

Volumes of Salt Excluding Water Shells, $V_2 - V_1$, and Radii, r, of Equivalent Spheres

Salt Rejection (%)	Fixed Ion Concentration (moles/Kg water)	$V_2 - V_1$ (Å^3)	r (Å)
70	2.73	426	4.7
63	2.81	372	4.5
51	2.25	376	4.5
45	1.90	394	4.5
42	1.35	515	5.0
39	1.07	605	5.2
33	1.44	381	4.5
5	0.35	238	3.8

Feed Concentration = 3.5%, applied pressure = 1500 psi

Equation (14) indicates that the salt rejection of ionic membranes is directly proportional to the fixed ion concentration, C*. This relationship was examined for block copolymer membranes of which C* was determined and was found to apply as shown in Fig. 24. Equation (16) indicates that the salt rejection of ionic membranes can be related to the water content of the membrane, a parameter considerably easier to obtain than C*. The validity of Eq. (16) is examined in Fig. 25 for the block copolymers

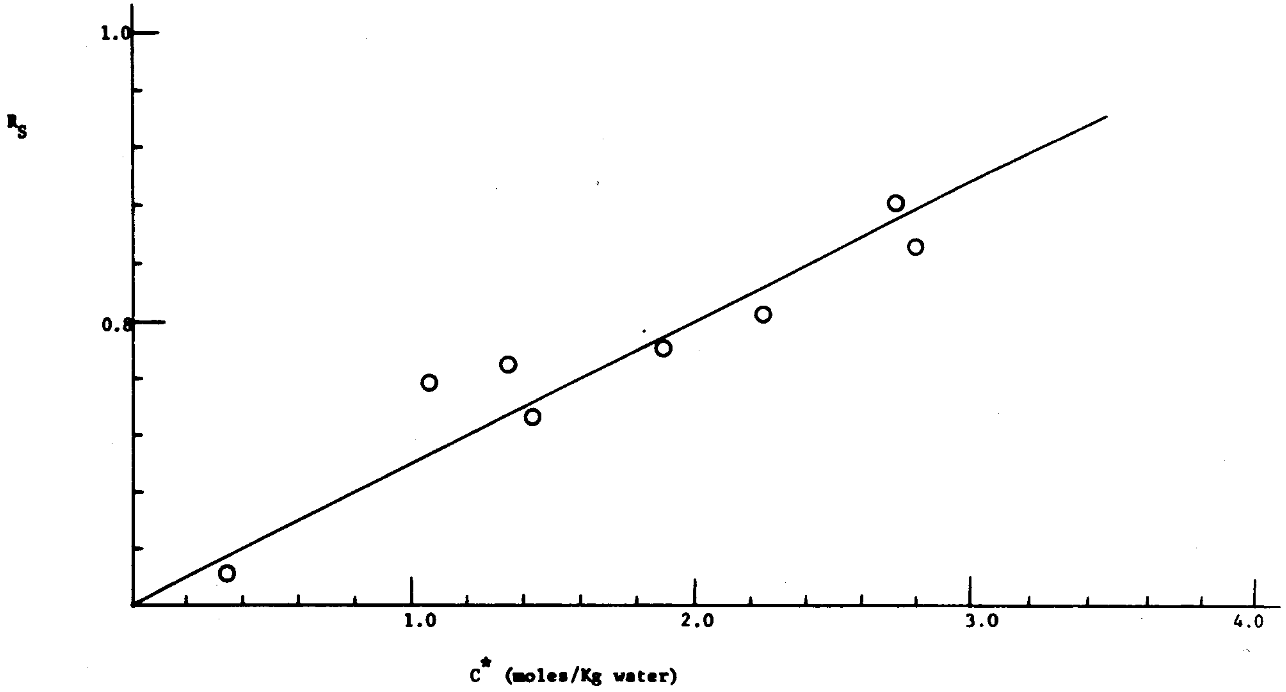


Figure 24 - Salt rejection versus fixed ion concentration in block copolymer membranes composed of styrene and 2-vinyl-N-methyl-pyridinium bromide.

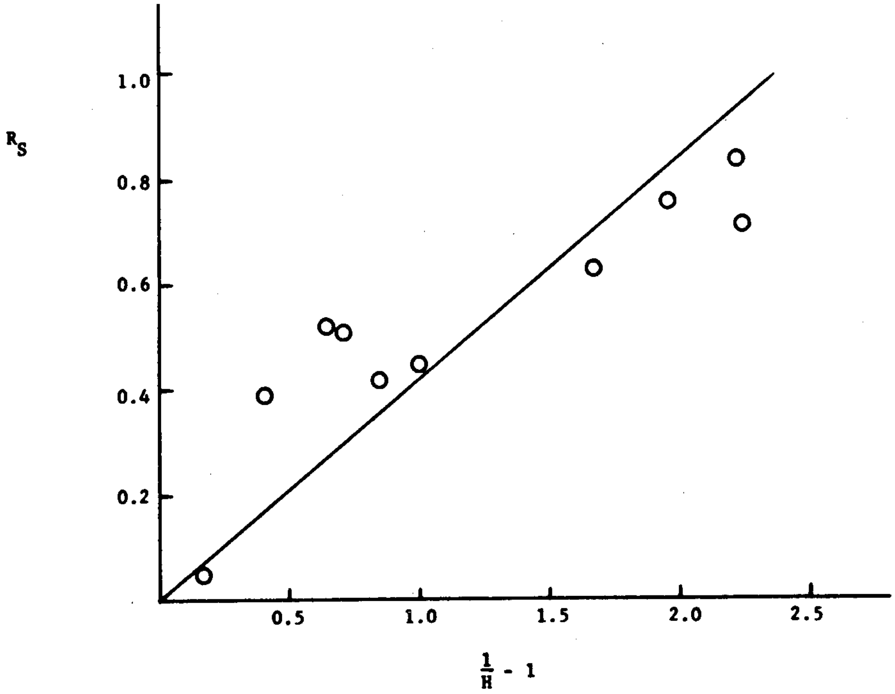


Figure 25 - Dependence of salt rejection on membrane hydration of block copolymer films composed of styrene and 2-vinyl-N-methyl-pyridinium bromide.

reported in Table V. Although there is a considerable scattering of points, the general trend agrees with Eq. (16). Some of the scattering might be caused by not considering the hydrophobic portions of the membranes, but such a consideration might be somewhat arbitrary by not knowing how much PS can participate in the swollen domains.

The hydraulic permeability constant of water for highly hydrated membranes can be approximated by an expression of the form[27]

$$K_1 = K_o \exp - B' \left(\frac{1}{H} - 1\right) \quad (17)$$

where K_o and B' are constants. It should be noted that the relationship given by Eq. (17) is empirical and only approximate for small values of 1/H - 1, though most ionic polymer membranes fall into this region.

The value of V_1 is closely related to the molecular volume of the macromolecule per ionic site, which is the molecular volume of the repeating unit for an ideal case. The water uptake in the actual ionic polymer membrane will be governed not only by the number of fixed ions but also by the film morphology and/or molecular and topological cross-linking. Therefore, V_1 in realistic membranes may not be directly proportional to the molecular weight of the monomer. Under these conditions, it may be rationalized, as the first approximation, that m/V_o is a constant, since $m/V_1 = V_2/V_1 - 1$. In this approximation it is assumed that the salt rejecting shell volume is proportionally larger with larger ionic groups.

With this assumption, Eq. (16) and Eq. (17) can be combined to give the general form as shown in Eq. (4). The relationship of Eq. (4) has an important practical value in characterizing reverse osmosis performance of ionic membranes, since K_1 and R_S are ordinarily the only parameters observable under the exact condition of the reverse osmosis.

In general, for a given membrane, the salt rejection increases with decreasing feed concentration. This increase demands an increase in the salt excluding shell volume, $(V_2 - V_1)$, provided that C* can be assumed to remain constant. The measurement of C* was done with membranes equilibrated with pure water and the values were assumed to remain unaffected by changing feed concentration. However, for more or rigorous treatment, the effect of feed concentration and pressure on the membrane hydration had to be considered.

Such an increase in the shell volume becomes reasonable if one considers that the closest average approach distance of two ions of similar charge is determined by the concentration of all ions present. The calculated equivalent radii of the salt rejecting shells are shown in Table VIII, which indicates a general increase of r with decrease of feed concentration.

TABLE VIII

Effect of Salt Concentration on the Radii of Equivalent Impermeable Sphere

Feed Concentration	r (Å) Membrane No.		
C_2' (mole/Kg water)	R-116 Bz	R-116	R-118
0.616	4.5	4.7	5.2
0.320	4.8	5.0	5.5
0.188	5.1	5.0	5.8
0.099	5.3	5.1	6.2
0.045	5.4	5.2	-

It is worth noting that many reverse osmosis data[28-30] reported by different investigators for various charged membranes all fit the general trend shown in Fig. 21, and also that the time-dependent changes observed with some membranes also follow the general quantitative relationship; i.e., the increase of flux with decrease of salt rejection and vise-versa. The latter fact may be reflecting the change of membranes under the conditions of testing. Namely membranes may swell or contract in the salt solution under higher pressure; however, this change will merely reflect in H, and consequently in C*, in such a way that all relationships given by Eqs. (14), (16), and (17) are followed; hence the results observed as R_S and K_1 are expected to follow the general relationship described by Eq. (4).

Salt rejection can be treated as a consequence of transport depletion of salt relative to the water flux rather than to the blocking of salt transport.[25] The transport depletion can be explained by consideration of volumes available for transport of water and salt in the homogeneous polymer membranes based upon the movement of water in the membrane phase of both ionic and nonionic polymers. It is worth noting that throughout this analysis the derivations are based on one model of membranes; i.e., homogeneous polymer membranes which are detailed in the literature,[25,31] and it was only necessary to characterize the movement of water (solvent) in the membrane to explain the phenomena observed with different types of membranes. It is also interesting to note that the relationship shown in Fig. 21 for ionic polymer membranes is converging to the identical point with nonionic membranes as R_S increases, or K_1 decreases, indicating that very high salt rejection by ionic polymer membranes no longer can be attributed to rejection by an ionic mechanism. As the water permeability approaches the diffusion region, the salt rejection by tight ionic membranes may be best explained by a solution-diffusion mechanism, in which the partition coefficient may be explained by or Donnan type equilibrium.

It may be concluded that the salt transport depletion relative to water transport is caused by the difference in the characteristic volumes or sizes of hydrated ions and water. In nonionic membranes, the difference depends on the physical size of hydrated solute and water. In ionic membranes, the size of the impenetrable ionic field (for similarly charged ions) over-rides the size of hydrated ions. In both cases, salt rejection and water flux seem to be best understood by the concept of "transport volume" described.

F. Charge Mosaic Membranes from Styrene-2-Vinyl Pyridine Block Copolymers

Block copolymers were hopefully considered to represent the best material for the preparation of charge mosaic membranes. The occurring phase separation provides discrete domains of both constituting polymeric blocks which can be chemically transformed into regions of oppositely charged polyelectrolytes by proper selection of the polymeric components. The selection of the polymeric component is restricted in several ways.

Block copolymers are prepared best by anionic polymerization mechanisms, and therefore, only monomers can be used which are not interfering with the free carbanions or the counter ions of the alkali metal. Furthermore, the pronounced differences in the basicities of different carbanions determine the possible block sequence in the polymer. For example, if one intended to separate the anionic and cationic blocks in a chain by a block of neutral polymer this would not be possible by the combination of S, VP, and MMA since these monomers could only be polymerized in this sequence. The VP, providing the cationic polymer, will always remain adjacent to an anionic block regardless whether the latter results from hydrolysis of the MMA or sulfonation of the S.

The chemical reactions by which the ionic centers are introduced should be mild but still effective ones because of the necessity to carry out these reactions with the polymer in film form. The film has to be swollen in order to admit the reagent but the swelling has to remain selective for one domain, the other domain providing the physical cross-links during the treatment. For this reason, it was not found possible to sulfonate the PS domains in a S-2VP block copolymer film in the usual way with concentrated sulfuric acid. The sulfonated PS as well as the P2VP salt are both soluble in concentrated sulfuric acid and the film dissolves. A similar situation might be anticipated for the hydrolysis of a 2VP-MMA block copolymer film in alcoholic potassium hydroxide solution. The P2VP is soluble in alcohols and with increasing hydrolysis of the PMMA these domains dissolve also. If the P2VP is quaternized prior to hydrolysis it is not soluble in alcohol but the prolonged treatment with a strong alkaline solution will partially decompose the quaternary pyridinium groups.

Solubility properties present one of the main problems in the selection of feasible polymer combination. In order to obtain a block copolymer with anionic and cationic domains separated by a neutral polymer block the combination B-S-2VP was investigated (ISV-1 to 4). The three monomers can easily be polymerized in the indicated sequence. It was intended to sulfonate the PB with a diethyl ether complex of chlorosulfonic acid, this complex being too weak to attack the PS. In several trials the films dissolved in the ether during treatment.

The introduction of cationic and anionic centers in the same film demands two subsequent reactions, the conditions of which should not be detrimental. Cationic groups can be introduced either by quaternization of already present tertiary amine groups or by amination of active chlorine atoms. These chlorines can be either initially present in the monomer or can be introduced into the polymer, e.g., by chloromethylation of PS. Anionic groups can be either carboxylic acid groups or sulfonic acid groups.

With anionic polymerization conditions the only polymers possessing tertiary amine groups are those derived from vinyl pyridines. Monomers possessing chlorines active in amination are prohibited for obvious reasons. The only chlorine containing monomer susceptible to anionic polymerization conditions is p-chlorostyrene but the corresponding polymer cannot be aminated easily. Polymers with carboxylic acid groups can be derived from their corresponding esters which allow anionic polymerization conditions to be applied. Unfortunately, the easily hydrolyzable esters of the acrylic acid polymerize very poorly under anionic polymerization conditions due to self-termination which prevents the reaction to go to completion. Esters of the methacrylic acid polymerize readily but the polymers hydrolyze extremely slowly even if in solution. In film form the hydrolysis of PMMA is still much slower.

Carboxylic acid groups for the anionic domains of block copolymer films are not easily obtainable and it was therefore decided to use sulfonic acid groups. These groups can be introduced into PS under mild conditions in a number of ways. With the use of the PS for the anionic domains the cationic domains had to be derived from P2VP. Quaternization of P2VP and sulfonation of PS are both specific reaction not interfering with each other. Methylbromide solely reacts with the P2VP and the latter, especially in its quaternized form is not attacked during the sulfonation of the PS. The insolubility of the quaternized P2VP in chlorinated solvents allows swelling of the PS domains for the sulfonation reaction without disintegration of the film.

The sulfonating agents were sulfur trioxide complexes with either triethyl phosphate or 2,2'-dichlorodiethyl ether.[32-34] These complexes are soluble in carbon tetrachloride, chloroform, or methylene chloride and were applied at room temperature. The quaternized block copolymer films were preswollen according to the solvent used. The reaction times varied from 15 min to several hours. The sulfonation reaction was terminated by placing the films in methanol. After washing the films were placed in dilute sodium hydroxide solution and then in a sodium chloride solution for conditioning.

All the amphoteric films were clear, of rubbery consistency, and very highly swollen (over 80%). With respect to the chemical aspect the approach to prepare charge mosaic membranes was successful. Unfortunately, none of these amphoteric membranes exhibited the desired piezodialysis effect, i.e., salt enrichment in the permeat with respect to the feed. All of the membranes had high water permeabilities and very low salt rejections, salt enrichment was never observed, not even a marginal one.

The reason for these negative results is a consequence of improper film morphology resulting from block copolymers. At first sight it seems surprising that a film of a block copolymer solely compose of S and 2VP is insoluble in water after both kinds of domains have been converted to polyelectrolytes. Chemical cross-links are not introduced by the quaternization reaction with methyl bromide, and also the sulfonation with sulfur trioxide complexes is claimed to yield products free of cross-links. Although cross-link formation in the latter reaction cannot be ruled out completely, the number of cross-links probably formed would remain insufficient to prevent the film from disintegration. Without the presence of chemically cross-links film strength is supplied by ionic cross-links at the phase boundaries.

The phase boundaries in block copolymer films are never ideally sharp and around each domain there exists a layer in which PS and P2VP chain segments overlap. In this region salt formation between the sulfonic acid groups and the quaternized pyridinium rings takes place. The resulting poly-poly salts are water insoluble and provide a thin network which supplies the mechanical strength. The existence of ionic cross-links is indicated by the swelling behavior of amphoteric block copolymer films in salt solutions.[35] The films swell strongly in salt solution and deswell in water. This behavior can be explained by the shielding effect of imbibed salt ions. The imbibed salt ions act as counter ions for the sulfonic acid and pyridinium groups thereby opening the ionic cross-links in the phase boundaries. As a consequence the cross-link density of the film decreases allowing an increased water uptake. Because of the films not showing the desired piezodialysis effect quantitative measurements of the swelling properties were not carried out.

The lack of piezodialysis properties in amphoteric block copolymer films is a consequence of unfavorable morphological structures. Mainly three film properties are responsible for the failures: (1) poly-poly salt formation at the phase boundaries, (2) lack of a rigid matrix which prevents swelling, and (3) three-dimensional instead of the necessary two-dimensional phase separation in the film.

The poly-poly salt regions in the phase boundaries cause undesirable swelling properties and provide regions of unhindered salt flow. Unhindered salt flow to occur in poly-poly salt regions was shown with different membranes derived from S-2VP block copolymers in which the P2VP domains were made amphoteric. With these membranes the PS remained uncharged preventing excessive swelling of the membranes.

In the first membrane investigated the amphoteric group corresponded to $\equiv N\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}SO_3^-$. This group was introduced by treating the membrane with propylene sultone in methanol. Under reverse osmosis conditions the membrane showed extremely high flux, 10 ml/min under experimental conditions corresponding to over 200 gdf-mil. The salt rejection was negligible, between 1-2%. After a test period of over 24 hrs. the supporting filter paper was completely free of rust spots indicating the absence of larger pinholes.

A series of membranes was prepared from a solution of a $(S\text{-}2VP)_n$ block copolymer with acrylic acid in an amount equivalent to the P2VP content of the polymer. About 2 wt.-% of ethylene dimethacrylate and 0.5 wt.-% azo-diisobutyronitrile were added to the solution. Films were cast on glass plates and cured at 50°C over night. Very tough membranes resulted. Again under reverse osmosis conditions the membranes showed extremely high flux and a negligible salt rejection below one percent.

These membranes were erroneously reported to exhibit a marginal salt enrichment of 1-2%. Although the effluent, sampled at the same time as the feed, exhibited an increase in conductivity over the latter, this increase was due to a slight increase in the temperature of the effluent as a consequence of the high flow rate. In repeated measurements both samples, effluent and feed, were allowed to stand in covered vials at room temperature for at least half an hour before conductivities were measured. Under these conditions the conductivity of the effluent was always slightly lower than the conductivity of the feed.

A detailed explanation of these results seems to be of importance firstly to correct an erroneous statement, and secondly to show the awareness of possible pitfalls in the determination of marginal piezodialysis effects. Therefore, the slight salt enrichment observed with a charge mosaic film derived from a polymer blend can be considered to be a true one with greater confidence.

The results obtained from poly salt membranes explain to a large extent the absence of piezodialysis effects in charge mosaic membranes solely composed of sulfonated PS and quaternized P2VP. Block copolymer membranes could be expected to exhibit piezodialysis effects only if the domains of both polyelectrolyte precursors were separated by a polymer remaining unaffected during subsequent chemical reactions. Because of the incompatibility of polymers the third polymer has to be incorporated into the block copolymer, i.e., a ternary block copolymer has to be used. The unreactive polymer block, which constitutes the matrix has to be inserted between both polyelectrolyte precursors. Unfortunarely, a feasible polymer was not found which could be used under anionic polymerization conditions. An attempt to use the combination B-S-2VP or IP-S-2VP failed because of the films dissolving in ether during the selective sulfonation of the PB or PIP blocks.

Provided the demanded ternary block copolymer could be synthesized, there remains still the open question whether the phase separation in the film would be the desired one. In such ternary block copolymers of structure A-M-B where A and B are anionic and cationic precursors, respectively, and M represents the matrix polymer, both blocks A and B would have to be considerably shorter than the M block in order to assure the formation of A and B domains isolated from each other by M. In order to obtain a permeable membrane the A and B domains must not possess a spherical shape completely surrounded by M but the separation of the three phases must be restricted to two dimensions. The smallness of the A and B domains would then demand extremely thin films.

The necessity for the presence of an unreactive matrix polymer in charge mosaic films has also a second reason besides the one of preventing poly-poly salt formation on the phase boundaries. As long as only the P2VP domains are quaternized the degree of swelling of these domains is limited by the rigidity of the PS matrix. With sulfonation of the PS domains this limitation ceases to exist and the water uptake of the P2VP domains will now be considerably higher than before. As a consequence the salt rejecting properties of the P2VP domains will now reach such low values that a piezodialysis effect cannot be expected to occur to a significant extent. In the same way the sulfonation of the PS domains increases the swelling of the P2VP domains the latter domains affect the former ones. The amphoteric film now consists of highly swollen anionic and cationic domains each one with very low salt rejecting properties. These domains are held together by regions of poly-poly salts on their phase boundaries which exhibit no salt rejection at all but possess the highest water permeability.

Whether the mutual increase in the degree of swelling of the ionic domains or whether the high volume fraction of the poly-poly salt regions contribute more to the unhindered salt flow depends on the membrane morphology. It seems to be most likely that the latter condition contributes most to the high salt flux. Membranes in which one or both domains were partially cross-linked still possessed high water permeabilities and negligible salt rejections.

In one series of membranes the P2VP domains were partially cross-linked by addition of 1,5-dibromopentane to the casting solution and curing at 70°C before the methyl bromide for complete quaternization was admitted. With 0.6 N NaCl at 1600 psi a typical membrane showed a salt rejection of 78% with 0.33 gdf-mil. The membrane was tight and strong enough to be sulfonated and retested. Retesting in reverse osmosis yielded 2.5% salt rejection with a flux of over 200 gdf-mil.

Some membranes of this series were swollen in dichloroethane after quaternization and an ether solution of aluminum trichloride was added to provide cross-links in the PS domains by Friedel-Crafts reaction. After sulfonation the membranes showed again high permeabilities and salt rejections between one and two percent.

For two reasons it seems to be very unlikely that the extremely low salt rejection observed with amphoteric membranes is caused by improper ionic balance between the anionic and cationic domains. It seems reasonable to assume that a film possessing the ideal morphology of a charge mosaic membrane will show decreasing salt enrichment the more the balance of anionic and cationic domains becomes disturbed. There should even come a point when the film exhibits low salt rejecting properties. All of the investigated amphoteric membranes showed very low salt rejection and salt enrichment was never observed at all. It seems very unlikely that all of these films were improperly balanced just to be marginally situated on the side of salt rejection.

Although improper ionic balance of the anionic and cationic domains could explain the absence of a piezodialysis effect, it could not explain the extremely high water permeabilities observed with amphoteric membranes. The latter membrane property must be a consequence of changes in membrane morphology or composition which are connected with the introduction of both kinds of ionic domains. As pointed out before these changes can involve either the formation of extended regions composed of poly-poly salts or can be a consequence of increased swelling of the individual domains due to the disappearance of a rigid matrix. Both changes which might act simultaneously would not only increase the permeability of the membranes but would also be detrimental for the piezodialysis effect.

The absence of a piezodialysis effect in the investigated block copolymer membranes could also be blamed on improper film morphology. The demanded phase separation in charge mosaic membranes for piezodialysis must be a two-dimensional one which means that domains of opposite charge should be adjacent only in the main dimensions of the film but not across its thickness. Each domain should extend uninterrupted through the film thickness.

It becomes immediately obvious that this arrangement of domains will be very unlikely to occur if the film thickness considerably exceeds the average domain dimensions. In order to make both dimensions commensurable either the domains have to be extremely large or ultrathin films have to be used. An average phase dimension of about 1000Å already demands an average molecular weight of about one million. Films of block copolymers of such large block lengths possess a very low cross-linking density and accordingly will swell very strongly. One has to consider that each chain in a domain is only anchored by its ends at the phase boundaries. Such domains will exhibit a very low salt rejection making these membranes useless in piezodialysis. Even with block lengths of one million in molecular weight the gain in film thickness remains small since the film thickness still has to remain below one micron.

The chemical modifications of thin block copolymer films of several microns thickness was not successful although the block lengths were far below one million. The main problem occurred during sulfonation of the quaternized films. Such thin films have a tendency to form folds and these folds could not be straightened out without rupturing the films. The strong adherence of touching film surfaces is very likely caused by salt formation between oppositely charged domains upon contact. In all trials it was not possible to obtain films free of holes after sulfonation.

Films with three-dimensional phase separation where oppositely charged domains are stacked in the direction of film thickness will not exhibit a piezodialysis effect. Such membranes should possess salt rejection and flow properties corresponding to a combination of two membranes, one being of anionic, the other of cationic nature. As anticipated, experiments showed that such a combination of membranes has higher rejection and lower permeability than each individual membrane. The high permeabilities and the negligible salt rejections of the investigated amphoteric membranes cannot be explained by the presence of overlapping domains in a three-dimensionally separated film.

Block copolymers applicable for piezodialysis would demand extremely large block lengths in order to obtain domain dimensions commensurable with film thickness. The high water uptake of these domains has to be suppressed by introducing chemical cross-links. Since it is hardly possible to prepare block copolymers yielding average domain sizes much in excess of 1000Å, film thickness has to remain very low which complicates the handling of these films. Because of the necessity to introduce chemical cross-links one might ask why to use block copolymers at all. Films with regular phase separations can be obtained also from polymer blends. Such films have average phase dimensions up to several hundreds of microns making the restrictions in film thickness less severe.

IV. Membranes From Random Copolymers of S and 4VP

In recent years considerable attention has been given to synthesizing and improving existing membranes for the purpose of removing certain undesirable solutes usually from aqueous mediums.[36-40] Perhaps the most attention has been given to the problem of removing salt from saline water. Often the membranes used for such separation processes work quite satisfactory over short periods of time, but fail over longer time intervals due to inherent drawbacks such as poor initial strength or compaction under the high pressure necessary to affect reverse osmosis conditions.[41] Numerous attempts have been made to stabilize membranes by chemical cross-linking and grafting techniques. In some cases, the presence of chemical cross-links has improved the problem of membrane compaction.[42] Often, however, it is difficult to incorporate certain cross-linking compounds in the membrane without having undesirable affects on the transport properties. With this viewpoint in mind, high-energy irradiation was used to investigate the effect of cross-linking on the properties of an alternating copolymer of styrene and 4-vinyl pyridine. Also, this system readily lent itself to the study of the influence of hydration on the transport properties of water and salt due to the easy quaternization of the copolymer. In addition, asymmetric membranes could be easily prepared by quaternization on a gradient and the unidirectional flow properties measured under reverse osmosis conditions.

Chapiro[43] has pointed out that for most polymers irradiation leads to more chain scissions than primary cross-links between chains, i.e., the G(value) for scission is much higher than that for cross-linking. As a result, the polymer is severely degraded before substantial cross-linking can take place. However, there is usually an optimum dose which varies from polymer to polymer where the tensile properties are at a maximum. The results of the present study will now be discussed in more detail below.

A. Experimental Procedure

The copolymer was prepared by introducing equimolar amounts of freshly vacuum distilled styrene and 4-vinylpyridine into glass ampoules. In the case of 4-vinylpyridine it was necessary to distill it through a spinning-band column prior to the vacuum distillation. A small amount of 2,2'-azobis(2-methyl-propionitrile) was added as the initiator. Each sample was then thoroughly degassed by the freeze-thaw method and sealed. Afterwards the samples were placed in a oven pre-set at 75°C and allowed to polymerize for two days.

Tetrahydrofuran was used as the casting solvent and was added directly to the glass ampoules until the polymer had a concentration of about 10 percent. All films were cast directly from this solution and allowed to dry slowly in air. Films were then thoroughly evacuated in glass ampoules to assure the complete removal of residual solvent or monomer and irradiated by Cobalt-60 for the desired dose at a dose rate of 0.1 megarads per hour.

Film quaternization was carried out using methyl bromide in the vapor state for various periods of time. The residual methyl bromide was then pumped away and the film again weighed. These films were then allowed to reach equilibrium with deionized water and the various properties were then measured. The percent hydration was taken as the grams of water absorbed per gram of swollen polymer on a percentage basis.

Transport properties were measured in high pressure cells with the applied pressure maintained at 1500 psi and the salt concentration at 2.5%. All measurements were carried out at ambient conditions, circa 25°C.

B. Effect of Film Irradiation

The random copolymer of styrene and 4-vinylpyridine used in these studies contained approximately equimolar amounts of each constituent based on nitrogen analysis. Also, the reactivity ratios for the two monomers favor an ideal copolymer.[44]

Prior to tensile tests, the quaternized membranes were allowed to come to equilibrium in distilled water and the tensile properties measured in the wet state. For these measurements duplicate samples were examined at each dose and the resulting values were then averaged. The influence of total dose on the resulting tensile properties is presented graphically in Fig. 26. Also, the pertinent data along with the values for hydration are summarized in Table IX. Clearly both the modulus and tensile strength increase initially with dose, pass through a maximum, and then decrease with further increase in dose. In this case, the optimum conditions correspond to a total dose of about 9 megarads which gives rise to a 60 percent increase in the modulus. As modulus is a good measure of a polymers resistance to deformation, compaction would be expected to be the lowest under these conditions.

Although the curves shown in Fig. 26 show a decrease in tensile strength at the higher doses this does not mean that the tensile strength continues to decrease for even higher doses. In fact, Charlesby, has shown that such curves will once again increase at the higher doses at which time the polymer usually becomes glassy and brittle but possesses a much higher tensile strength.[45]

Introduction of cross-links by direct irradiation in the random copolymer was sufficient enough even at the highest degrees of quaternization to prevent complete solubilization of the quaternized copolymer. (Without irradiation, the highly quaternized copolymer was readily water soluble.) At the doses investigated, however, the highly quaternized films became too highly hydrated in water and were not strong enough to withstand the high pressures encountered in reverse osmosis. It should be pointed out, however, that a random copolymer membrane that has been quaternized to the extent to give optimum values for salt and water flux is very tough and shows good mechanical properties as indicated by the data of Table IX.

In a separate series of experiments, several of the alternating copolymer membranes were quaternized to various extents and the hydration and transport properties were then measured. When the percent hydration was plotted as a function of degree of quaternization a sigmoid-shape curve as shown in Fig. 27 was obtained. It is interesting to note that the optimum conditions for water flux with good salt

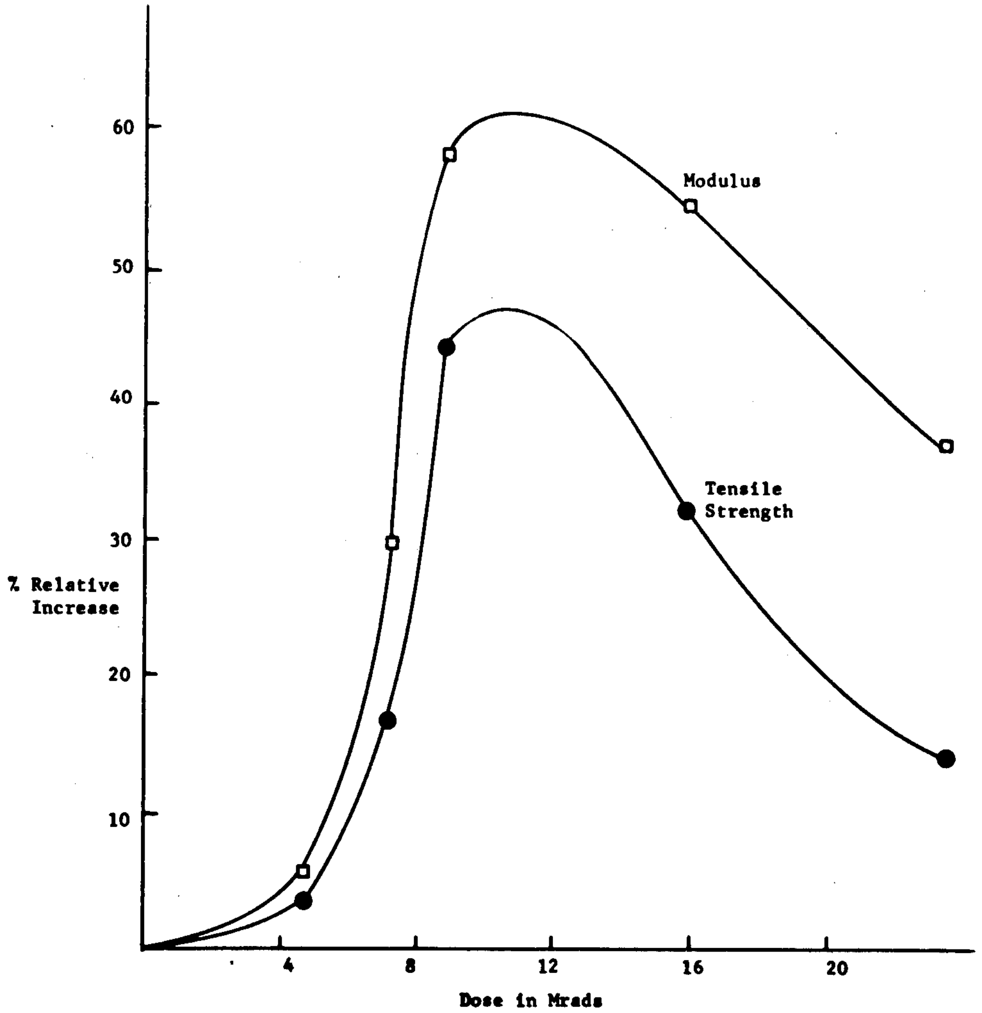


Figure 26 - The effect of irradiation dose on the tensile properties of random copolymer films of styrene and 4-vinyl pyridine.

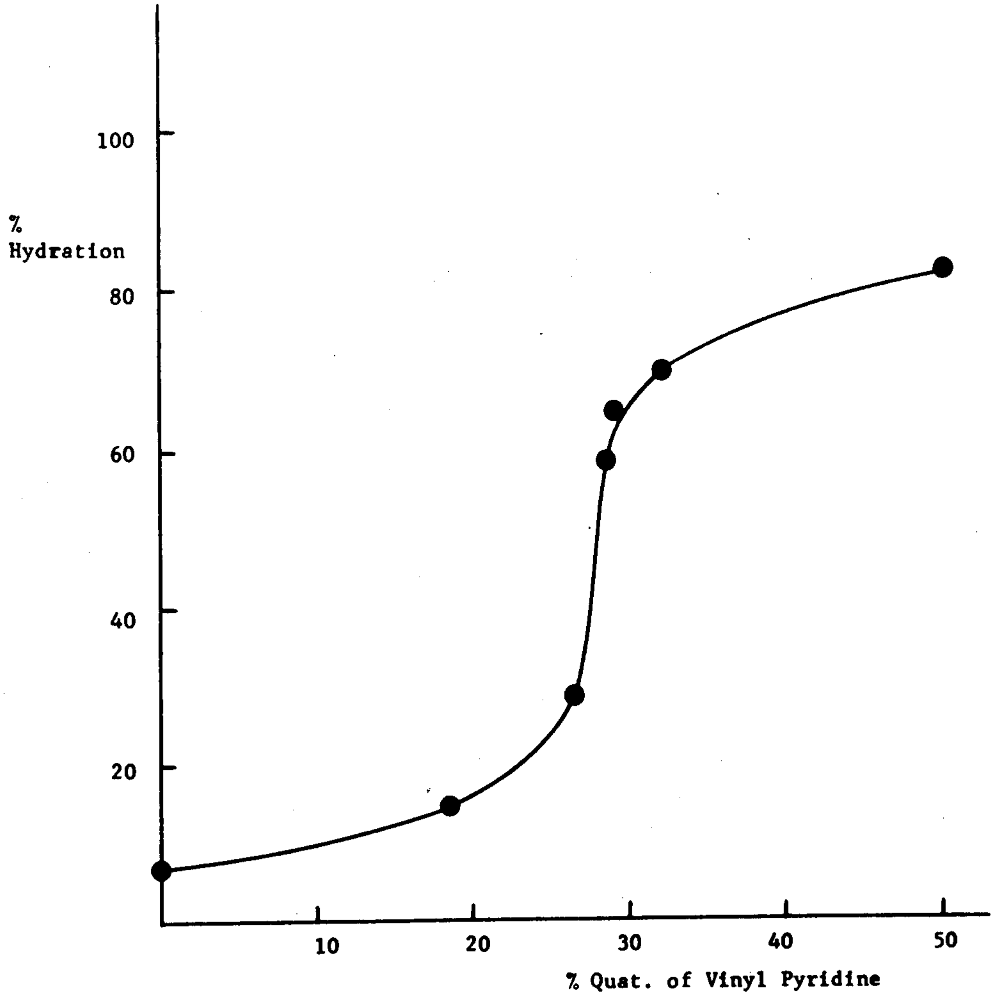


Figure 27 - Effect of the degree of quaternization on the hydration of styrene-4-vinyl pyridine copolymer films.

TABLE IX

The Influence of Irradiation Dose on the Tensile Properties of a Quaternized Alternating Copolymer of Polystyrene and Poly 4-Vinyl Pyridine

Sample No.	Dose (Mrads)	*Percent Increase in Modulus	**Percent Increase in Tensile Strength	% Hydration
13	0	0	0	28.2
7	4.7	5.4	3.5	29.1
8	7.2	29.4	16.8	25.4
9	8.8	57.9	44.2	20.2
10	15.9	54.2	31.9	22.9

---

* Modulus of Control Sample - 670 $kg/cm^2 \cdot cm$

** Tensile Strength of Control Sample - 113 kg/cm^2

TABLE X

The Influence of Quaternization on the Degree of Hydration for an Alternating Copolymer of Polystyrene and Poly 4-Vinyl Pydridine

Sample No.	*% CH_3Br	% Hydration	% Sorbed
Control	0	6.7	7.2
14	18.6	14.4	16.9
13	26.4	28.2	39.2
2	28.6	58.7	142.0
5	29.0	64.5	181.8
4	31.8	69.8	231.3
3	50.0	81.9	453.0

---

* Based on Vinyl Pyridine Portion Only.

TABLE XI

The Effect of Degree of Quaternization on the Transport Properties of Water and Sodium Chloride Under Reverse Osmosis Conditions for an Alternating Copolymer of Polystyrene and Poly 4-Vinyl Pyridine

Sample No.	% Quat.	% Hydration	$P\times10^9$	% Salt Rejection
2	28.6	58.7	0.292	91
5	29.0	64.5	1.16	78
4	31.8	69.8	2.53	61
3	50.0	81.9	16.96	22

$P = \left(\frac{g \cdot cm}{cm^2 \cdot sec \cdot atm}\right)$

rejection seems to occur at the inflection point in this curve. The exact significance of this, if any, is not completely clear. However, work with asymmetric membranes of the alternating copolymers indicates that perhaps the inflection point might be associated with the quaternization of the inner depths of the membrane, i.e., when the middle of the film is quaternized then and only then is the membrane free to swell. Upon quaternization of the middle portion, the membrane swells more freely and as a consequence the water flux increases along with the salt flux, i.e., poor salt rejection. The actual values for the water permeability constants and salt rejection values along with the other pertinent data are presented in Tables X and XI. It is quite evident that the water permeability increases and the salt rejection decreases as the film becomes more and more hydrated. Also, that the degree of hydration continues to increase with increasing quaternization until the film eventually becomes water soluble.

When the permeability constants were plotted in a semilog fashion as a function of the reciprocal hydration a curve as shown in Fig. 28 was obtained. For such a relationship, it follows that the dependency of the permeability constants on hydration may be expressed as

$$P = P_o \exp(-\gamma/H) \tag{18}$$

Other experiments indicate that a similar relationship can be obtained for different polymer systems. The value of γ in this case was found to be 3.64. The corresponding values for the salt rejection are shown in Fig. 29 as a function of reciprocal water concentration in the film.

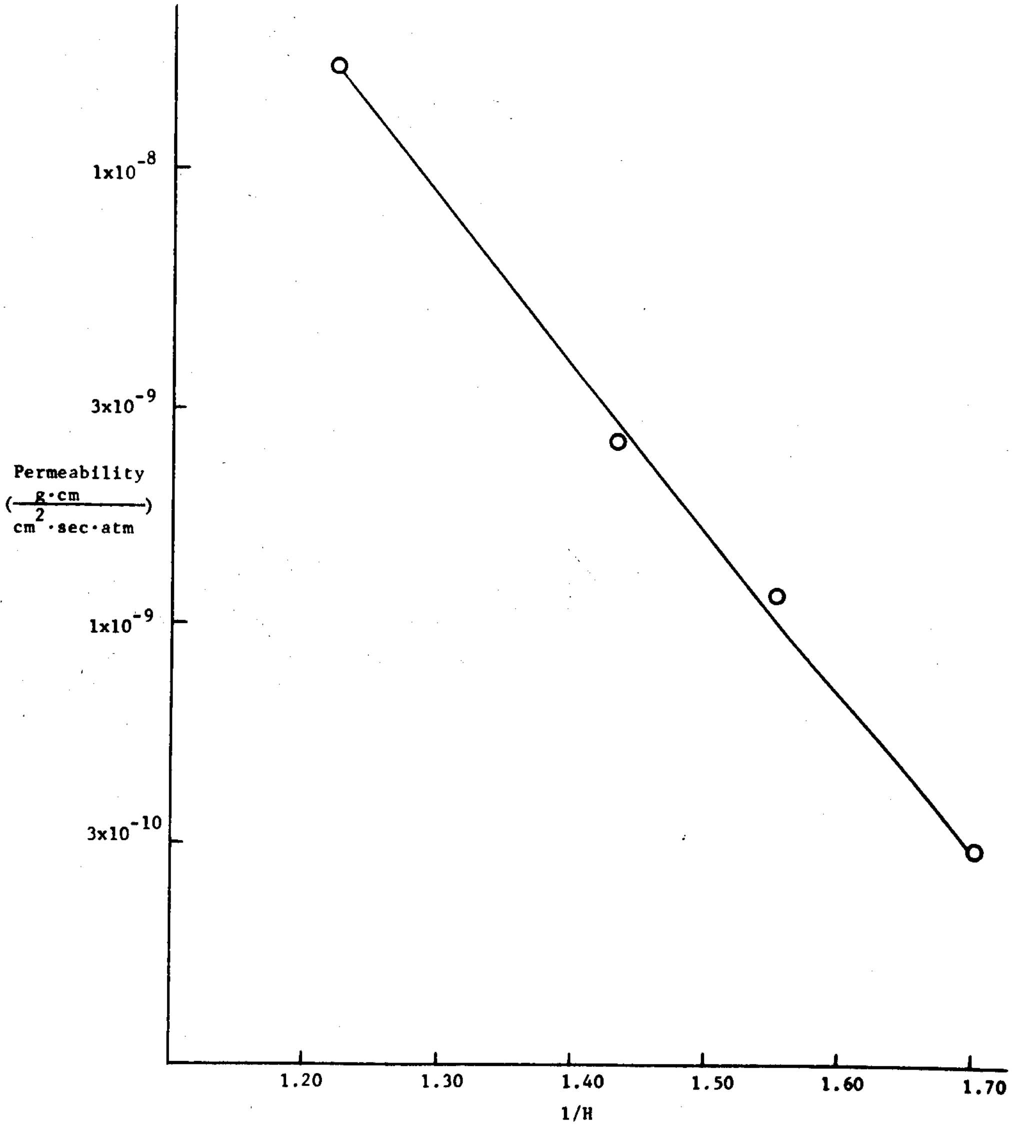


Figure 28 - Effect of hydration on water permeability in random copolymer films of styrene and 4-vinyl-N-methyl-pyridinium bromide.

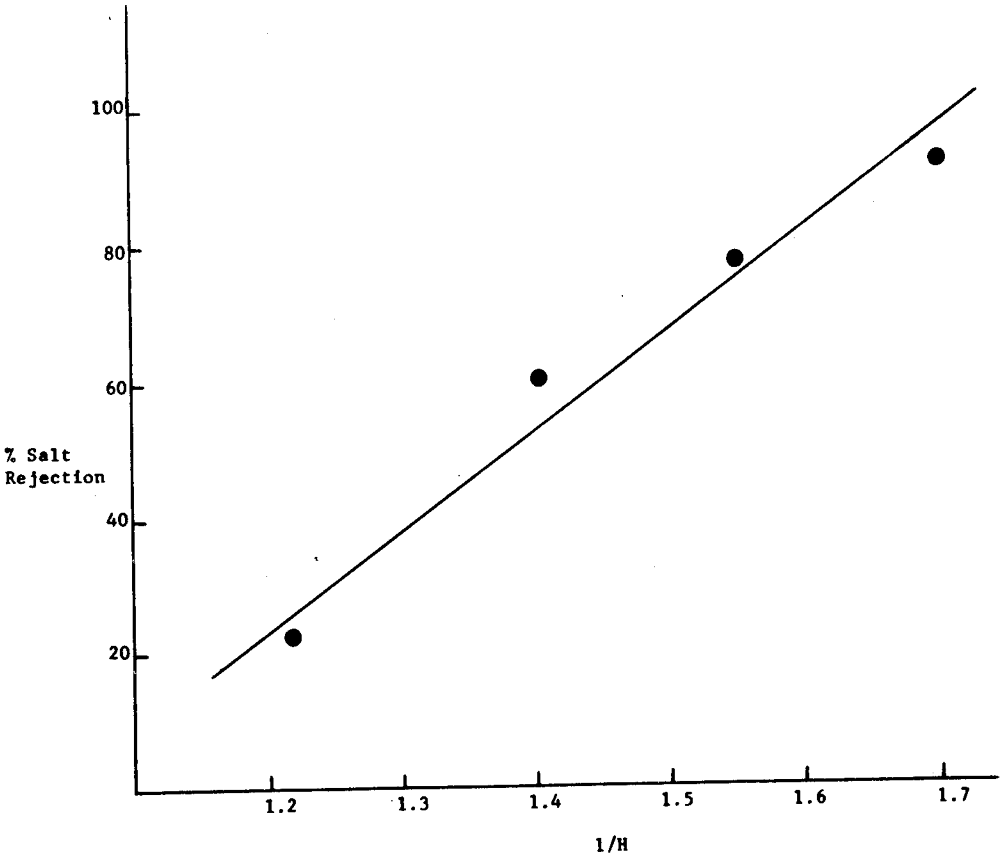


Figure 29 - Effect of hydration on salt rejection in films of random copolymers of styrene and 4-vinyl-N-methyl-pyridinium bromide.

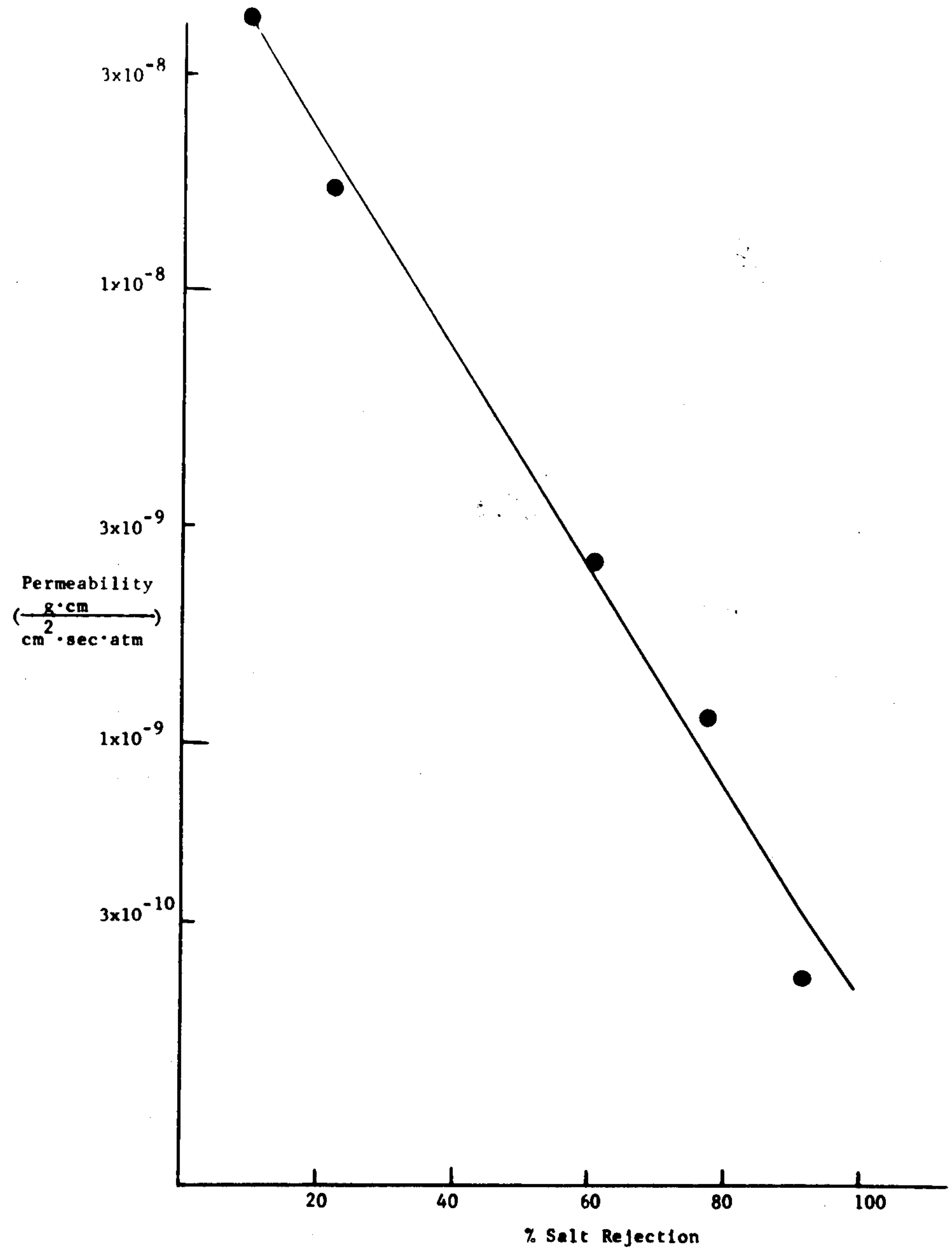


Figure 30 - Relationship between salt rejection and water permeability in films from random copolymers of styrene and 4-vinyl-N-methyl-pyridinium bromide.

Since for saline water purposes it is nice to be able to relate directly the water permeability to salt rejection such a plot is shown in Fig. 30. From such a curve it is quite apparent that as one obtains a higher and higher water flux it must be done so at the sacrifice of salt rejection. However, for a small sacrifice in salt rejection a considerable increase in water flux results. Such a relationship seems to be quite general and is not dependent on the nature of the ionic polymeric membrane except for what point it might fall on the curve.

C. Effect of Graded Quaternization

It had been shown previously by Stannett-Williams-Gosnell-Gervasi[46] that anisotropic flow properties were obtained when polyethylene-2-vinylpyridine grafted films were quaternized on a gradient. In their study, the transport of water took place in the vapor state and at very low pressures, i.e., pressures well below the forces required for membrane compaction. Rogers[47] has also found similar vectored permeability characteristics in the case of polyethylene films that had been grafted on a gradient with various monomers. In an earlier paper, Rogers-Stannett-Szwarc[48] presented a quantitative explanation for such effects in the case of gas permeation through laminated films.

In the present work the influence of graded membranes on the transport properties of water and sodium chloride under reverse osmosis conditions has been examined. Alternating copolymers of styrene-4-vinylpyridine were prepared by free radical polymerization and films were then cast from a suitable solvent. Before removal of the film from the glass plate, quaternization was carried out by subjecting the exposed side of the film to methyl bromide vapor for various time intervals. The degree of quaternization and quaternization profile could be varied easily by time of exposure or vapor activity employed.

Several graded membranes were prepared as above and their behavior under reverse osmosis conditions were examined both with and against the direction of the quaternization gradient. Typical results for water flux and salt rejection are summarized in Table XII. It is quite clear that when the highly quaternized side is exposed to the salt solution there is a considerably higher water flux than when the gradient is reversed. In the first case for example, the water flux is 1.3 gfd along the gradient and is reduced to 0.80 gfd against the gradient. Also, the salt rejection values are less along the gradient as compared to rejection against the gradient again in support of the asymmetric nature of the membrane. This type of membrane selectivity for the respective transport of water and salt would be expected based on the results presented in Fig. 27 and 30, i.e., the highly water permeable direction would be expected to have a low salt rejection and vice-versa.

The calculation[49] of water permeability for a membrane with a hydration gradient demonstrates the following features:

1. There is no asymmetry in membrane permeability if the hydration is independent of applied pressure or if the permeability has the same pressure dependence $d\ell nP/dp$ through the membrane;
2. The permeability is higher for the pressure gradient having the same direction as the hydration gradient if the actual pressure the membrane has to sustain (compacting pressure) reduces the hydration and hence the permeability more on the high than on the low hydration side. If the total pressure inside the membrane goes from p_o to 0. the compacting pressure at any length of the membrane is $p_o - p$ where p is the pressure in the liquid at that point.

The results of Table XII hence imply that the highly quaternized side of the membrane with the high hydration and permeability is more affected by pressure than the less quaternized side. Therefore, the flux through the membrane is less reduced if the high pressure is applied to the highly quaternized side because in that case the compacting pressure is much less than in the reverse orientation of the membrane.

This can perhaps best be seen schematically in Fig. 31 and in consideration of Dracy's law:

$$j_{\pm} = K_{\pm} \left(\frac{\partial p}{\partial x}\right)$$

where j is the volumetric flow rate, K the permeability, and $\partial p/\partial x$ is the pressure gradient across any element of the membrane. The positive and negative subscripts for K refer to flow with the highly quaternized side exposed to the high pressure, and the reverse orientation, respectively. When the highly quaternized side is exposed to the high pressure the compacting pressure on it is much less than in the reverse case which results in the inequality:

$$\int_o^{\ell} K_+ \frac{dp}{dx} > \int_o^{\ell} K_- \frac{dp}{dx}$$

i.e.,

$$j_+ > j_-$$

The actual water flux along the quaternized gradient is about 50% more than against the gradient for the values given in Table XII. Undoubtedly, the magnitude of this difference can be varied appreciably by the severity of the gradient imposed on the original membrane.

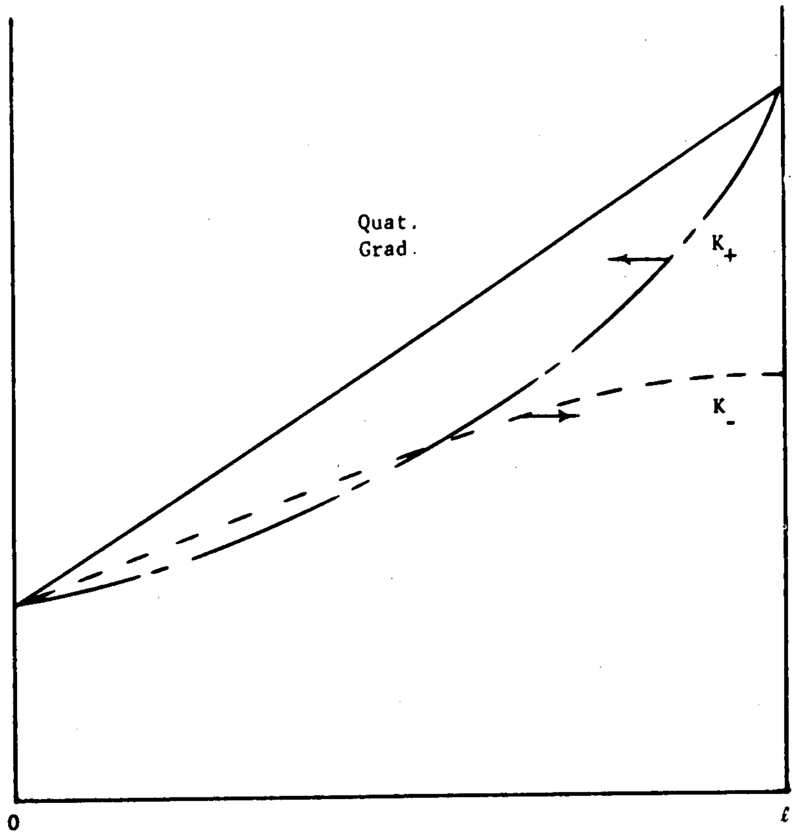


Figure 31 - Schematic representation of an anisotropic membrane with directional properties.

TABLE XII

Directional Water Permeability Effects brought about by Quaternization of an Alternating Copolymer of Polystyrene and Poly 4-Vinyl Pyridine on a Gradient

Sample No.	Flux ($\frac{\text{gals.}}{\text{ft}^2 \text{ day}}$)	$Px10^9$	% Salt Rejection
1-Quat. "Up"	1.26	1.19	45
1-Quat. "Down"	0.80	0.73	67
2-Quat. "Up"	0.52	0.49	25
2-Quat. "Down"	0.37	0.35	45

$P = (\frac{g \cdot cm}{cm^2 \cdot sec \cdot atm})$

V. Membranes from Polymer Blends

Because of the covalent bond between the different polymeric blocks of a block copolymer phase separation is restricted to molecular dimensions. If in a block copolymer A-B the component A forms a separated phase simultaneously a phase B is formed adjacent to A. The sizes of the A domains is restricted by the sizes of the B domains and vice versa. Such restriction does not apply in the phase separation of blends of homopolymers where each phase can grow independent of the other one.

The individual phases in films from polymer blends can be arranged in a very regular fashion depending on casting conditions. In Fig. 32 there is shown a film obtained from a 1:1 mixture of homo PS and homo P2VP. Both polymers were dissolved separately in THF and the solutions were mixed before casting. Phase separation already takes place in the combined solutions. The mixture becomes turbid and silk-like schlieren form upon shaking and stirring. If the mixture is left undisturbed for some time two layers separate. Therefore, casting has to be performed with the well stirred blend.

The film from the PS-P2VP blend was cast the usual way on a glass plate by applying a doctor knife and then dried on air. During drying distinct circular P2VP domains form regularly arranged in the PS matrix. The dimensions of the P2VP phases are in the range of 300 to 500 microns which is several times larger than the film thickness (about 30 microns). For this reason the P2VP phases extend through the film thickness as could be shown by treating the film with methanol. By this treatment the P2VP was leached out and only a lace like PS network remained. The remaining PS lace was used as the negative for making the print of Fig. 32, and therefore, the P2VP domains appear as dark holes. Films with corresponding phase

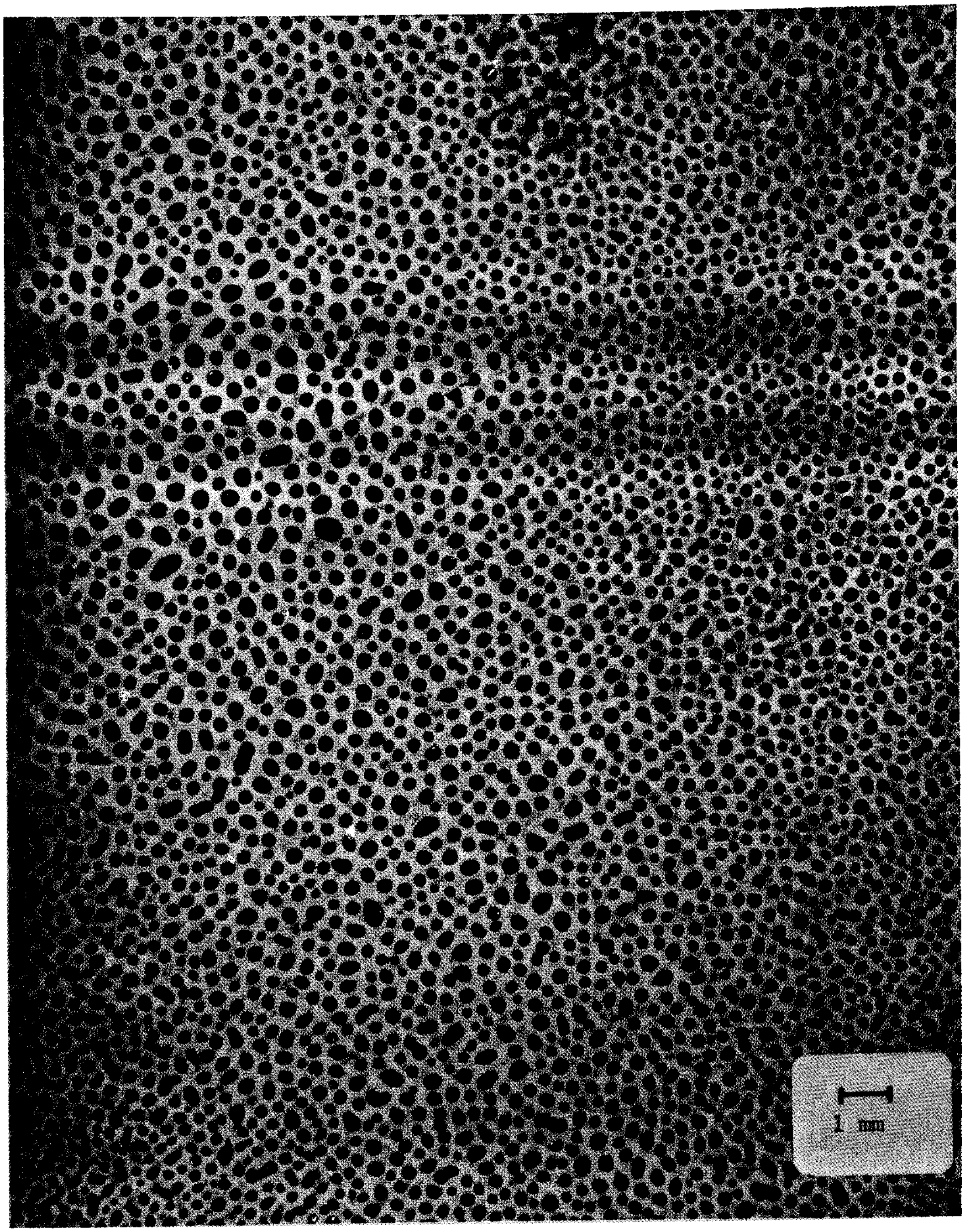


Figure 32 - Photoprint of a phase separated film cast from
a blend of homopolystyrene and homopoly(2-vinyl
pyridine)(1:1).
Poly(2-vinyl pyridine) domains eluted with methanol.

arrangements were obtained with other homopolymer combinations, such as PS-PMMA and P2VP-PMMA.

The arrangement and size of phases in films derived from homopolymer blends would make them ideal ones for charge mosaic membranes in piezodialysis provided the films could be sufficiently cross-linked. Cross-linking can be accomplished if the homopolymers were substituted by copolymers containing small amounts of curable units.

Phase separated membranes made from polyblends have the advantage of greatly increasing the number of useable polymer combinations. There exists no restriction with respect to the polymerization mechanism, and the polymers have to meet only three conditions. The polymers have to be (1) sufficiently incompatible to exhibit good phase separation, (2) curable to form sufficiently dense networks, and (3) easily convertible into polyelectrolytes. It is obvious that also in polyblends only one of the components can be a polyelectrolyte. The curing process has to meet three conditions. Firstly, the generated cross-links must remain stable during subsequent film treatments whereby the ionic groups are introduced. Secondly, the cross-linking process has to be applicable in a reaction medium in which both of the polymer components are insoluble but swell sufficiently to allow the reaction to proceed. Thirdly, the reactive groups for the cross-linking reaction should be easily incorporated into the polymer by copolymerization reactions.

Considering all three conditions governing the selection of curing reactions, the most promising approach seemed to be cross-linking by means of olefinic chain segments. Such segments are easily incorporated by copolymerization with either butadiene or isoprene. A free radical polymerization was preferred in copolymer synthesis over anionic polymerization because of the general applicability of the former and also because of resulting in a greater randomness in the distribution of cureable units along the polymer chain. A random distribution of cureable units, and therefore, of cross-links, in the film could be expected to result in tougher films with low degree of swelling. Furthermore, the even distribution of cureable groups was hoped to facilitate the formation of interfacial cross-links.

The synthetic work on charge mosaic membranes derived from polyblends was carried out in two phases. In the first phase prospective copolymers were selected and synthesized. These copolymers were used to make films composed of one component only in order to evaluate the best cross-linking reaction. The films were then characterized by their salt rejection and permeation properties under reverse osmosis conditions. In the second phase blends of copolymers were used for film preparation. These films were investigated with respect to their morphology and their behavior under reverse osmosis. With one of these films a marginal piezodialysis effect was observed for the first time.

A. Cross-Linking Studies With Isoprene Containing Block Copolymers

Cross-linking studies were carried out with two kinds of block copolymers available from previous studies. The block copolymers contained either S or 2VP in combination with isoprene. The following cross-linking methods were tried.

1. UV Irradiation of films containing small amounts of azo-bis(isobutyronitrile) as photosensitizer for free radical generation.
2. Gamma-irradiation of films without additives.
3. Film treatment with low pressure helium plasma.
4. Curing with benzoyl peroxide at 80°C and with cumyl peroxide at 140°C.
5. Treatment of films containing small amounts of tert-butyl hydroperoxide with sulfur dioxide gas.
6. Vulcanization with sulfur monochloride.

With the first four methods free radicals are generated in the polymer which lead to non-specific cross-linking over carbon-carbon linkages. In the presence of olefinic sequences in the copolymers the carbons in α-position to the double bonds are preferentially attacked and cross-linking takes place mainly in the olefinic domains. All curing processes involving free radicals demand polymers free of stabilizers and prematurely cross-linking of the copolymers during storage or dissolving can take place.

Both irradiation methods, UV and gamma-irradiation, yielded cross-linked but extremely brittle films which disintegrated during handling. Nevertheless the PS containing film still swelled rather strongly in toluene. Similar results were obtained from film curing with cumyl peroxides. Benzoyl peroxide was not effective at all. Peroxide curing of 2VP containing polymers is not possible because of the accelerated peroxide decomposition in the presence of amines. The polymer solutions in benzene colored immediately upon addition of the peroxide and no cross-linking effect was observed on the films.

Film treatment with low pressure helium plasma resulted in films solely cross-linked on the surface. Upon treatment these films with a solvent a very thin and incoherent skin remained.

The reaction of a polymer with sulfur dioxide gas in the presence of a hydroperoxide is specific for relatively long sequences of cis or trans double bonds.[50] Presumably the reaction involves a free radical initiated addition of sulfur dioxide to the double bonds with the formation of 5 or 6 membered sulfone rings along the chains. The amount of sulfur dioxide addition depends on the polymer structure, 1,2-vinyl structures which interrupt the sequence of 1,4-butadiene or 1,4-isoprene units interfere with the sulfone formation. Diene polymers from emulsion polymerization with 1,2-placements in excess of 15% are less satisfactory for sulfone formation than all cis or all trans polymers. Being a free radical process this cross-linking method also demands stabilizer-free polymers.

With the S-IP block copolymers the cross-linking reaction was successful although the films still swelled considerably in toluene due to the large size of the PS domains. 2VP containing block copolymers could not be cross-linked at all very likely because of the interaction between the pyridine rings with the hydroperoxide. In this connection it might be mentioned that 2VP containing copolymers of either toluene or butadiene did not cross-link during storage whereas the corresponding styrene containing copolymers cross-linked very easily if free of stabilizers.

The reaction of sulfur monochloride with unsaturated polymers results in cross-linking over sulfur bridges (formation of β,β'-dichloro-di-thioethers). The vulcanization of films derived from unsaturated polymers can be carried out in two ways, either by adding the sulfur monochloride to the polymer solution before casting,[51] or by placing the cast films in a dilute solution of the sulfur monochloride. Both methods worked equally well with S-IP block copolymers.

Polymers containing 2VP cannot be vulcanized in this way because of the pyridine groups reacting with the sulfur monochloride. With the addition of the latter to a benzene solution of the block copolymer gelation takes place nearly immediately. Vulcanization of the cast films with dilute solutions of sulfur monochloride in heptane was not effective either. The reaction of the sulfur monochloride with the P2VP can be avoided if the latter is quaternized before treatment. A series of vulcanization experiments was carried out with quaternized films and varying sulfur monochloride concentrations and reaction times. All these experiments with heptane as solvent yielded negative results.

In further vulcanization experiments with 2VP containing copolymers different solvents for the sulfur monochloride were investigated. The choice of solvents was rather restricted by the high reactivity of the sulfur monochloride and the second demand that the reaction medium must be a nonsolvent for the film. It was found that the dielectric constant (ε) of the reaction medium plays a decisive role in the vulcanization reaction. Three solvents of high dielectric constant were finally selected, nitroethane ($\varepsilon = 28.0$), acetonitrile ($\varepsilon = 38.8$), and nitromethane ($\varepsilon = 39.4$). The 2VP containing copolymer films were quaternized with methyl bromide on the glass plate and were then placed into solutions of freshly distilled sulfur monochloride (5 vol.-%) in the dry solvents (dried over calcium hydride). Only in the last two solvents vulcanization took place, apparently the dielectric constant of nitroethane still being too low. The pronounced dependence of the vulcanization reaction on the dielectric constant of the reaction medium is rather interesting and might be connected with the polar nature of the polymer. Indeed, vulcanization of random copolymers of butadiene with methacrylic acid exhibited an identical behavior. Also this copolymer could be effectively vulcanized only in either nitromethane or acetonitrile but not in nitroethane solutions of sulfur monochloride. For further work with random copolymer films nitromethane was used as vulcanization medium since it was found that this solvent gave the most stable solutions of sulfur monochloride.

Although block copolymers of S or 2VP with IP could be cross-linked by vulcanization, these films were not useful as membrane materials, either by themselves or in form of blends, because of their high degree of swelling in their ionic forms. The high water uptake was a consequence of the large size of the ionic domains resulting from the block structure. This undesirable swelling behavior could be overcome by introducing the vulcanizable monomer units randomly along the chains.

B. Films Derived from Random Copolymers Containing Butadiene

A series of random copolymers of butadiene was prepared by free radical polymerization utilizing the following comonomers: styrene, methyl methacrylate, methacrylic acid, 2-chloroethyl methacrylate, 2-, and 4-vinyl pyridine. The reactivity ratios of butadiene in these monomer combinations are in the range of 0.2-1.4, and the reactivity ratios for the comonomers in the range of 0.3-0.5. The butadiene content of the copolymers was in the range of 20-45 mole-%. In Table XIII the polymerization conditions are summarized of those random copolymers which were used for film preparation.

After polymerization the copolymers had to be stabilized with N-phenyl-2-naphthylamine since several of them cross-linked prematurely during isolation and drying. The presence of the stabilizer had no detrimental effect on the vulcanization reaction with sulfur monochloride indicating that the reaction does not involve free radicals. The ionic nature of the vulcanization reaction might also be indicated by the strong effect of the dielectric constant of the reaction medium.

The first films investigated were composed of one random copolymer only in order to investigate their behavior during conversion into polyelectrolytes. It was especially of interest whether the sulfur bridges would withstand the sulfonation reaction, quaternization or amination reactions being rather mild one.

The vulcanized styrene films were swollen in chloroform or 1,2-dichloroethane and sulfonated in the same medium either with chlorosulfonic acid or with a sulfur trioxide-bis-(2-chloroethyl)-ether complex (1:3). Chlorosulfonic acid is soluble in chlorinated solvents except perchlorinated ones and concentrations of 2-10 vol.-% were applied. During sulfonation by both methods a purple color developed in the films which deepened during the reaction. The color was very likely caused by the presence of the stabilizer (N-phenyl-2-naphthylamine). During washing the films

Co-polymer No.	Co-monomer	Polymerization system	Initiator		Polymerization		mole-% butadiene in		Polymer conversion	Purification of the copolymer
			mole-%		Temp. °C	Time hrs.	monomer feed	co-polymer	%	
BS-10	styrene	bulk	0.24	AIBN	50	90	10	18	55	polymer bulk dissolved in THF + 0.2% PNA; precipitated in methanol
BS-6	styrene	emulsion	0.30 0.15	$Fe^{2\oplus}$ BPO	25	7	25	24	75	polymer emulsion precipitated in methanol + 1% conc. HCl + 0.1% PNA
BS-9	styrene	emulsion	0.16 0.80	$K_2S_2O_8$ n-heptyl-mercaptane	50	20	28	30	78	polymer emulsion precipitated in methanol + 1% conc. HCl + 0.1% PNA
BV-5	2-vinyl pyridine	bulk	0.23	AIBN	50	44	18	23	90	polymer bulk dissolved in THF + 0.2% PNA; precipitated in n-hexane
BV-1	2-vinyl pyridine	bulk	0.23	AIBN	50 65	16 6	18	24	73	polymer bulk dissolved in THF + 0.2% PNA; precipitated in n-hexane
BV-3	2-vinyl pyridine	bulk	0.23	AIBN	50 70	24 15	26	37	92	polymer bulk dissolved in THF + 0.2% PNA; precipitated in n-hexane
BV-2	4-vinyl pyridine	bulk	0.23	AIBN	50 65	16 3	18	29	87	polymer bulk dissolved in ethanol + 0.2% PNA; precipitated in water
BMA-9	methacrylic acid	bulk	0.12	BPO	50	45	38	45	30	polymer bulk dissolved in THF + 0.2% PNA; precipitated in water
MAB-1	methyl methacrylate	bulk	0.24	AIBN	50 65	16 31	28	29	45	polymer bulk dissolved in THF + 0.2% PNA; precipitated in methanol
BCM-1	2-chloro-ethyl methacrylate	bulk	0.32	AIBN	50	20	20	34	51	polymer bulk dissolved in THF + 0.2% PNA; precipitated in methanol

TABLE XIII. Copolymerization data of different random copolymers containing butadiene.

with fresh chloroform after sulfonation the color disappeared and completely clear and faintly yellow films resulted. The chloroform was then replaced by methanol and the latter by water. The films were finally placed into a 0.5 N NaOH solution to be converted into their salt form.

After vulcanization the films were sometimes slightly opaque due to finely dispersed elemental sulfur. The opaqueness remained during swelling prior to sulfonation but vanished during the sulfonation reaction. One might speculate that the sulfur particles in this finely divided form were oxidized by the sulfonating agent. If this were true attack of the sulfonating agent on the sulfur bridges cannot be completely excluded although weakening of the films by the sulfonation reaction could not be observed.

Quaternization of 2VP copolymers was carried out in the usual way by treatment with gaseous methyl bromide at 70°C prior to vulcanization. The copolymers of 2-chloroethyl methacrylate were aminated in the gas phase at 70°C with trimethyl amine. The methyl methacrylate copolymer was hydrolyzed with alcoholic NaOH solution. The copolymer of acrylic acid was converted into the salt form by placing into 0.5 N NaOH solution. All films were conditioned in 0.2 N NaCl solution before being tested in reverse osmosis (1200 psi). The preparation and the reverse osmosis properties of the random copolymer membranes are summarized in Table XIV.

Reverse osmosis data of the vulcanized random copolymer films are graphically presented in Fig. 33 by plotting salt rejection versus logarithm of film permeability. Again a straight line is obtained as previously shown in Fig. 21 for anion exchange membranes derived from S-2VP block cpolymer films. The slope of the line in Fig. 33 is somewhat steeper than of the line in Fig. 21 due to the difference in reverse osmosis conditions (0.2 N versus 0.6 N NaCl and 1000 versus 1600 psi, respectively). For comparison some of the quaternized block copolymer films shown in Fig. 21 were retested under the reverse osmosis conditions of Fig. 33 and are included in the latter. There are also included in Fig. 33 some grafted polyethylene membranes in order to show the general validity of the relationship between salt rejection and water permeability for ionic membranes.

C. Charge Mosaic Membranes from Vulcanized Polymer Blends

For the preparation of charge mosaic membranes from blends of random copolymers, utilizing the phase separation taking place in films, the combination of S and 2VP containing copolymers was selected. With this combination very good phase separations were observed and domains of strong polyelectrolytes can be obtained.

The copolymers, each containing about 20 mole-% of butadiene, were dissolved separately in THF. The solutions were combined and the resulting turbid mixture was cast on glass plates with the use of a doctor knife. Phase separation occurred

Membrane No.	Copolymer No. (see Tab.II)	Treatment of the membrane	Thickness of the Membrane [mm]	Water Permeability $\left[\frac{1 \cdot mm}{m^2 \cdot day}\right]$	Salt Rejection [%]
1	BS-10	5 vol.-% S_2Cl_2 in CH_3CN for 90 min.; SO_3:bis-(2-chloroethyl)ether = 1:3 in 1,2-dichloroethane at 0°C for 30 min.	0.016	9.8	52.2
2	BS-6	20 vol.-% S_2Cl_2 in CH_3NO_2 for 120 min.; SO_3:bis-(2-chloroethyl)ether = 2:3 in 1,2-dichloroethane at 20°C for 15 min.	0.018	2.9	78.0
3	BS-6	10 vol.-% S_2Cl_2 in n-hexane for 120 min.; SO_3:bis-(2-chloroethyl) ether = 2:3 in 1,2-dichloroethane at 20°C for 5 min.	0.026	27.8	36.2
4	BS-9	5 vol.-% S_2Cl_2 in CH_3CN for 120 min.; 10 vol.-% HSO_3Cl in chloroform for 5 min.; 0.5n NaOH for 5 min.	0.065	19.8	41.3
5	BS-9	5 vol.-% S_2Cl_2 in CH_3CN for 120 min.; 2 vol.-% HSO_3Cl in chloroform for 15 min.; 0.5n NaOH for 5 min.	0.088	39.2	25.9
6	BV-5	CH_3Br gas at 70°C for 30 hrs.; 5 vol.-% S_2Cl_2 in CH_3CN for 180 min.	0.032	8.4	54.7
7	BV-1	CH_3Br gas at 70°C for 85 hrs.; 10 vol.-% S_2Cl_2 in CH_3NO_2 for 180 min.	0.088	11.5	50.0
8	BV-2	CH_3Br gas at 70°C for 48 hrs.; 5 vol.-% S_2Cl_2 in CH_3NO_2 for 120 min.	0.028	8.2	57.8
9	BV-3	CH_3Br gas at 70°C for 48 hrs.; 5 vol.-% S_2Cl_2 in CH_3NO_2 for 120 min.	0.030	5.3	67.7
10	BMA-9	20 vol.-% S_2Cl_2 in CH_3NO_2 for 120 min.; 0.5n NaOH for 15 min.	0.053	17.1	43.6
11	BMA-9	5 vol.-% S_2Cl_2 in CH_3CN for 150 min.; 0.5n NaOH for 15 min.	0.027	6.9	51.6
12	MAB-1	10 vol.-% S_2Cl_2 in n-hexane for 120 min.; 10 wt.-% NaOH in CH_3OH at 40°C for 24 hrs.	0.035	2.8	72.3
13	BCM-1	10 vol.-% S_2Cl_2 in n-hexane for 120 min.; $N(CH_3)_3$ gas at 70°C for 15 hrs.	0.030	1.6	67.9

TABLE XIV. Preparation and Reverse Osmosis Properties of Different Ionic Membranes Derived from Random Copolymers Containing Butadiene.

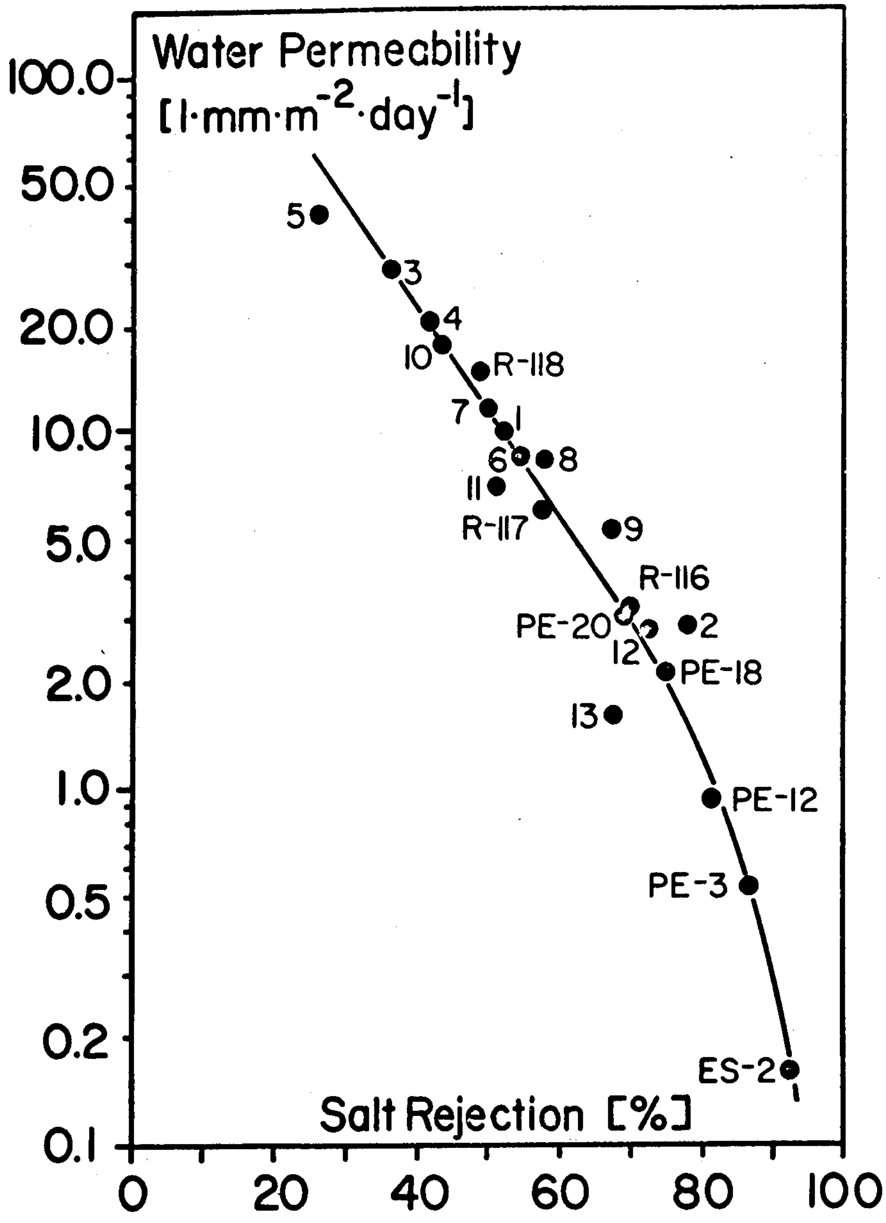


Figure 33 - Salt rejection versus water permeability of different ionic membranes derived from vulcanized random copolymers containing butadiene. Reverse osmosis conditions: 0.2 N NaCl at 1000 psi.

immediately, size and form of the domains depending on the blending ratios. For better observation a good contrast between the phases could be obtained by a simple staining technique. The P2VP swells slightly in water and by painting the film surface with a water soluble dye stuff (feltpen) the dye is sorbed by the P2VP domains. After rinsing the films with water the PS domains become colorless whereas the P2VP domains are deeply colored. Films treated this way were directly used as negatives for making the prints shown in Fig. 34-36. The white domains in the photoprints correspond to the P2VP domains, the dark areas corresponding to the PS.

Especially with a blending ratio of S-co-B to 2VP-co-B of 1:2 well separated large domains resulted. The film morphology consists of a continuous PS matrix with elongated P2VP domains imbedded. The elongation of the P2VP domains occurs in the casting direction and is caused by the shearing forces generated. The average width of both kinds of domains is about equal and corresponds to several hundred microns. Because of the large average domain size as compared with the film thickness (about 30-50 microns) all of the domains extend from one film surface to the other.

The size of the P2VP domains decreases rapidly in films of higher PS contents. This might be caused by partial dissolution of the P2VP copolymer in the PS copolymer which is enhanced by the common butadiene contents of both components. Films from copolymers of lower butadiene content did not cross-link sufficiently by vulcanization and therefore were not used for polymer blends.

Films corresponding in their structure to Fig. 35 were quaternized with methyl bromide in the gas phase while still attached to the glass plate. The treatment was extended to 48 hrs in order to avoid the formation of graded films. Floating of the films prior to quaternization resulted in weak films after vulcanization because of the uneven swelling of the non-cross-linked films during floating. The plates with the quaternized films were submerged in 10% solutions of sulfur monochloride in either nitromethane or acetonitrile and the vulcanization reaction was allowed to proceed for 15 hrs. After washing with heptane the plates were placed in 1,2-dichloroethane and a solution of a sulfur trioxide-bis-(2-chloroethyl)-ether (2:3) complex was slowly added. During the sulfonation reaction one kind of domains slowly turned purple whereas the other kind remained colorless. Such a color change was previously observed during the sulfonation of vulcanized butadiene-styrene copolymer films and it was therefore assumed to be indicative for the PS domains in the blended film. Indeed, vulcanized films of 2VP-co-B remained colorless under these conditions.

With proceeding sulfonation reaction the films started to float which assured complete sulfonation of the PS domains. After the films were completely floated, methanol was added slowly in small portions to destroy surplus sulfonating complex. After washing with methanol the films were placed in a salt solution. The films

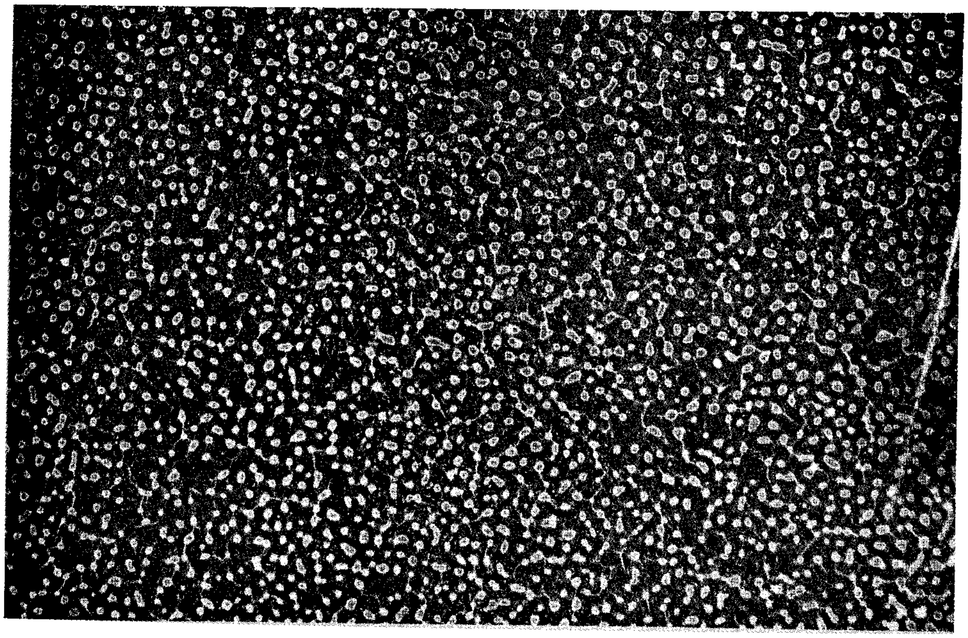


Figure 34 - Photoprint of a composite membrane derived from a 1:1 blend of poly(styrene-co-butadiene). Both copolymers containing about 20 mole-% butadiene.

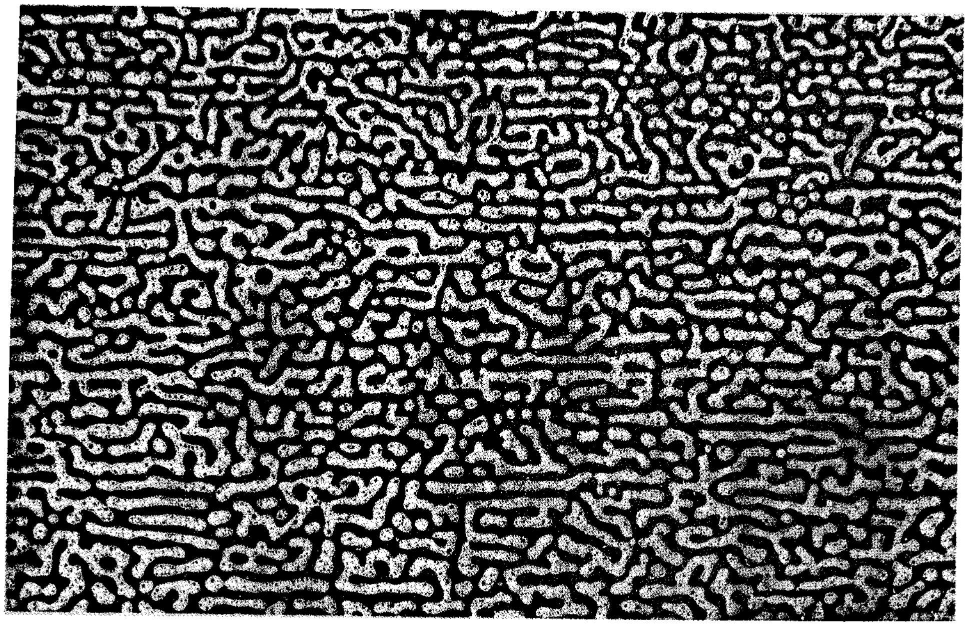


Figure 35 - Photoprint of a composite membrane of the same copolymers as in Fig. 34 but a blending ratio of 1:2.

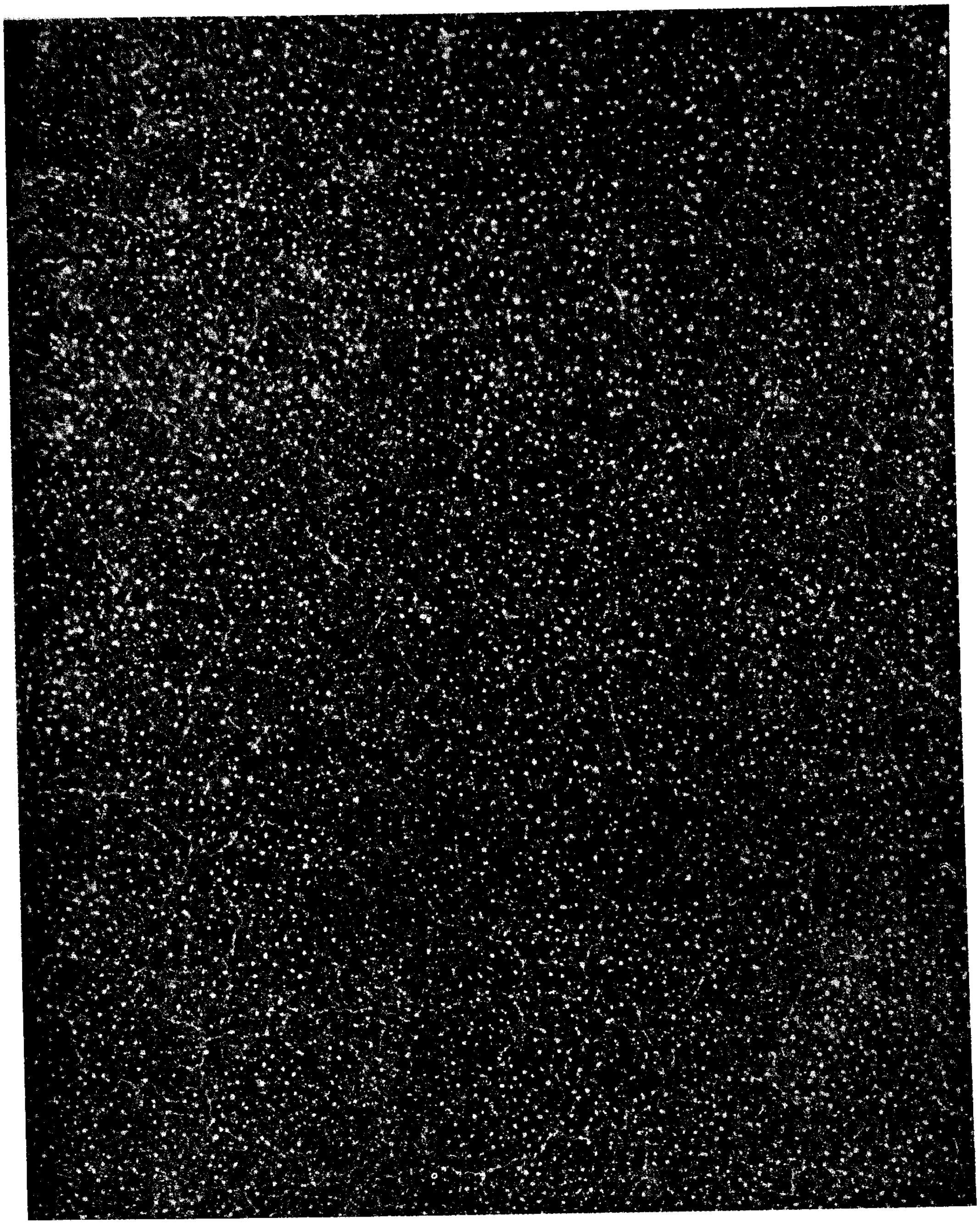


Figure 36 - Photoprint of a composite membrane of the same copolymers as in Fig. 34 but at a blending ratio of 2:1.

did not disintegrate but were too highly swollen to be tested under reverse osmosis.

Observation under the microscope of a series of such charge mosaic films revealed the formation of microcracks at the phase boundaries with time. Upon prolonged keeping under water some of the films completely disintegrated after several weeks. The P2VP domains formed small, isolated gel particles leaving behind the PS part of the film in the form of a lace. The weakness of the films is caused by the unequal swelling of both domains whereby high stresses develop at the phase boundaries (stress cracking). Variations in the vulcanization and sulfonation procedures did not result in any improvements of film properties.

The effect of the selective swelling of one phase could be seen better by making the individual phases considerably larger. A glass plate was covered with narrow stripes (about 2 mm width) of Scotch tape at equal spacings of about 2mm. Across this plate a solution of butadiene-methacrylic acid copolymer was cast. After drying the Scotch tape was removed leaving plain glass surface between the copolymer stripes. The latter were then covered with Scotch tape of equal width and a solution of butadiene-vinyl pyridine copolymer was cast across the plate. After drying the tape was pealed off and a film was left on the plate composed of equally spaced stripes of both copolymers. The film was then swollen in THF vapor to improve the contact between the stripes. On the phase boundaries of the stripes salt formation seemed to take place as could be judged from the formation of a narrow turbid zone which contrasted with the clear interior of the stripes. After drying the film could be floated in water. The film was then quaternized and vulcanized as before.

The film demonstrated clearly the difficulties encountered with all films composed of macroscopic domains. Upon placing the film in NaCl or NaOH solutions, the P2VP phase swelled more rapidly than the methacrylic acid phase. In the directions normal to the stripes the film expanded evenly during swelling. In the direction of the stripes an increasing number of wrinkles formed in the P2VP stripes at the phase boundaries where the swelling of the P2VP phase was hampered by the slowly swelling methacrylic acid phase. After a short time the film started to rupture at the phase boundaries.

The problem of differences in the swelling behavior of separated phases is of minor importance as long as the domain dimensions remain small. Apparently under this condition the generated stresses can equalize. With decreasing domain sizes the mechanical strength of the films is improved but the probability for the domains to extend from one film surface to the other decreases. Domains with average dimensions being smaller than the film thickness will not extend through the film. Optical microscopy in reflected light revealed that in films with large domain dimensions (Fig. 35) each domain is surrounded by a relatively deep depression in the film surface. This observation might explain the facile disintegration of charge mosaic membranes along the phase boundaries.

In order to test the effect of domain dimensions films were prepared from blends of S and 2VP copolymers which separated into very small domains (about 10 microns). Copolymers of higher butadiene content had to be used, and therefore, the effect of domain dimensions is somewhat blurred by the higher cross-linking density. The copolymers selected were BS-9 and BV-3 (Table XIII) which contained 30 and 37 mole-% butadiene, respectively. At a blending ratio of BS:BV=3:2 films were obtained with average domain dimensions of about 10 microns diameter (Fig. 37). After quaternization, vulcanization, and sulfonation, these films possessed sufficient mechanical strength to be tested under reverse osmosis. The films were sulfonated with dilute chlorosulfonic acid in chloroform for different lengths of time (3-5 min). One of these films (5 min. sulfonation time) exhibited a marginal salt enrichment of 4-5% (0.2 N NaCl at 1000 psi). The value of salt enrichment fluctuated very strongly and during some intervals the membrane exhibited either zero rejection or a rejection of 1-2%. One might interprete these results as presenting normal scattering in the effluent concentration of a membrane exhibiting no salt rejection at all. Such kinds of membranes were often encountered in previous studies but none of them ever showed the slightest indication of salt enrichment in the effluent. Generally, in such cases the fluctuations were always between zero rejection and a rejection of 1-2%.

For morphological investigations the film exhibiting marginal salt enrichment was selectively stained with a universal indicator. One part of the film was stained in an acidic medium (dilute HCl) the other part in an alkaline medium (dilute NaOH solution). After staining the films were thoroughly washed in deionized water to remove all of the invaded acid or base. The film stained in NaOH was deeply blue and microscopic investigation revealed that it was composed of blue circular domains imbedded in a faintly yellow matrix (Fig. 38). The intensitity distribution of the colored domains indicated that only the largest domains might have extended through the film. The film stained in HCl was bright red. Under the microscope it could be seen that circular, faintly yellow domains were imbedded in the red matrix (Fig. 39). The size of these yellow domains approximately corresponded with the size of the largest blue domains of the film stained in NaOH.

Under these staining conditions the P2VP domains will be stained blue in an alkaline medium by formation of the free base, and the PS domains will be stained red in an acidic medium by formation of the free acid. Both kinds of domains should be stained green if the corresponding polyelectrolytes are transformed into their salt forms. These color changes were verified by staining experiments with grafted

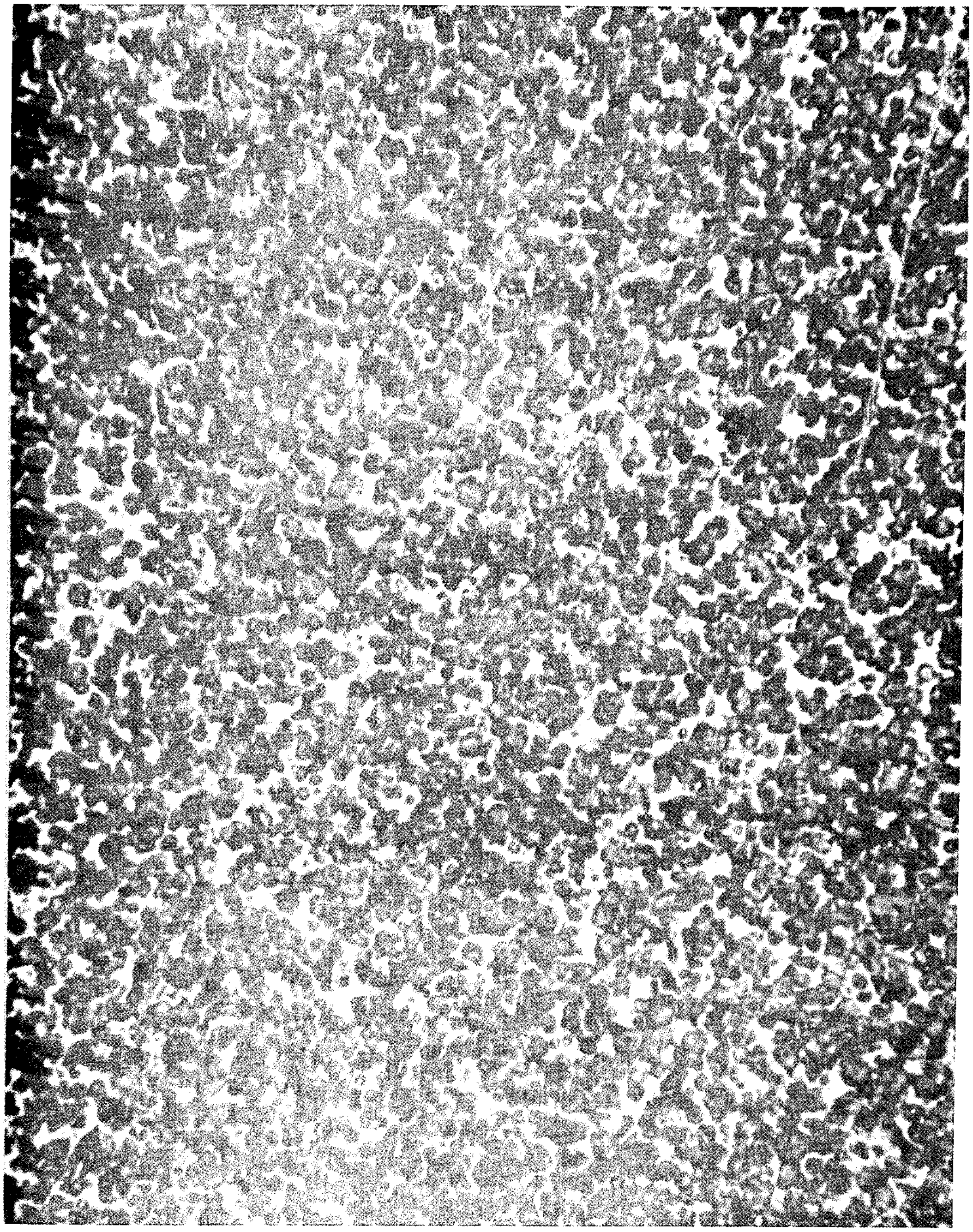


Figure 37 - Optical micrograph of a charge mosaic membrane precursor derived from a 3:2 blend of poly(styrene-co-butadiene) and poly(2-vinyl pyridine-co-butadiene) containing 30 and 37 mole-% butadiene, respectively.

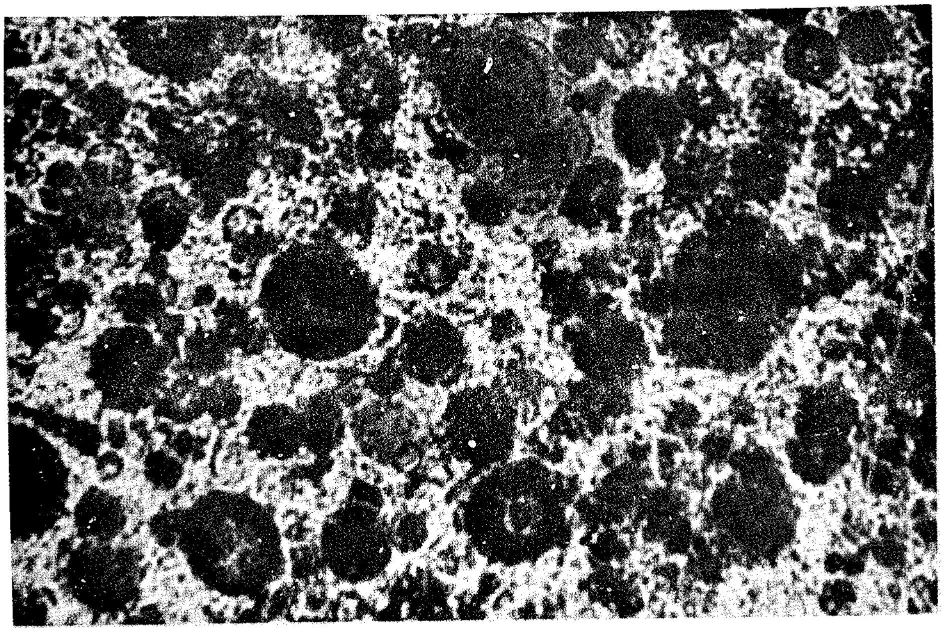


Figure 38 - Optical micrograph of a charge mosaic membrane derived from the composite film shown in Fig. 37. Film was stained with a universal indicator in dilute NaOH and washed.

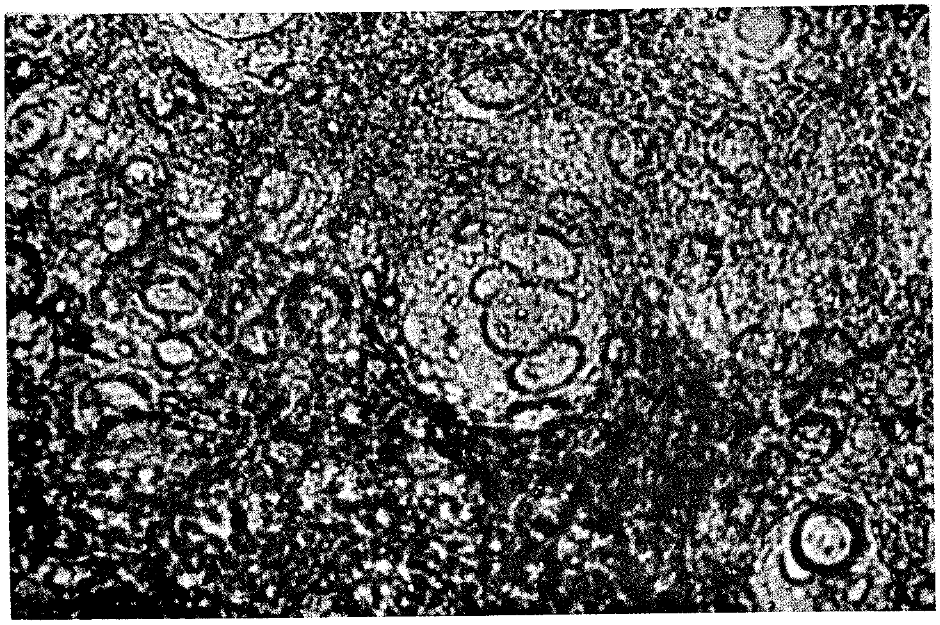


Figure 39 - Optical micrograph of a charge moasic membrane derived from the composite film shown in Fig. 38. Film was stained with a universal indicator in dilute HCl and washed.

polyethylene films. The green color of the domains in their salt form was not observed with the charge mosaic membrane although there was a distinct color difference between the phases at each staining condition. In order to explain the absence of the green coloration indicating a polyelectrolyte in its salt form one might speculate that none of the domains represented a pure polyelectrolyte of one kind. This assumption would explain the low salt enrichment observed.

In addition to incomplete phase separation the high degree of swelling of the charge mosaic membrane might have contributed most to its low efficiency. Comparison of the average dimensions of the P2VP domains before and after transformation of the membrane into its ionic form revealed an increase in size by an order of magnitude. This means that each domain by itself will have very low salt rejecting properties, and therefore, the concerted effect of both domains in piezodialysis can only be marginal. If one considers that the high swelling was observed on a membrane containing 30-40 mole-% butadiene, a value which cannot be exceeded without further deterioration of the phase separation, cross-linking by vulcanization does not seem very promising.

In order to separate the PS and P2VP domains better in the film a ternary polymer blend was investigated. The matrix polymer selected was a copolymer of butadiene and methyl methacrylate which was available. The low hydrolysis rate of this polymer should allow the sulfonation of the PS without effecting the ester groups of the matrix polymer. During the preparation of the blend an unexpected observation was made. Upon addition of the MMA copolymer solution to the turbid mixture of the other two copolymer solutions the ternary blend became completely clear. Films were cast from this clear blend which possessed very small domains. The films were quaternized and then vulcanized in the usual way. A film which was only quaternized did not swell in water and was completely impermeable in reverse osmosis. Obviously all of the P2VP domains were completely surrounded by the PMMA matrix. The complete occlusion of the PS domains in the PMMA matrix was also indicated by the sulfonation reaction. The film developed a purple color very slowly which was very persistent during washing with methanol. Also this amphoteric film had no permeation in reverse osmosis.

As far as film morphology is concerned, phase separated films from polymer blends are most promising. Such films possess regularly arranged domains of proper size which extend undisturbed through the film. The main problem of these films concerns their mechanical strength. The films investigated were cross-linked by introducing chemical bonds in curing or vulcanization reactions. This approach demands the use of random copolymers containing reactive groups. Because of the presence of a common comonomer in both film components the incompatibility of the latter is impaired. As a consequence the resulting domains are not pure and after transformation of the film into the amphoteric form each domain will contain anionic and cationic centers thus decreasing their selectivity in ion transport. Furthermore, it cannot be ruled out that the common comonomer will remain completely unreactive during the sulfonation reaction.

Films from polymer blends can also be cross-linked by physical means similar to the physical cross-linking of block copolymer membranes. This could be shown in some preliminary experiments with blends of S-2VP block copolymers and homo PS. It was observed previously that block copolymers of S and 2VP containing small amounts of homo PS due to impure polymerization conditions yielded films exhibiting macroscopic phase separation. These films were extremely weak in their quaternized form. Under these conditions of preparation the homo PS has the same molecular weight as the PS block in the block copolymer. Blending alternating block copolymers of S and 2VP with homo PS of high molecular weight resulted in phase separated films which were surprisingly strong even after quaternization.

The films derived from 1:1 blends were composed of a continuous PS matrix with the block copolymer imbedded in circular domains of several hundred microns diameter. After quaternization these domains swelled in water to spherical shapes protruding from the film surface. Testing under reverse osmosis condition (0.2 N NaCl at 1000 psi) revealed the absence of pinholes or microcracks. Indeed, compared with a film of the same block copolymer the salt rejection of the composite film was practically identical, 58% versus 56%, respectively. The slightly lower value of the composite film was very likely caused by a small leakage around the O-ring gasket due to the roughness of the film surface.

It was very surprising that physical cross-linking by means of an amorphous matrix homopolymer yielded stronger films than chemical cross-linking of butadiene containing copolymers. The higher stress cracking resistance of homopolymer-block copolymer blends might be caused by a more intimate blending in the phase boundaries than takes place in blends of incompatible copolymers. Also in the latter case the stress cracking resistance could be improved by increasing the content of the common comonomer in both copolymer components but such an increase results in partial miscibility of both components and the formation of very small domains.

In films derived from polymer blends a matrix polymer has to be used which remains inert during the sulfonation reaction. It was first intended to use PMMA for this purpose. Unfortunately, experiments with ternary blends composed of PS, P2VP, and PMMA revealed that the presence of the latter polymer strongly decreased the incompatibility of the other two polymers. Clear solutions resulted and the films exhibited very poor phase separation.

A good matrix polymer would be polyethylene. This polymer has excellent film forming properties and its semicrystalline state provides strong physical cross-links, Good crystallization of the polyethylene chains demands relatively long polyethylene sequences uninterrupted by the comonomer. Therefore, block copolymers of polyethylene can be expected to yield the best results. Block copolymers of ethylene and vinyl monomers can be prepared by combining a Ziegler-Natta process with a free radical process.[52,53] Ethylene is polymerized by means of a Ziegler-Natta catalyst system in the presence of diethyl zinc in order to obtain chains terminated by carbon-zinc bonds. These terminal groups are reacted with t-butyl hydroperoxide whereby zinc salts of alkyl hydroperoxides are formed. The latter compounds exhibit catalytic activity in the polymerization of a number of vinyl monomers.[52,54]

Block copolymers of polyethylene can be expected to exhibit good phase separation because of the strong incompatibility between all vinyl polymers and hydrocarbons. Furthermore, polyethylene sulfonates very slowly especially with concentrated sulfonic acid. All these properties make the use of polyethylene block copolymer blends very promising for the preparation of charge mosaic membranes.

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