Translated from *Uspekhi Khimii*, **57**, 1001-1009 (1988)

New Trends in the Development of Polymeric Materials for Reverse Osmosis Membranes

Yu.E.Kirsh and Yu.M.Popkov

Synthetic polymeric materials used for the preparation of asymmetric and composite membranes are examined. The reactions leading to the synthesis of these polymers and ways of obtaining a thin barrier layer which determines the principal quality parameters of the membranes are described. Attention is specially concentrated on the interfacial polycondensation reaction between acid chlorides and amines in order to create a barrier layer with a high selectivity and permeability.
The bibliography includes 32 references.

CONTENTS

I. Introduction 566
II. Polymeric materials for asymmetric membranes 566
III. Polymeric materials for composite membranes 567

I. INTRODUCTION

Membranes for reverse osmosis have found most extensive application in devices and apparatus designed for the desalination of brackish waters and sea water, for the conversion of industrial waste water into high-quality fresh water, for the separation of valuable side products in the petroleum, petrochemical, chemical, electrochemical, and cellulose-paper industries, for the concentration of food products in the food industry, etc.[1-3]

Numerous papers and patents concerning the preparation of reverse osmosis membranes incorporating synthetic polymers have been published during the last 10–15 years. Despite the considerable advances made, the interest in the search for new approaches in this field has not waned. A series of unsolved problems remain in the science of membranes of the type considered. Certain difficulties still exist in the interpretation of the mechanism of the segregation of water from aqueous salt solutions. Ideas concerning the influence of the chemical structure of the polymer and the processes occurring during its synthesis, its conformational and configurational states under the conditions of the formation of the membrane, and the arrangement of the macromolecules and their associated species on the surface as well as other macromolecular characteristics on the separation of substances under the conditions of reverse osmosis have been inadequately developed.

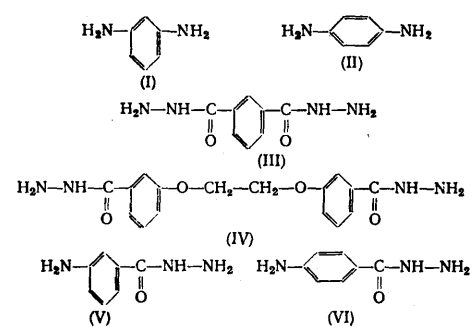
A survey of the available information about the polymeric materials used in the manufacture of the membranes can promote the development of these ideas and can stimulate the development of membranes for reverse osmosis with a high selectivity and permeability and capable of working at low pressures.

II. POLYMERIC MATERIALS FOR ASYMMETRIC MEMBRANES

Qualitatively new acetylcellulose membranes were first prepared in 1959,[2,4] which promoted a vigorous development of the application of reverse osmosis in the desalination of water. Such membranes are prepared by pouring a solution containing a water-soluble pore-forming additive over a solid surface with subsequent evaporation of the solvent at low temperature, coagulation in ice water, and annealing in hot water. Cellulose acetate containing 39.8% of acetyl groups is normally employed.[4] In this case, the membrane has an asymmetric structure, because it consists of a very thin dense surface layer, called the barrier layer, and a more porous lower layer. The molecules of the permeating solution encounters most resistance in a thin barrier layer, where they are in fact separated. However, such membranes also suffer from a series of disadvantages. The susceptibility of the acetate groups of acetylcellulose to hydrolysis in acid and alkaline solutions limits the employment of the membranes in practice and their sensitivity to microbial infection dimishes their useful life in the purification of water.

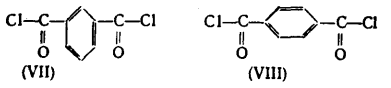
For this reason, membranes for reverse osmosis, which have a higher chemical stability than traditional acetylcellulose membranes, began to be developed since 1969. New polymeric materials distinguished by a high chemical and thermal stability have been found and new approaches have been devised to the creation of a thin barrier layer[5,6] in asymmetric and composite membranes. The latter differ from the former by the fact that their barrier layer consists of a polymeric material differing from the material of the coarsely porous base.

The first asymmetric membranes made from a non-cellulose material[5] found extensive application in the desalination of brackish waters and sea water. The modular devices for this purpose consists of hollow fibres made from aromatic polyamines or polyhydrazides. These polymers are synthesised by condensing aromatic diamines, aromatic dihydrazides, or aromatic aminohydrazides with aromatic acid chlorides in a solvent—*N*-methylpyrrolidinone (or dimethylacetamide).[5-8] *m*-Phenylenediamine (I), *p*-phenylenediamine (II), the dihydrazides (III) and (IV), for example, the dihydrazide of isophthalic acid (III), and aminohydrazides, for example, the hydrazides of *m*-aminobenzoic acid (V) and *p*-aminobenzoic acid (VI), are used as the first component:



The second component is a mixture of isophthaloyl chloride (VII)

and terephthaloyl chloride (VIII) in proportions of 7 : 3.



(VII) (VIII)

The polymers obtained are readily soluble in organic solvents. When only the acid chloride is used instead of the mixture, the resulting polymer can undergo rapid crystallisation, which hinders the preparation of the casting solution.

The casting solution for the preparation of asymmetric planar membranes can contain, for example, 15 wt.% of the polymer in dimethylacetamide with added $LiNO_3$ (35% of the weight of the polymer[5]). The film obtained on a glass plate after casting is kept in air and then placed in ice water for 1 h, after which it is washed with distilled water. The influence of the concentration and nature of the solvent and also of the nature of the salts on the formation of an asymmetric membrane has been considered.[8] The data presented in Table 1 show that the structure of the polymer influences the permeability of the membrane to water, while the selectivity remains equally high. The flux of liquid through a homogeneous film prepared from one of the aromatic polyamides [the diamine (I) and (VII/VIII) in proportions of 7 : 3] is smaller by a factor of almost 180 than that through an asymmetric membrane of the same thickness made from the same material and having the identical selectivity.[5]

Table 1. The flux of water (P) and the selectivity (S) of certain polyamide membranes.*[6]

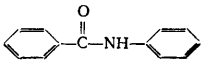
Composition of initial monomer mixture		P, litre m^{-2} h^{-1}	S, %
component 1	component 2		
(I)	(VII)/(VIII) (7:3)	8.5	99.8
(IV)/(III) (5:8)	(VII)/(VIII) (7:3)	22	99.3
(V)/(VI) (8.3:1.7)	(VII)/(VIII) (7:3)	28	99.5

*Conditions of the test: 30 °C; 3.5% NaCl solution; pressure over the membrane 10.3 MPa.

Electron microscopy of the thin barrier layer in the asymmetric polyamide-hydrazide membrane showed a closer-packed layer comprising "micelles" having a diameter of 40–60 nm. This layer consists of spherical aggregates or globular domains between which there are 7.5–10 nm cavities.[8]

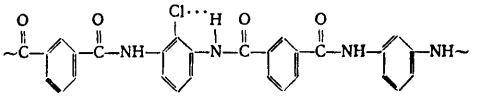
Membranes based on aromatic polyamides are manufactured in the form of hollow fibres with an external diameter of 85 μm, an internal diameter of 42 μm, and a barrier layer whose thickness ranges from 0.1 to 1 μm.[5] These membranes have a high mechanical strength, which eliminates the need for the employment of a support capable of withstanding a high pressure, and their chemical stability is also high at neutral pH.

After prolonged use of such membranes, their sensitivity to the chlorine dissolved in water was observed.[5] In order to elucidate the mechanism of the decrease in the selectivity of the membrane prepared from compounds (I), (VII), and (VIII) [for (VII)/(VIII) = 7 : 3], a study was made of the interaction of a compound modelling the material of this membrane with bromine dissolved in water.[9] Benzanilide (IX), which contains all the principal groups present in the polymer, was chosen as the model compound:



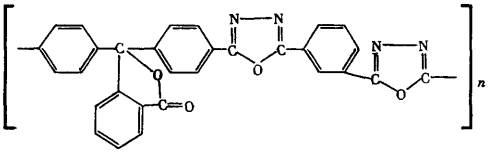
(IX)

As bromine acted on compound (IX), it gradually replaced the hydrogen in the benzene ring of the amino-component. The results obtained permitted the conclusion that, when the polymer was treated with chlorine, substitution took place in the ortho-position of the benzene ring of the diamine, i.e.



and that intramolecular hydrogen bonds between the halogen atom and the H–N group in the compound formed arose instead of the intermolecular hydrogen bonds –C=O...N–N–. Naturally such chemical changes disturb the structure of the polyamide chains and alter the submicrostructure of the polymer and hence increase the flux of liquid and reduce the selectivity of the membrane with respect to the salt. This confirms the existence of a close relation between the initial structure of the polymer, the conformation and state of the macromolecules in the aggregates, and the arrangement of the macromolecules in the barrier layer, on the one hand, and the permeability of the membrane to water and its selectivity in the reverse osmotic process, on the other.

Poly-1,3,4-oxadiazole is also used as the polymeric material for an asymmetric membrane:[10]



The membranes are obtained by casting a 20–40% solution of the polymer in methylpyrrolidinone onto a glass or metallic surface polished to a mirror finish with subsequent maintenance of the film in an atmosphere with a humidity of 80–100% for 1 h and the coagulation of the film in a precipitation bath containing water. As a result, the barrier layer is generated at the support–film boundary and not at the film–air boundary, as happens, for example, in the preparation of polyamide membranes with rock-forming additives. The membrane obtained is capable of retaining 98.5–99.2% of the salt from a 1% NaCl solution and its permeability to water is 20–25 litre m^{-2} h^{-1}.

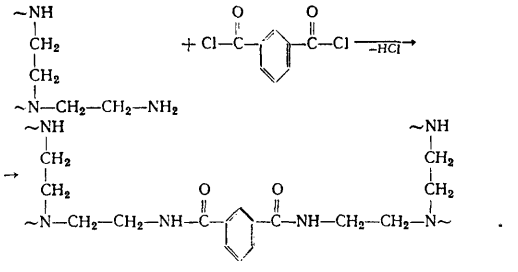
III. POLYMERIC MATERIALS FOR COMPOSITE MEMBRANES

A composite membrane for reverse osmosis consists of a thin barrier layer, a microfilter, and a base, usually a polyester base, which serves to increase the mechanical strength. Microfilters made of a polysulphone, which possesses high chemical and mechanical stability, are usually employed. Numerous investigations have been devoted to the preparation of a barrier layer,[11] from which it can be seen that the creation of this layer requires a high degree of technological sophistication and constitutes to some extent an art, scientifically well-founded criteria for the selection of the type of polymer (structure and type of functional groups) being so far lacking.

One can distinguish several principal approaches to the creation of the barrier layer. They are based on the possibility of the occurrence of the following chemical reactions on the surface of the support: (1) interfacial polycondensation between the amine and the acid chloride; (2) acid polycondensation; (3) radiation-induced cross-linking and plasma polymerisation.

1. Interfacial Polycondensation

Polyethyleneimine + aromatic acid dichlorides. In 1970 a new method was developed for the creation of the barrier layer by the interfacial polycondensation of the low-molecular-weight isophthalic acid chloride (VII) with high-molecular-weight polyethyleneimine (PEI).[11] The polysulphone support is saturated with an aqueous solution of PEI (0.5–1% solution) and is transferred to hexane containing compound (VII) (0.1–1% solution). The chemical polycondensation reaction with evolution of HCl takes place rapidly at the water–hexane interface. Since the PEI used contains primary and secondary amino-groups (the ratios of the primary, secondary, and tertiary groups are 3 : 4 : 3) and has a high molecular weight (from 10^4 to 6×10^4), interchain cross-linking of the PEI molecules takes place via the mechanism



The presence of cross-linked or branched polymer molecules at the interface between two liquids leads to the arrest of the reaction owing to the restriction of the diffusion of the amine from the aqueous phase and of the acid chloride from the organic phase. PEI which failed to react therefore remains under this layer. In order to obtain a high quality membrane, heat treatment at 110 °C, which promotes the cross-linking of the pure PEI with evolution of ammonia, is necessary.

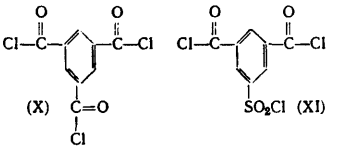
A membrane of the NS-100 type[12] consists of three layers of different porosity: the barrier layer made up of the cross-linked polyamide, the transversely cross-linked PEI layer which enters into the pores of the support, and the polysulphone microfilter. The role of the first and second layers in the creation of a high-quality membrane has been demonstrated by the following two experiments. When PEI is simply cross-linked without polycondensation, the resulting membrane has a low selectivity (70% with respect to NaCl) combined with a high water flux (92 litre m^{-2} h^{-1}).[11] If the NS-100 membrane is subjected to heat treatment at 75 °C and not at 110 °C, its selectivity falls from 99 to 96%.

Although the NS-100 membrane has a high salt-retaining capacity, it also suffers from a number of disadvantages: an insufficiently large water flux at a pressure of 10.3 MPa (~30 litre m^{-2} h^{-1}), a high sensitivity to chlorine, and a low mechanical strength of the upper layer.

In order to overcome these disadvantages, attempts have been made to replace PEI by other polymeric amines.

Polymeric aliphatic amines + dichlorides and trichlorides of aromatic acids. It has been suggested that compounds obtained from polyepichlorohydrin and ethylenediamine [13] and from polyepiiodohydrin and 4-(aminomethyl)piperazine [14] be used as the polymeric amines. A barrier layer more resistant to oxidation by chlorine can be obtained by condensation with compound (VII).[15]

Polymeric amines of other structures have been obtained by the reaction of amines with a polymeric anhydride, for example, by the reaction of triethyleneamine with the copolymer of maleic anhydride and methyl acrylate.[16] It has been suggested that a mixture of compound (VII) with the chloride of benzene-1,3,5-tricarboxylic acid (X) be used as the second reaction component:



After the interfacial polycondensation between the above polymeric amine and the mixture of acid chlorides, the membrane was dried at 115–120 °C. The flux at a pressure of 4.1 MPa and 25 °C was 98 litre m^{-2} h^{-1} for a 0.5% NaCl solution with a selectivity of 96.8%.

In order to alter the permeability and selectivity of the barrier layer, methods have been developed for its preparation from polyamides containing different numbers of free amino- and carboxy-groups.[17] Partly protonated or partly alkylated PEI and the chloride of benzene-1,3,5-tricarboxylic acid (X) and 3-chlorosulphonylisophthaloyl chloride (XI) were used. However, the barrier layer obtained was extremely hydrophilic and possessed a low selectivity.

Low-molecular-weight amines + dichlorides and trichlorides of aromatic acids. In order to obtain a barrier layer resistant to the prolonged action of chlorine, low-molecular-weight diamines (in particular, piperazine[18,19]) have also been used. The interaction of piperazine with compound (VII) makes it possible to produce a layer fairly resistant to chlorine and having a selectivity of 90–96% with respect to sea water. However the NS-300 membranes obtained in this way have not come to be widely used because they are inferior to the NS-100 membrane in their selectivity and permeability.

There exist interesting data concerning the influence of the composition of the mixture of compound (VII) with compound (X), interacting with piperazine, on the characteristics of the membranes for reverse osmosis.[6] The change in composition influences significantly the selectivity and permeability of the membrane relative to NaCl solution and solutions of bivalent metal salts ($MgCl_2$) (Table 2).

The conditions governing the formation of the barrier layer are as follows: the aqueous phase containing 1% of piperazine, 1% of Na_3PO_4, and 0.5% of dodecyl sulphate and the hexane phase containing 1% of the acid chlorides. The membrane obtained from a mixture of 33% of compound (X) with 67% of compound (VII) and piperazine is most effective for the separation of $MgCl_2$. It is characterised by a very high permeability combined with an extremely high degree of salt retention. The membrane obtained from 10% of compound (X) and 90% of compound (VII) possesses a high capacity for the retention of the salt from NaCl solution. The presence of free carboxy-groups in the barrier layer, formed as a result of the

hydrolysis of the residual acid chloride groups, promotes the retention of salts with bivalent ions:

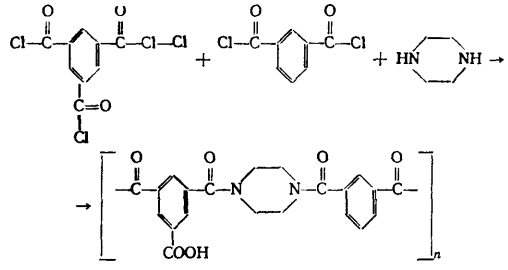


Table 2. The influence of the composition of the mixture of isophthaloyl chloride and the chloride of benzene-1,3,5-tricarboxylic acid on the properties of the membrane with respect to $MgCl_2$ and NaCl solutions.[11]

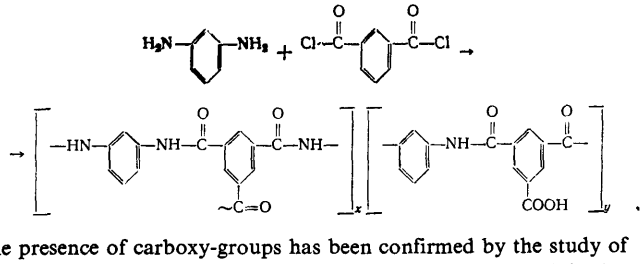
Composition, %		0.5% $MgCl_2$ solution (1.4 MPa)		3.5% NaCl solution (10.3 MPa)	
(X)	(VII)	P, litre m^{-2} h^{-1}	S, %	P, litre m^{-2} h^{-1}	S, %
100	0	43	99.3	133	68
75	25	52	99.3	160	64
33	67	128	99.9	157	65
25	75	97	99.6	121	78
10	90	30	99.9	55	96
0	100	6.7	99.0	33	98

Notation: P is the water flux and S the selectivity.

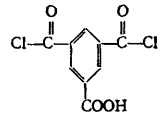
The NS-300 membranes are not manufactured on an industrial scale because of the considerable non-reproducibility of their properties.[11] The reaction of piperazine with the acid chloride is itself probably difficult to control. When piperazine is replaced by aromatic diamines, it is possible to obtain high-quality membranes for reverse osmosis.

Aromatic diamines + aromatic tricarboxylic acid chlorides. The creation in 1978 of the FT-30 membrane was a major step foward in the development of the technology for the preparation of highly efficient membranes for reverse osmosis.[20,21] The barrier layer on a polysulphone support is created in this case by the interfacial polycondensation of aromatic diamines, for example, compound (VII), with aromatic acid trichlorides, for example, compound (X). Linear chain sections, sections with branched macromolecules, and regions of cross-linked macromolecules arise during the reaction.

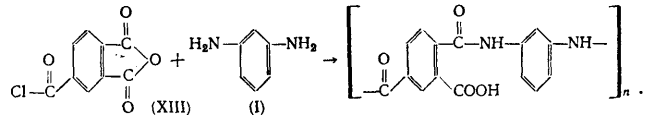
It has been demonstrated by the ESCA method that the polymer in the barrier layer contains 72% of cross-linked and branched forms (x) and 28% of linear sections with a carboxy-group (y):[22]



The presence of carboxy-groups has been confirmed by the study of the adsorption of cationic dyes. The lack of solubility in sulphuric acid indicates a cross-linked structure of the polyamide barrier layer. The presence of the cross-linked structure influences significantly the characteristics of the membranes for reverse osmosis.[11] Thus, if the barrier layer is obtained from the bifunctional acid chloride (XII)



mixed with compound (I), whereupon a cross-linked structure does not arise, then the membrane exhibits a low selectivity with respect to NaCl (from 60 to 80%). The layer obtained from the acid chloride of trimellitic anhydride (XIII) and the diamine (I) has the same characteristics:



These data indicate the existence of a definite relation between the degree of cross-linking and the morphology of the formations (aggregates) generating the barrier layer.

It has been observed by electron microscopy that the barrier layer in the FT-30 membrane consists of several layers of different density with an overall thickness of ~0.25 μm.[11] It possesses a high chemical stability and resistance to wear. The membrane can be sterilised in boiling water without change in its properties. The recommended pH range in the solutions where the membrane is sufficiently stable is between 3 and 11. The membrane can be regenerated by treatment with phosphoric and nitric acids. It is more resistant to chlorine than the NS-100 membrane, the greatest stability being observed at pH 5–6. With increase in pH, the properties of the membrane subjected to the action of dissolved chlorine are impaired. This membrane has found extensive practical application in roll-type elements and is characterised by 99.0–99.2% salt retention and a flux of 40 litre m^2 h^{-1} when a 3.5% solution is used under pressure of 5.5 MPa.

A new composite membrane for reverse osmosis, obtained by employing interfacial polycondensation, has been developed recently.[23] The barrier layer consists of a cross-linked aromatic polyamide, whose structure is close to that of the series FT-30 membrane. The membrane is characterised by an extremely high (99.5%) salt retention with respect to NaCl (0.15% solution), a high water flux (40–50 litre m^{-2} h^{-1} at 1.5 MPa), and resistance to chlorine and hydrogen peroxide.

Thus the interfacial polycondensation method gives rise to considerable possibilities for the preparation of highly efficient membranes for reverse osmosis. Presumably more efficient membranes with a high selectivity and permeability at a reduced working pressure (1–2 MPa) can be developed in this way. A low working pressure is extremely significant from the standpoint of reducing the energy consumption in the desalination process.

2. Acid Polycondensation

In order to obtain a barrier layer on the surface of the polysulphone microfilter, the acid polycondensation reaction of low-molecular-weight hydroxyl-containing compounds is used.[24,25] For

this purpose, one prepares a mixture of furyl alcohol, sulphuric acid, and a solution of polyoxyethylene (molecular weight 10^4) in proportions of 2:2:1. Polyoxyethylene is introduced in the form of a solution of 80:20 mixture of water and isopropyl alcohol. The reaction mixture is deposited on the surface of the support and dried at 125–140 °C. This results in acid polycondensation of furfuryl alcohol with formation of a polymeric barrier layer. However, after prolonged tests the membrane selectivity with respect to NaCl falls, which is associated with the irreversible swelling of the layer in the salt solution, the hydrolysis of the sulphate linkages, and oxidation (by the oxygen and chlorine dissolved in water).

When 1,3,5-tri(hydroxymethyl)isocyanuric acid (XIII) is used together with furyl alcohol for the condensation reaction, it is possible to obtain a membrane with better parameters.[25] The surface of the support is treated with a mixture of one part of compound (XIII) and two parts of furyl alcohol. The polymerisation on the surface is carried out at 150 °C. The membrane obtained is characterised by the following parameters: 99.5% salt retention with respect to NaCl (0.25% solution) and a flux of 20.5 litre m^{-2} h^{-1}. The Toray Industries (Japan) Company developed an extremely effective membrane (PEC-1000) for reverse osmosis apparently using the above condensation reaction between furyl alcohol and compound (XIII) in the presence of an acid.[26]

The cross-linking of sulphonated polysulphone on the surface of the support can also be included among the acid polycondensation reactions.[6] For this purpose, the initial polysulphone is sulphonated with chlorosulphonic acid in order to obtain a water-soluble polymer. The surface of the microfilter is coated with an aqueous solution of the polymer and is subjected to heat treatment at 100° to 140 °C, which results in the formation of a barrier layer comprising the cross-linked sulphonated polysulphone. Together with a high selectivity with respect to NaCl (98%), this membrane has a small water flux (2.5 litre m^{-2} h^{-1}). A major advantage of the membrane is its high resistance to chlorine after very prolonged action of the latter (5000) h).[27]

3. Radiation-induced Cross-linking and Plasma Polymerisation

The method consisting in the cross-linking of a surface film made up of sulphonated poly(phenylene oxide) (SPPO) by ^{60}Co γ-radiation has been applied to produce chlorine-resistant membranes with a high permeability.[8] The SPPO film is deposited on a porous polysulphone support, dried, and exposed to radiation. Best results have been obtained for doses of 2–5 Mrad; the salt retention increased from 88 to 98% and the water flux rose from 20 to 40 litre m^{-2} h^{-1}.

It has also been suggested that plasma polymerisation of vinyl and other organic compounds be used to create a barrier layer on a dry macroporous support.[29–32] However, these studies have not so far gone beyond laboratory research.

The data presented indicate the existence of a wide variety of approaches to the creation of membranes for reverse osmosis. The use of the interfacial polycondensation reaction between amines and an acid chloride is most promising. The possibility of extensive variation of the structure of both the low-molecular-weight components and of the polymers has been demonstrated in this instance. This helps in its turn to establish a relation between the structure of the polymer and the properties of the barrier layer under the conditions of reverse osmosis and hence to elucidate the mechanism of the segregation of water from aqueous salt solutions under pressure.

REFERENCES

1. R.E.Lacey and S.Loeb (Editors), "Industrial Processing with Membranes" (Translated into Russian), Izd.Mir, Moscow, 1976, 370 pp.
2. S.-T.Hwang and K.Kamermeyer, "Membranes in Separation" (Translated into Russian), Izd.Khimiya, Moscow, 1981, 464 pp.
3. V.N.Smagin, I.N.Medvedev, N.E.Khozhevnikova, and T.P.Sadchikova, "Primenenie Membrannykh Metodov Razdeleniya Veshchestv" (Application of Membrane Methods in the Separation of Substances), Izd.NIITEKhIM, Moscow, 1985, No.10, p.40.
4. S.Sourirajan, "Reverse Osmosis", Acad.Press, New York, 1970.
5. H.H.Hoehn, "Materials Science of Synthetic Membranes" (Edited by D.R.Lloyd), ACS Symposium Series, No.269, Washington, 1985, p.81.
6. H.Finken, "Materials Science of Synthetic Membranes" (Edited by D.R.Lloyd), ACS Symposium Series, No.269, Washington, 1985, p.245.
7. J.M.Richter and H.H.Hoehn, US P. 3 567 632.
8. M.Panar, H.H.Hoehn, and R.R.Hebert, Macromolecules, 1973(6), 777.
9. J.Glafer and M.R.Zacharian, "Reverse Osmosis and Ultrafiltration" (Edited by S.Sourirajan and T.Matsuura), ACS Symposium Series, No.281, Washington, 1985, p.345.
10. A.P.Bogdanov, K.M.Saldadze, R.S.Gotsiridze, and G.A.Gorokhova, USSR P. 1 248 629; Byul.Izobret., 1986(29).
11. J.E.Cadotte, "Materials Science of Synthetic Membranes" (Edited by D.R.Lloyd), ACS Symposium Series, No.269, Washington, 1985, p.274.
12. L.T.Rozelle, J.E.Cadotte, K.E.Cobian, and C.V.Kopp, "Nonpolysaccharide Membranes for Reverse Osmosis: NS-100 Membranes for Reverse Osmosis and Synthetic Membranes" (Edited by S.Sourirajan), National Research Council of Canada, Ottawa, 1977, p.249.
13. R.L.Riley, R.L.Fox, C.R.Lyons, et al., Desalination, 1976, **19**, 113.
14. M.Kurihara, K.Uemura, and K.Okada, US P. 4 387 024.
15. A.Al-Cholaikah, N.El-Ramly, J.Janyoon, and R.Seaton, Desalination, 1978, **27**, 215.
16. T.Kawaguchi, Y.Taketani, N.Sasaki, et al., US P. 4 303 336.
17. T.Kawaguchi, H.Minematsu, Y.Hayashi, et al., US P. 4 360 434.
18. L.Credali, A.Chiolle, and P.Perini, Desalination, 1974, **14**, 137.
19. P.Parrini, Desalination, 1983, **48**, 67.
20. J.E.Cadotte, R.J.Petersen, R.E.Larson, and E.E.Erickson, Desalination, 1980, **32**, 25.
21. J.E.Cadotte, US P. 4 277 344.
22. Ja-Young Koo, R.J.Petersen, and J.E.Cadotte, "International Congress on Membranes and Membrane Processes", Tokyo, 1987, p.350.
23. M.Kurihara, Y.Himeshima, and T.Uemura, "International Congress on Membranes and Membrane Processes", Tokyo, 1987, p.428.
24. J.E.Cadotte, US P. 3 926 798.
25. M.Kurihara, T.Watanaba, and T.Unoue, US P. 4 366 062.
26. M.Kurihara, N.Kanamaru, K.Harumiya, et al., Desalination, 1980, **32**, 13.

27. R.B.Davis, D.K.Schiffer, and C.E.Kramer, "Hollow Fiber Reverse Osmosis Composite Membranes. Process and Properties", ACS Symposium, Series, No.153, Washington, 1981, p.367.
28. E.Y.M.Huang and J.J.Kim,"Reverse Osmosis and Ultrafiltration" (Edited by S.Sourirajan and T.Matsuura), ACS Symposium Series, No.281, Washington, 1985, p.83.
29. K.R.Buck and V.K.Davan, Brit.Polym.J., 1970, **2**, 238.
30. H.Yasada and C.E.Lamaze, J.Appl.Polym.Sci., 1973, **17**, 201.
31. P.Y.Hollahan and T.Wydeven, Science, 1973, **179**, 500.
32. S.Suzuki, T.Ogawa, and N.Hitotsuyanagi, "Reverse Osmosis and Ultrafiltration" (Edited by S.Sourirajan and T.Matsuura), ACS Symposium Series, No.281, Washington, 1985, p.69.

Karpov Physicochemical
Institute, Moscow