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Synthesis of Ion-exchange Membranes

O.D.Savenko, F.T.Shostak, and B.N.Laskorin

Extensive research has been conducted during recent years on the synthesis, properties, and applications of ion-exchange membranes. On the basis of the periodical and patent literature the paper gives a systematic account of membranes and methods for their production, the various ways of synthesising them, and brief information on their application and the laws of membrane processes. Classification is based on various criteria, primarily the homogeneity, the nature of the skeleton and the character of functional groups, electrochemical properties, etc.
Numerous methods of synthesising and producing polymerisation and polycondensation membranes, activated films, and heterogeneous membranes are described and critically examined. The main reactions are given. From an analysis of the literature, patents, and other sources the prospects are given for possible future developments in the synthesis of ion-exchange membranes. A list of 367 references is included.

CONTENTS

I. Introduction 920
II. Classification of membranes 920
III. Properties of ion-exchange membranes 922
IV. Methods of synthesising ion-exchange membranes 922
1. Heterogeneous membranes 922
2. Homogeneous membranes 922
3. Interpolymer membranes 927

I. INTRODUCTION

Ion-exchange polymers are used in many fields of science and technology. Depending on the character of the process, the exchangers are employed in the form of particles varying in geometrical shape and size. They are most widely used as granules and sheets (membranes). Methods for the synthesis of ion-exchange resins of the former type are well known and have been widely described [1,2]. Methods which have hitherto been proposed for the synthesis of ion-exchange membranes have been reported almost exclusively in the patent literature and in a few review papers [3-14], which contain a brief list of processes for obtaining membranes, published over a definite period of time.

The first specimens of membranes (heterogeneous), based on industrial exchangers, were obtained in 1950 by Wyllie and Patnode [15]. The synthesis of homogeneous membranes was first described by Manecke [16] and by Sollner and Neihof [17] in 1951, and later Gregor and his co-workers [18,19] synthesised interpolymer membranes.

With expansion in the possible fields of application of membrane processes, the demands made on membranes have risen, and consequently new types of membranes and methods for synthesising them have appeared.

The applications of ion-exchange membranes show great variety. Particularly important uses are the desalination of salt-water and of brackish waters, the preparation of high-purity metals, and recently the production of fuel cells. Membrane methods of desalination—electrodialysis [20-31,33,34], ion-osmosis [32], and hyperfiltration [35-37]—have aroused great interest. Promising uses of ion-exchange membranes are the preparation of pure metals, the isolation of certain metals from their mixtures with others, the separation of elements of closely similar properties, etc. [26,38-45].

Fuel cells provide a new field for the application of ion-exchange membranes [46-52], whose use has such advantages as decreasing the weight of the fuel cells, the absence of a liquid electrolyte, and the possibility of obtaining pure water when hydrogen and oxygen are employed. The prospects for the use of membrane processes are very promising.

II. CLASSIFICATION OF MEMBRANES

The literature on ion exchange contains no papers specially devoted to the classification of membranes. This question is sometimes touched on in review papers and monographs. Laskorin et al. [45], Morgan [53], Lyubman and Shostak [14], and Hasenberg [54] discuss ion-exchange membranes mainly from the point of view of structure. There is as yet no rigorous scientific classification of membranes and methods of synthesis, based on a single common criterion. It is difficult to make such a classification.

An attempt is made in the present paper to give a practical classification, based on various criteria, of the membranes which have been described in the periodical and the patent literature. A distinction must be made between films and ion-exchange membranes: films consist of inert, uncharged polymers, whereas ion-exchange membranes are insoluble polyelectrolytes, containing positively or negatively charged groups, in the form of sheets, plates, discs, rods, etc. The term "diaphragms" is applied in most cases to inorganic membranes [55-57].

Ion-exchange membranes are of either natural or synthetic origin. Each type is divided according to its chemical character into organic and inorganic [55-65]. Examples of organic natural membranes are proteins, the skin of frogs, and ox bladder; while inorganic natural membranes include insoluble minerals containing calcium, several zeolites, and clays.

Depending on their type of selectivity, membranes are either (1) permeable to ions having charges of one sign and impermeable to oppositely charged ions and water, or (2) permeable to water but impermeable to ions. The former type are used in electrodialysis, mainly for demineralising water [66-77] and separating metals [38-40,78-83]; while the latter are still in the research stage, and may find application predominantly in hyperfiltration processes for the demineralisation of water [35,64-121].

Membranes are divided into ionogenic, complexing, and redox membranes according to the character of the fixed groups. Ion-exchange membranes contain acidic or basic functional groups. In complex-forming membranes the functional groups are able to form complexes with various

elements [122-126]. Such membranes have been obtained, for example, from a copolymer of di-isobutyl vinylphosphonate and acrylic acid [122], the resin Dowex A-1 and poly(vinyl chloride) [124], etc. These membranes have not yet found sufficiently wide application. Redox membranes contain oxidation–reduction groups instead of ionogenic groups.

According to the acid–base function of the ionogenic groups we can distinguish cation-exchange, anion-exchange, and amphoteric membranes. Cation-exchange membranes containing the strongly dissociated sulpho-group are said to be strongly acidic [127-169], while groups of moderate or low degree of dissociation (phosphoric, carboxylic) are said to be weakly acidic [170-173]. On this criterion anion-exchange membranes are in turn divided into strongly basic, containing the strongly dissociated pyridinium, quaternary ammonium, or rarely phosphonium or sulphonium groups [174-190], and weakly basic, having tertiary, secondary, or primary nitrogen atoms [191-199]. Amphoteric membranes contain both negatively charged and positively charged ionogenic groups [200-203]. These membranes play an important part in the vital activity of living cells. They are mostly membranes of animal (mainly proteins) or vegetable (mainly lignin) origin. Depending on the pH of the surrounding medium, protein membranes function as inert at a hydrogen-ion concentration corresponding to the isoelectric point, as anion exchangers at lower pH values, and as cation-exchange membranes at higher pH. It has been proposed to synthesise amphoteric membranes, containing quaternary ammonium and carboxyl groups, by the copolymerisation of a homogeneous solution of a 5-ethyl-1-methyl-2-vinylpyridinium salt, methacrylic acid, styrene, and divinylbenzene in the presence of a plasticiser [201]. In another case a copolymer of methacrylic acid and 2-diethylaminoethyl methacrylate is used as the active component [200]. The main theoretical principles of membrane processes, worked out by Meyer and Sievers [204] and by others (see below) extend also to membranes of this type.

Depending on their structure, membranes are subdivided into heterogeneous, homogeneous, interpolymer, isoporous (synthesised by the Reviewers), bipolar, mosaic, and coated with an inert polymer film.

Heterogeneous membranes are two-phase systems, the ion-exchange resin being distributed in an inert binder [159-164,205-223]. Since a continuous phase of the ion-exchange component is not present in this case, transport of ions takes place as a consequence of contact between the resin particles or through solution present between them, the process often being governed by both factors.

Homogeneous membranes consist solely of the ion-exchange component, forming one continuous phase [127-154,224-298]. In most cases they are transparent and uniform for visible wavelengths (~ 4000 Å). Homogeneous membranes are now finding preferential dissemination in connection with their successful use in electrodialysis. According to their mode of production these membranes can be divided into condensation [133-139] and polymerisation [228-238] membranes, together with those based on inert polymer films [240-298]. This last group are divided in turn into sheet [141,142], graft [240-274], and film [275-298] membranes.

Interpolymer membranes, obtained by the molecular blending of two polymers, are similar in properties and structure to homogeneous membranes [74,76,299-338]. In membranes of this type molecular chains of the two components are closely interlinked, and the polyelectrolyte forms one phase, although chemical bonds are not usually present between the two polymers. This has a good effect on the properties of the membranes, in particular their mechanical stability, since on swelling in water no great stresses are produced in the membrane, owing to the mobility of one polymer molecule relative to another. Two types of interpolymer membranes—dynel [299-305] and those based on inert polymer films [306-315,330-336]—can be distinguished.

Membranes exist in which one surface is a cation exchanger, while the other is an anion exchanger. These are bipolar membranes [339-343]. Their most important feature is their selectivity towards hydrogen. A Japanese patent [343] proposes the synthesis of a bipolar membrane from a polyethylene film, styrene, and 4-vinylpyridine by the use of γ-radiation. A bipolar membrane can be obtained by sticking together sheets of cation-exchange and anion-exchange membranes prepared from the appropriate resins and a solution of poly(vinyl chloride) in cyclohexanol by a method of pouring [342]. The use of bipolar membranes has not become widespread.

Little is known about mosaic membranes [292,344]. They consist of sharply divided regions, one of which is permeable to cations, while the other is permeable to anions. A synthesis of mosaic membranes has been described [292]: polyethylene film is treated with sulphuryl chloride or a mixture of sulphur dioxide and chlorine, after which individual portions are treated with tetraethylenepenta-amine.

According to the state of aggregation membranes are divided into ordinary and liquid [345,346], and according to their physical structure into porous [347,348] and those having limited swelling (gel membranes). A further distinction is made between reinforced and unreinforced membranes. The reinforcement—unilateral, bilateral, or between the sheets—confers great mechanical strength on the membranes, but at the same time lowers their exchange capacity and their electrochemical parameters, while considerably increasing the cost [349].

Reference is made in the literature to the possibility of using as reinforcing material glass fibres [79,129,138], Saran [136,137,192], Teviron [299], and Vinyon [136] fabrics, nylon [163], capron [186], poly(vinyl chloride) and poly(vinylidene chloride) fibres [175], polyacrylonitrile [163,181,206], linear polyesters and polyamides [163,206], paper [208], etc. Glass cloth, poly(vinyl chloride), and other rigid materials are less suitable as reinforcements owing to their hydrophobic character and differences in the variation in their linear dimensions compared with the membrane material on contact with polar solvents and water. Use of an unsuitable reinforcing cloth encourages the appearance of microcracks and other chemical defects as a result of differences in the coefficients of expansion and also internal stresses. Investigations on the effects of reinforcements on the electrochemical properties of heterogeneous membranes of Ankalit A-7, synthesised from the anion-exchange resin AT-1 and low-density polyethylene, have established [349] that bilateral reinforcement greatly increases the mechanical strength and permits the amount of the ion-exchange component to be increased at the expense of the binder; the electrical conductivity of the membrane is almost doubled. Capron, Saran, and Vinyon provide the most suitable reinforcement for this type of membranes. The improved adhesion of the resin to such fibres is explained by the presence of identical groups (e.g. amino) in the two structures.

Membranes can be distinguished from one another also by the location of the functional groups: an ionogenic group may be situated in the main chain [66,67,128,130] or in a side-chain [193] of the polymer.

Finally, the ion-exchange membranes can be subdivided according to the nature of the starting material, which may be a monomer [69,72], a monomer containing an

ionogenic group[131,145], a polymer containing an ionogenic group[159-164,205-223] or none[229,230], a copolymer[130,228], or various polymer films[287-298].

Neither in the Soviet nor in the foreign literature does there exist a unified chemical terminology for membranes, and arbitrary names, given by individual authors or firms, have become widely used. In the USA, for example, Amberplex, Nepton, Permutit, Nalfilm, Amfion, Jonac, etc. brands of membranes are marketed; in England, Permaplex, Zerolit, etc.; in Japan, Selemion, Scrion, Neozeplan, Neozepta, etc.; and in the USSR, MK-40, MA-40, MA-41, MK-100, MA-100 Ankalit, etc.

III. PROPERTIES OF ION-EXCHANGE MEMBRANES

An ideal ion-selectively permeable membrane allows ions of only one sign to pass through on application of an electric potential gradient, independently of the concentration of the external solution. Ion-selective permeability should be combined with high electrical conductivity, mechanical strength, elasticity, and thermal and chemical stability. Some of these properties are completely incompatible, and therefore ideal membranes cannot be obtained. The electrochemical properties of membranes are independent of their geometrical shape: membrane potentials, among the most important of properties, are identical for discs, rods, and strips provided that these are of the same composition[350].

The founders of the theory of selectively permeable membranes and their electrochemical properties were Teorell[351] and Meyer and Sievers[204]. According to this theory the selective permeability of ion-exchange membranes can be explained by the presence of mobile charged ions and counter ions in the membrane phase.

A considerable contribution to the study of the electrochemical properties of ion-exchange membranes has been made by Soviet scientists. The theoretical foundations of the process of electrodialysis were established by I.I. Zhukov[352], and his pupils Laskorin, Smirnova[353,354], Nikol'skii, Materova, Stefanova[355], Belinskaya[218], and others have made detailed investigations of the properties of various ion-exchange membranes. Some of the results of these investigations have been used in the book by Laskorin et al.[45].

IV. METHODS OF SYNTHESISING ION-EXCHANGE MEMBRANES

1. HETEROGENEOUS MEMBRANES

All the methods which have been proposed for producing heterogeneous membranes are based on combining a finely divided ion-exchange resin with an inert binder and then forming the mass into a film. These methods are distinguished by the technology of preparation, the state of aggregation of the binder, or its chemical nature. The properties of the membranes depend in considerable measure on the quantity and the degree of subdivision of the initial exchanger. The content of active component in the membrane usually varies over the range 60–80%. Increase in its content is accompanied by a considerable decrease in mechanical strength as well as the increases in electrical conductivity and in exchange capacity of the membrane. The proportions of ion-exchange resin and of binder must therefore by selected so that the membrane does not deform or disintegrate during use.

A fraction of particle size not exceeding 100 μm is usually taken. Thermoplastic substances—polyethylene, polystyrene, poly(vinyl chloride), phenolic resins, polymethacrylic ester, synthetic and natural rubber, etc.—are especially widely used as binders. Inert materials are employed in the form of granules, powder, film, viscous mass, or solution.

A heterogeneous membrane can be obtained from practically any ion-exchange resin. It has been proposed[214,356] to compress the finely divided exchanger into sheets, which are then impregnated with a monomeric liquid, the latter being polymerised on further treatment.

In some cases the ion-exchange resin is introduced into the semi-liquid binder. Such a state is achieved either by adding a plasticiser or by keeping at an elevated temperature. After careful stirring the viscous mass is passed between rollers or pressed into sheets. If a plasticiser has been used, it is usually removed[75,187,215]. Membranes of this type possess improved mechanical strength. However, the use of high temperatures in the process of synthesis often impairs the properties of the exchangers, and it is therefore best to mix the resin and the binder at lower temperatures. A rubber latex can conveniently be used as the inert component[210,213].

A very interesting and effective way of modifying and improving heterogeneous membranes has been suggested by Laskorin et al.[222,357], who use a method of cross-linking with surface-active substances. Introduction of the latter enables a stable bond to be produced between the poorly compatible hydrophilic ion-exchange resin and the hydrophobic polymeric binder, with consequent decrease in the electrical resistance and increase in mechanical strength. The absence of reinforcement in cross-linked heterogeneous membranes considerably lowers their cost, and hence the cost of the demineralised water.

The following bands of heterogeneous ion-exchange membranes—Amberplex C-1 and A-1 (USA), Permaplex C-10, C-20, A-10, and A-20, Zerolit C-20 and A-20 (England), MK-40, MA-40 (USSR), etc.—are widely known at the present time.

Heterogeneous membranes possess several important defects—low electrical conductivity, high permeability to water, low resistance to the diffusion of electrolyte, and the possible formation of deposits inside the membrane—their high mechanical strength being due to reinforcement.

2. HOMOGENEOUS MEMBRANES

Because of the unsatisfactory electrochemical properties of heterogeneous membranes, extensive research has been undertaken during recent years on the synthesis of homogeneous membranes. The foundations of their synthesis are the reactions of polycondensation, polymerisation, and the chemical activation of inert films.

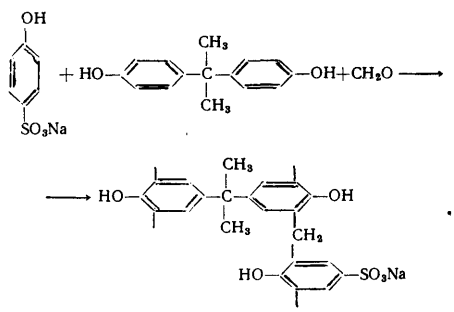
(*a*) Polycondensation Membranes

The starting materials most often used for this type of membranes are monohydric or polyhydric phenols, aromatic and aliphatic amines, urea and its derivatives, certain hydrocarbons, and other products. Choice of monomer is guided primarily by its chemical structure: the more reactive groups the initial compound contains the higher usually are the chemical stability of the final product and the three-dimensional interlocking of the individual chain units[358].

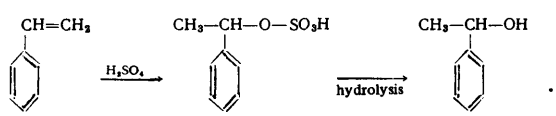
Ways of synthesising polycondensation membranes differ according to the medium in which the reaction is conducted, the nature of the initial monomers, and the process conditions. The first membranes were obtained from acidic aqueous mixtures containing hydroxybenzenesulphonic acid, melamine, or other similar monomer, formaldehyde, and a catalyst. It has been proposed to conduct polycondensation in an organic medium, e.g. methanol [138]. Morgan [53] refers to the production of polycondensation membranes by pouring the solutions on to the surface of mercury in a closed vessel. The more uniform and improved structure of the product is explained by the high thermal conductivity of mercury preventing the occurrence of local overheating.

Methods for the synthesis of polycondensation membranes have been most widely developed on the basis of hydroxybenzenesulphonic acid and formaldehyde [128,147]. The reaction can be conducted either in acid or in alkaline medium. The hydroxybenzenesulphonic acid can be replaced by the viscous product of the initial condensation of phenol with formaldehyde in the presence of acid or alkaline catalysts, followed by sulphonation of the resulting polymer [129]. In neither case do the membranes obtained possess adequate mechanical strength.

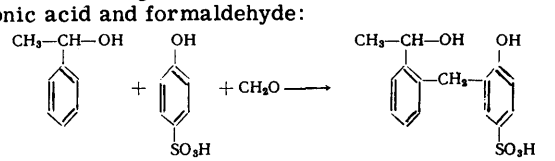
Improved membranes are obtained by condensing sodium hydroxybenzenesulphonate with phenol and formaldehyde [133,154]. Replacement of phenol by 2,2-diphenylpropane-*pp'*-diol yields specimens of enhanced stability, e.g. in solutions containing oxidising agents at 40°C [227]. The increased stability of the polymer is probably explained by the chemical nature of tne diol:



An interesting method has been suggested by Japanese chemists [143]. They took a mixture of phenol, styrene, and 98% sulphuric acid, preheated at 100–110°C, for cocondensation with formaldehyde and paraformaldehyde. Under these conditions sulphuric acid adds to the styrene at the vinyl bond, and the resulting partial sulphuric ester is hydrolysed:



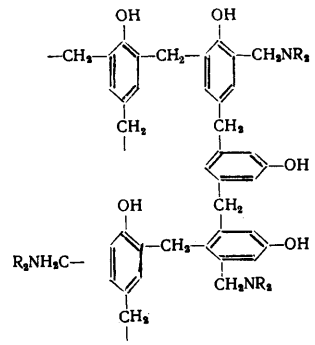
The product undergoes cocondensation with hydroxybenzenesulphonic acid and formaldehyde:



The use of styrene in the synthesis of polycondensation membranes apparently enables stronger specimens to be obtained, possessing diminished electrical resistance (in the present case 4 ohms cm^{-2}).

It has been proposed [153] to synthesise anion-exchange membranes by the polycondensation of tetraethylenepentaamine, ammonium sulphate, phenol, and formaldehyde in the presence of sulphuric and acetic acids. Replacement of the penta-amine by *o*-dimethylaminomethylphenol confers greater chemical resistance on the membrane, e.g. to the action of oxidants [193].

Japanese authors [198] suggest an original process for the industrial manufacture of anion-exchange membranes having a long service life. They use a resin in which the nitrogen atom constituting the central atom of the exchange base is not involved in the network structure of the resin:



For this purpose a compound of phenolic type containing a tertiary amino-group (e.g. $HOC_6H_4CH_2NR_2$) or a quaternary ammonium group is condensed with phenol and formaldehyde. The viscous resol resin is then formed into a film, and the gel ripened by heating. A membrane of this type is probably less suitable for use in electrodialysis, owing to its polyfunctionality.

Because of poor stability and low selectivity, especially in relatively concentrated solutions of electrolytes, polycondensation membranes have limited application.

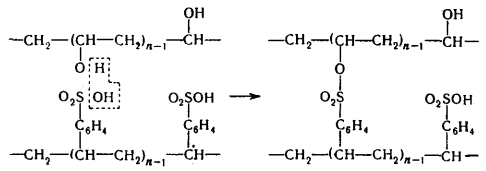
(*b*) Polymerisation Membranes

Membranes of this type are synthesised by the polymerisation or copolymerisation of unsaturated compounds, one of which should contain an ionogenic group or a group capable of transformation into such. Compounds containing vinyl groups are used, among them the aromatic compounds styrene, styrenesulphonic acid, and vinylpyridine, and the aliphatic vinylsulphonic, acrylic, and methacrylic acids, as well as salts, esters, and other derivatives of these compounds. The bridge-forming agents used are polyfunctional vinyl compounds—di- and tri-vinylbenzene, ethylene dimethacrylate, allyl acrylate, bismethylallyl ether, and other dienes and polyenes.

The above monomers are known to exhibit differing tendencies to polymerise, this constituting the main factor determining choice of the initial monomer in the synthesis. For example, cation-exchange membranes could have been more conveniently synthesised from styrenesulphonic acid, since sulphonation goes more easily with monomeric than with polymeric styrene; furthermore, polystyrene films on treatment with sulphonating agents undergo partial loss of their mechanical strength, and are deformed. But since styrenesulphonic acid is difficult to polymerise, in most cases polymerisation or copolymerisation of monomeric styrene with subsequent sulphonation is used.

Membranes possessing satisfactory electrical conductivity together with high mechanical strength are obtained from styrene and vinylsulphonic acid [145,152,182].

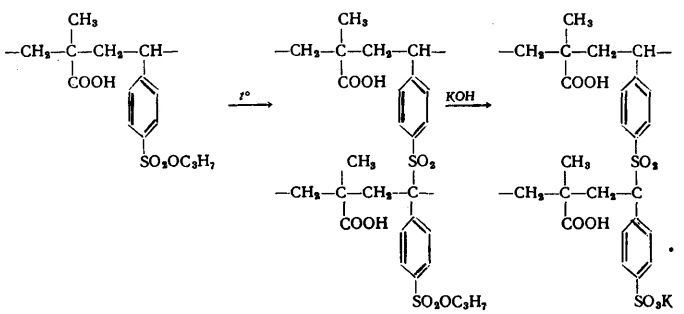
Synthesis is sometimes accomplished by using together styrene and styrenesulphonic acid [72] or styrenesulphonic acid with poly(vinyl alcohol) [134,232]. It has been suggested [314] that the combination of poly(vinyl alcohol) with poly(styrenesulphonic acid) occurs in conformity with the equation



To avoid the aqueous solubility of such a membrane and to ensure good electrochemical properties, the synthesis has been suggested of poly(styrenesulphonic acid) having a maximum content of sulpho-groups. An increase in the content of the acid in the copolymer from 20% to 60% is accompanied by an increase in the exchange capacity of the membrane from 1.1 to 2.8 mg-equiv. g^{-1}, while the electrical resistivity is halved. Even in the best specimens, however, the latter exceeds 500 ohm cm.

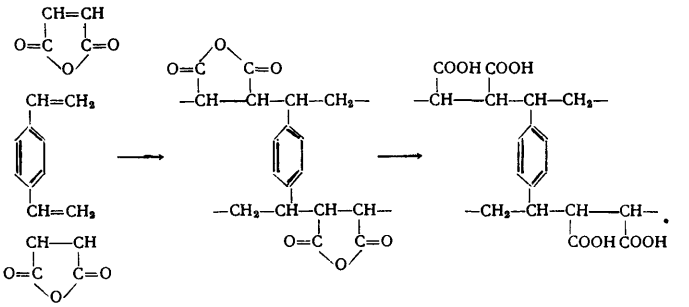
More promising is the use of styrenesulphonic esters mixed with other monomers. These esters polymerise more easily than does the acid itself, and are better combined with vinyl monomers (styrene, divinylbenzene, vinyl acetate, etc.).

Trostyanskaya et al. [131] synthesised cation-exchange membranes by the copolymerisation on various fabrics of toluene-*p*-sulphonic ester and divinylbenzene with subsequent sulphonation. The membranes possessed a high electrical resistance [131]. Sigodina et al. [66] obtained a cation-exchange membrane of low electrical resistance, but of poor mechanical strength, on the basis of copolymers of propyl styrenesulphonate and vinyl acetate. These workers [66] suggested the preparation of polyfunctional membranes based on copolymers of propyl styrenesulphonate and methacrylic acid, the membrane being vulcanised at 100°C for 5 h and then saponified. The process can be represented by the scheme



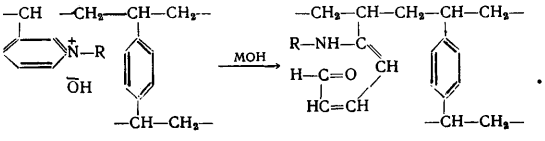
These membranes have greater mechanical strength than have monofunctional membranes. However, such membranes can hardly be used in electrodialytic desalination apparatus.

A carboxylated membrane of capacity 2.1 mg-equiv. g^{-1} has been synthesised by the copolymerisation of maleic anhydride with divinylbenzene in the presence of azoisobutyronitrile [231]. The reaction is conducted on the reinforcing fabric between two glass plates, the anhydride group then being hydrolysed [231]:



A Dutch patent [230] proposes the use of a complicated mixture—(1) a monomer (styrene, methacrylic or acrylic acid, methyl methacrylate), (2) its polymer, (3) a cross-linking agent (divinylbenzene or a mixture thereof with butadiene), and (4) a plasticiser not involved in the reaction—as starting materials for the synthesis of strongly and weakly acidic cation-exchange and anion-exchange membranes. Polymerisation is conducted in two stages, with partial (~25%) conversion of the monomer, addition of the remaining components, and completion of polymerisation. Ionogenic groups are introduced in the usual way. The final membranes are claimed to possess increased mechanical strength. Such membranes probably constitute a variety of ion exchangers of isoporous structure; the improved mechanical strength may therefore be assumed to be due to a more ordered polymer structure.

It has been proposed to synthesise most anion-exchange polymerisation membranes from vinylpyridine or its derivatives mixed with other components—polyepoxide compounds [78], quinol, styrene, butadiene [180], etc.—the vinyl-pyridine being alkylated during the synthesis with the formation of a pyridinium base. Membranes based on pyridinium compounds possess strongly basic properties, and are unstable in alkaline media [359]:

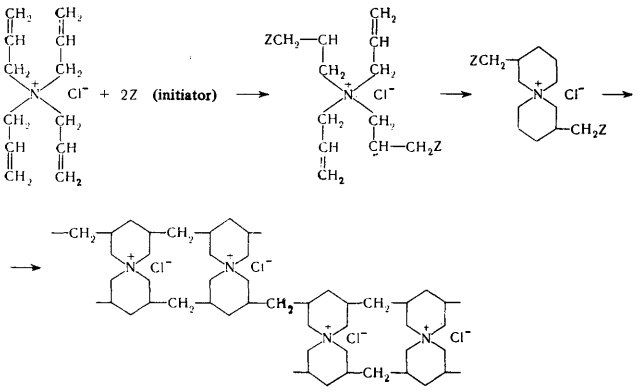


Tevlina et al. [238] first synthesised a water-soluble polymeric base (by the chloromethylation of polystyrene and polyvinyltoluene followed by amination), and then combined it with poly(vinyl alcohol). The resulting films were heated at 120–140°C for 20 h in order to cross-link them. The authors [238] suggest a scheme for formation of the water-soluble polymeric base, but give no mechanism by which the three-dimensional structure is produced. The poly(vinyl alcohol) probably undergoes cross-linking by the formation of ether bonds [360]. It is hardly possible in this case that a cross-linked membrane of homogeneous type could be obtained by interaction of unchanged chlorine in the chloromethyl group with the poly(vinyl alcohol). This is supported also by the fact that the polyelectrolyte is gradually eluted from the membrane [238]. The membranes possess quite low electrical resistance (1–2 ohm cm^{-2}) and an exchange capacity of around 1–2 mg-equiv. g^{-1}. The swelling is greatly dependent on the amount of polyelectrolyte introduced, which usually varied over the range 25–75%.

The swelling in water, and especially in alkaline solutions, was found to increase at polyelectrolyte contents of 50% and above. When it was increased to 75%, the capacity of the membranes dropped sharply after the first regeneration (owing to elution of the water-soluble polymeric base).

Syntheses of anion-exchange membranes have also been suggested from but-3-en-2-one, styrene, and divinylbenzene[312], styrene, divinylbenzene, and butadiene[230], etc.

An interesting synthesis of anion-exchange membranes is based on poly(tetra-allylammonium chloride). The polymer is obtained in aqueous solution in the presence of ammonium persulphate at 50°C, and is treated with triallylamine hydrochloride[197]. The work of Butler et al.[361,362] established that tri- and tetra-allyl derivatives form insoluble three-dimensional structures on polymerisation. They suggest that the mechanism of polymerisation involves radical formation from the initial monomer, intra- and inter-molecular chain transfer, and formation of a three-dimensional polymer from alternating piperidine rings and methylene groups. It is probable that synthesis of the membranes[197] involves also formation of stable six-membered rings, which then undergo cross-linking:



Many polymerisation membranes have not found wide industrial use owing to their low mechanical strength and the difficulty of obtaining large sheets. The following membranes are manufactured by industry—Nepton CR-51, CR-61, and AR-111, Permutit C-1373 and A-1374 (USA); Zerolit C-60, DK-1, A-60, and DA-1 (England); Serion C-100 and A-100 (Japan); MK-100 and MA-100 (USSR); etc.

(c) Activated Films

The chemical modification of inert polymer films is the most convenient way of synthesising ion-exchange membranes, since it is considerably simpler to obtain films from an inert thermoplastic polymer than from a polymer containing ionogenic groups. Furthermore, this method enables very thin membranes to be obtained.

Matrix membranes. The way in which membranes of this type are synthesised is in effect to obtain a film from a copolymer (mostly a styrene–divinylbenzene or a styrene–butadiene copolymer), and then to introduce ionogenic groups into the film.

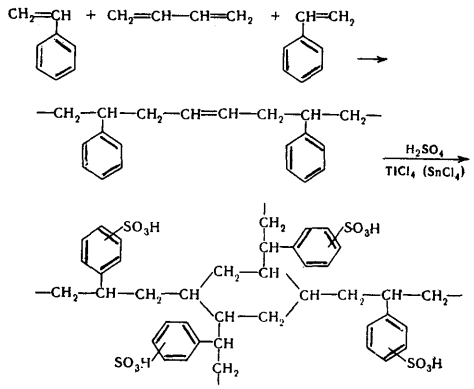
An example is the method proposed by the Japanese chemists Tsunoda and Seko[141], who used a copolymer of styrene, divinylbenzene, and ethylbenzene to form the matrix. The partly polymerised copolymer was dissolved in monomeric styrene, and the reaction completed by heating the mixture in a closed vessel at 100°C for 50 h. The copolymer was sulphonated.

Several analogous membranes have been obtained based on a styrene–divinylbenzene copolymer[142,195].

A ready prepared rubber latex can be used for film formation. The technique of this process is usually to impregnate a reinforcing cloth with a butadiene–styrene latex, dry, and treat with sulphonating or aminating agents. In an example described in a Japanese patent[149], a latex consisting of 29% of styrene and 71% of butadiene is applied to glass fibre, and the dried film is sulphonated with 96% sulphuric acid. Other membranes are obtained similarly[70,130]. The properties of this type of membranes depend on the film thickness, the proportions of styrene and butadiene, the concentration of sulphuric acid, and the time of treatment. The optimum concentration of sulphuric acid is 96%, and the styrene content 40–50%.

Nishihara[79] suggests a synthesis of a cation-exchange membrane which is selective with respect to individual cations. A matrix consisting of glass fibre and a styrene–butadiene latex (1 : 1) is placed in a 25% aqueous solution of resorcinol at 30°C for 20 min, and then in an aqueous solution containing hydrogen chloride (20%) and formaldehyde (15%) at 30°C. After half an hour the membrane is washed with water and 0.5 *N* sodium chloride. The presence of a three-dimensional structure helps to increase selectivity and improve other properties of the membrane[79].

Cyclisation is often used to form a cross-linked structure. Reactions of this type can be accomplished in the presence of such reagents as titanium and tin tetrachlorides. The former is the more effective catalyst, polymers having a greater degree of cross-linking being obtained in its presence, while the membranes are characterised by better electrochemical characteristics. Japanese chemists[189,239] suggest the synthesis of cation- and anion-exchange membranes based on a styrene–butadiene copolymer, cross-linking being effected by cyclisation. An advantage of this method is the simultaneous occurrence of the reactions in a single stage. The mechanism of formation of a cross-linked sulphonated polymer can probably be represented by the scheme



To obtain a strongly basic anion-exchange membrane a film of a copolymer of butadiene with 2-methyl-5-vinylpyridine is treated with methyl iodide. A disadvantage of such membranes is[185] that they can be used only in solutions of pH < 6.

Methods of synthesising matrix membranes have the advantage that a ready made copolymer is usually used, and films of large dimensions are fairly simply obtained. In

most cases, however, the membranes do not possess sufficient mechanical strength for their practical utilisation.

Graft membranes. Membranes having comparatively good electrochemical properties and mechanical strength can be synthesised on the basis of graft polymers formed by attacking the main chain of the polymer with reaction-initiating radicals. In practice initiation by ultraviolet radiation or by a cobalt-60 source is most often employed. The production of radicals by means of peroxide initiators is also widely used. In the synthesis of graft membranes based on polymer matrices and obtained by radiation grafting the source most often used is cobalt-60 [246-259].

Polyethylene, poly(vinyl chloride), polytetrafluoroethylene, etc. films are used as base for radiation grafting. The monomers which are grafted on are styrene [240,245-254], vinylpyridine and its derivatives, methyl acrylate, acrylonitrile [255,265], vinyltoluene, vinylnaphthalene [258], etc.

Ballantine et al. [363] studied the initiation by γ-rays of the formation of graft copolymers from polyethylene films and styrene. Ion-exchange membranes obtained by grafting styrene (20–30%) to polyethylene at a radiation dose of 1.06 Mrad possess the following characteristics [364]: thickness of damp membranes ~ 0.15 mm, exchange capacity 1.2 mg-equiv. g^{-1}, surface electrical resistance in 0.6 N potassium chloride solution 30 ohms cm^{-2}, selectivity 91.0, resistance to tearing in damp state 2.32 kg cm^{-2}, tensile strength in damp state 147.7 kg cm^{-2}, and elongation 190% [364].

Carbon–halogen bonds are more susceptible to attack by a radical and to the reaction of chain transfer than are carbon–hydrogen bonds. Therefore a membrane based on poly(vinyl chloride) is more easily obtained than one based on polyethylene.

In the synthesis of graft polymers, including those used for membranes, various changes produced by the action of radiation—formation of chemical bonds, degradation, oxidation, evolution of gas—are often observed, and these affect the properties of the final products [365].

An interesting generalisation applying to the action of radiation on vinyl polymers, which are usually employed in the synthesis of ion-exchange membranes, was made by Wall [366]: on irradiation in the absence of oxygen, cross-linking processes predominate in polymers having a fairly high heat of polymerisation, whereas degradative processes predominate in polymers possessing a lower heat of polymerisation. The heat of polymerisation is small for stressed molecules (poly-α-methylstyrene) and high for systems having sterically unstressed molecules (polystyrene, polypropylene, polyethylene). This is probably the reason why compounds of the latter type have been suggested almost exclusively for the synthesis of membranes.

Kargin, Cherneva, and their coworkers [71,266] among others have described the preparation of homogeneous graft membranes by initiation with ultraviolet radiation.

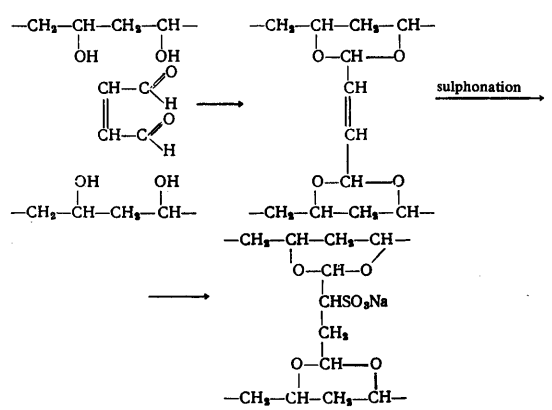
Zenftman [132] proposes the preparation of a graft ion-exchange membrane based on a styrene–polyethylene copolymer. Grafting is conducted in the presence of benzoyl peroxide in an inert gas (nitrogen). Treatment of the matrix with chlorosulphuric acid at 52°C for 30 min yields a cation-exchange membrane having a resistance of 37.7 ohms cm^2 and a selectivity of 0.97.

From a technical point of view the use of radiation polymerisation gives several advantages in comparison with well known methods of polymerisation. In particular, it becomes possible to avoid severe conditions for polymerisation, and unnecessary to employ expensive catalysts, traces of which cannot now contaminate the polymer. Opportunities for controlling the polymerisation process are considerably improved [367]. However, a disadvantage of radiation-grafted membranes is the difficulty of obtaining them under industrial conditions: this method has hitherto been still at the stage of laboratory research. The greatest interest attaches to chemical methods, since they enable graft polymers of desired composition and structure to be obtained in a pure form.

Film membranes. Ready made polymer films—hydrophilic or hydrophobic—are taken in all the proposed methods of synthesising film membranes. An inert film is transformed into an ion-exchange membrane in a single stage. Active groups are introduced by treatment with sulphonating agents, or else by chloromethylation followed by amination. Membranes based on either hydrophilic or hydrophobic films often have diminished mechanical strength.

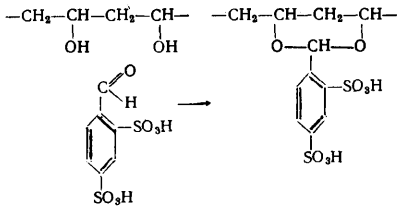
Membranes based on hydrophilic films. A cellulosic material—parchment, cotton cloth, cellulose acetate or regenerated cellulose sheets—or poly(vinyl alcohol) is used as the base. Polyisocyanates, bishydroxymethyladipamide, xanthates, etc. can be used as bridging agents. The use of parchment paper as starting material in the industrial production of large membranes is due mainly to its cheapness and availability. The ability of membranes based on parchment paper to withstand the stresses arising during heat-treatment and on subsequent immersion in water is attributed to the fibrous structure of the cellulosic base. The high water content of membranes of this type leads to low selectivity in relatively concentrated electrolyte solutions; the electrical resistance of such membranes is not large. In spite of the widespread use of membranes of this type, they have several important defects—poor chemical stability, cumbersome mode of production in most cases, etc.

Hydrophilic films of poly(vinyl alcohol) and cellulose can be modified in various ways, the most suitable being acetalisation or etherification of the hydroxyls with compounds containing ionogenic groups [158,173,176,275-286]. Cation-exchange membranes based on poly(vinyl alcohol) are obtained by treatment of the film under mild conditions with malealdehyde followed by addition of sodium hydrogen sulphite [158]:



The strength of the specimens obtained exceeds that of viscose rayon fibres, but the exchange capacity is around 0.2–0.25 mg-equiv. g^{-1} [158]. A greater effect is achieved

by using 4-formylbenzene-1,3-disulphonic acid:



Treatment with formaldehyde makes the membranes insoluble in water. The exchange capacity reaches 0.5–1.0 mg-equiv. g^{-1} [158].

Weakly acid membranes are obtained by heating a high-viscosity poly(vinyl alcohol) in a current of oxygen at 175°C for 5–15 min. Degradation is accompanied by an increase in crystallinity, cleavage of the chains, cross-linking, and oxidation to ketonic and carboxylic groups. Membranes obtained by the thermo-oxidative degradation of poly(vinyl alcohol) under milder conditions are less selective [173].

Weakly acid membranes are obtained by treating sheets of cellulose with an aqueous solution of phosphates of poly(vinyl alcohol) and then heating without a catalyst at 150°C for 15 min [176]. Treatment of poly(vinyl alcohol) films with various aliphatic, aromatic, and heterocyclic amines yields anion-exchange membranes [150,177,194]. The action of pyridine on a dry poly(vinyl alcohol) film at 100°C for 2 h gives a membrane having a low resistance. Insolubility in water (cross-linking) is effected by treating the final product with an organic polyisocyanate [177].

Membranes based on hydrophobic matrices. In this case industrial films of polystyrene, polyethylene, poly(vinyl chloride), polychlorotrifluoroethylene, and several others serve as base for the membranes. Ionogenic groups are introduced by direct sulphonation or amination of the film. The reagents usually employed in these reactions are hydrophilic in character and it is difficult to combine them with a hydrophobic film of compact structure. A further series of difficulties arise in the preparation of such membranes. For example, if the initial hydrophobic films are more than 0.07–0.08 mm thick, a very long time (usually exceeding 24 h) is required for complete swelling of the film. Thinner films are easily deformed, and the membranes obtained have poor mechanical strength. These difficulties, which usually occur in the chemical treatment of hydrophobic sheet material, can probably be overcome by using agents which promote swelling, or plasticisers, the presence of which facilitates sulphonation and has a favourable effect on the mechanical properties of the membranes. Phthalates are most often used as the plasticisers.

Cation-exchange membranes are obtained predominantly by sulphonation, more rarely by phosphorylation. Anion-exchange membranes are produced by chloromethylation of aromatic rings followed by amination or, in the case of halogenated polymer films, by direct amination.

Polystyrene films is the most convenient from the point of view of reprocessing and the chemical stability of the resulting membranes. Westermark [140] prepared a cation-exchange membrane by treating sheet polystyrene with sulphuric acid mixed with an organic solvent. The action of a strong sulphonating agent (e.g. chlorosulphuric acid) effects cross-linking through sulphonyl bridges. A disadvantage of these membranes is their poor mechanical strength.

Abrams and Adrian [178] obtained anion-exchange membranes from sheet polystyrene by the action of a mixture of formaldehyde, a polar organic liquid containing oxygen, and a halogenated sulphonic acid. This mixture forms a complex capable of cross-linking a linear polystyrene matrix. At the same time active groups are included in the polymer structure, and these can be subsequently transformed into quaternary bases by treatment with the appropriate amines. A negative aspect of this method is that the complex of the halogenated sulphonic acid with formaldehyde gradually ages.

Polyethylene [168,287–292] and poly(vinyl chloride) [77,293–297] films are most often used as the hydrophobic base. In view of the chemical resistance of these films to the action of sulphuric acid, sulphonation is accomplished predominantly with strongly acting agents (chlorosulphuric acid, oleum, sulphuryl chloride).

Vasil'ev et al. [289] prepared homogeneous membranes by sulphonating polymer films, and investigated the possibility of their use in electrochemical processes. Films of high-pressure polyethylene were sulphonated with sulphuric acid, oleum, or chlorosulphuric acid at 30°C; the resistance of the membrane was 20 ohm cm^{-2} in 10 *N* potassium hydroxide solution, and its exchange capacity 1.5 mg-equiv. g^{-1}. At 40°C chlorosulphuric acid destroys the film. Low-pressure polyethylene is broken down by chlorosulphuric acid above 50°C, but at 45–50°C sulphonation yields a membrane having an exchange capacity of 4 mg-equiv. g^{-1}. The crystallinity of polyethylene is preserved during sulphonation for 2 h, but is completely destroyed at 50°C after 4 h. Transition of the crystalline into an amorphous structure probably accompanies sulphonation throughout the thickness of the films, as is proved by the sharp increase in the electrical conductivity of the membranes. Degradation of the polyethylene is also possible, of course. The investigations made it clear that the homogeneous membranes obtained could have no practical application owing to their inadequate mechanical strength, chemical stability, and electrical conductivity.

Improvement in mechanical and chemical stability is achieved when the matrix of the membrane consists of polymeric chlorotrifluoroethylene or tetrafluoroethylene, but these membranes exhibit a tendency to intermembrane deposits.

Membranes based on poly(vinylidene fluoride) have been described. Direct sulphonation of a film of the latter takes place mainly on the surface owing to the difficulty of access by the sulphonating agent to the interior of the polymer. Sulphonation of a previously swollen film of the same material takes place throughout the film. In the latter case the rate of sulphonation is increased, and a membrane of relatively low electrical resistance is obtained [254].

The synthesis of ion-exchange membranes based on hydrophobic films has not become widespread. This is because the introduction of ionogenic groups into inert films takes place under severe conditions (high temperature, strong sulphonating agents, etc.) and causes degradation of the polymer. Owing to the difference in chemical nature between the film and the reagent introducing the active groups, the distribution of the latter in the membrane is non-uniform. This has an unfavourable effect on the electrochemical properties of the resulting membranes, which in most cases have a high resistance and low selectivity.

3. INTERPOLYMER MEMBRANES

Increasing attention has been paid during recent years to this type of membranes, because of their interesting combination of properties. Several of them possess

excellent electrochemical characteristics together with satisfactory mechanical strength. Interpolymer membranes are closely similar to homogeneous membranes in properties and structure, since the macromolecules of polyelectrolyte and inert polymer are closely interlinked and appear to form one phase, although chemical bonds are not usually formed. The interlinking of the active component of the membrane with the inert component should hinder and practically exclude its elution during operation. However, the absence of cross-linking bridges may be a reason for gradual partial elution of the active component.

Dynel Membranes

These membranes obtained their name from the original product "dynel" (a copolymer of vinyl chloride and acrylonitrile)[70,76,169]. Poly(styrenesulphonic acid), poly(acrylic acid), a copolymer of maleic acid and methyl vinyl ether, polyvinylimidazole, polyamines, etc. are used as the polyelectrolyte. A mixture of the two polymers is dissolved in a solvent for both hydrophilic polyelectrolytes and hydrophobic inert polymers, this requirement being met by dimethylformamide, dimethyl sulphoxide, and γ-butyrolactone.

Dynel membranes were first synthesised by Gregor and his coworkers[18,19]. A cation-exchange membrane was synthesised by dissolving poly(styrenesulphonic acid) (23%) and dynel (77%) in a mixture of cyclohexanone and methanol, and then pouring the film at 50°C and removing the solvent. For the synthesis of an anion-exchange membrane it is proposed to dissolve a linear poly(vinylbenzyltrimethylammonium chloride) (27%) with dynel in the same solvents. Such a membrane possesses an electrical resistivity of 200–300 ohm cm in 0.1 *N* sodium chloride and a selectivity of around 99%.

The difficulty of producing dynel membranes of large dimensions, the consumption of large quantities of solvents, the complexity of obtaining pure polyelectrolytes, and the relatively low electrical conductivity of the synthesised specimens create obstacles to their industrial utilisation.

Lyubman, Shostak, and their coworkers[316-329] suggested original syntheses of the interpolymer membranes Ankalit K-1 and K-2. The former are obtained by blending polystyrene and polyethylene on rolls in the presence of a hydrocarbon–formaldehyde resin, which functions as both cross-linking agent and plasticiser, lowering the melting points of both polymers. The electrical resistivity of the membrane does not exceed 130 ohm cm[316]. The K-2 membranes were synthesised by dissolving poly(vinyl chloride) and styrene–formaldehyde resin in a common solvent and then pouring the film. Introduction of ionogenic groups (sulphonation) takes place at the same time as cross-linking. The cross-linking–sulphonating reaction takes place at low temperatures of 0–20°C[320]. Introduction of a sulphogroup into the polymer at high temperatures (80–100°C) has an adverse effect on the strength of the membranes. Ankalit K-2 membranes are noteworthy in this respect, their synthesis involving rapid cross-linking at temperatures close to 0°C.

Activated Interpolymer Membranes

These membranes have been acquiring increasing importance during recent years. Combining a ready made inert polymeric film with a monomer which is activated by further treatment may yield mechanically strong membranes possessing adequate electrochemical characteristics.

Polystyrene[74,309,311], a copolymer thereof with divinylbenzene[306,308,310,313,315] or with butadiene[184,185], or a copolymer of styrene, divinylbenzene, and but-3-en-2-one[312] is usually taken as the polymer into which ionogenic groups are introduced. Polyethylene[306-310,316,317], poly(vinyl chloride)[311,315,332], polypropylene[303], and poly(vinylidene chloride)[313,314] are used in the form of films.

The synthesis of interpolymer membranes by the activation of a ready made thermoplastic film is accomplished by impregnating the initial polymer in a monomer or a mixture of monomers, polymerising (or copolymerising) the latter within the film in the presence of an initiator, and introducing ionogenic groups by the usual methods.

Activated interpolymer membranes will probably be given the principal role in electrodialysis processes, although at the present time most of them possess insufficiently low electrical resistance (~ 150–300 ohm cm). The above methods do not ensure good electrochemical characteristics, and moreover membranes of great mechanical strength are rarely obtained.

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In spite of the great scope of the investigations, the problem of synthesising ion-exchange membranes remains unsolved. The effective life of even the best of them does not exceed 3–5 years, whereas for a granular exchanger it sometimes reaches 15 years. No practical methods have been developed for synthesising membranes possessing selective properties towards individual ions of the same sign. Theoretical investigations on membrane processes considerably outstrip corresponding researches on the synthesis of membranes. An urgent problem is also the production of biologically active membranes, which might fulfil the functions of membranes in animal and vegetable organisms.

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Institute of Chemical Sciences, Kazakh SSR Academy of Sciences, Alma-Ata