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MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Aromatic Polysulfone Imides and Membranes Based on Them

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Abstract—Aromatic polyimides containing diphenyl sulfone fragments in the backbone were prepared. Asymmetric microporous films of the synthesized polymers were prepared by wet forming under the conditions of a phase-inversion process. The morphologies and the mechanical and transport properties of nonporous and phase-inversion films as materials for pervaporation membranes were studied. Multilayer composite membranes with diffusion layers of an aromatic polyether imide were prepared on the basis of microporous polyamido imide films. These membranes showed high performance in pervaporation separation of ethanol–cyclohexane mixtures of various compositions.

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Extensive search for polymers for membranes showing high selectivity in separation of mixtures of gases and liquids by the diffusion–sorption mechanism has been performed. Among promising materials for such purpose are rigid-chain aromatic polyimides and polyamido imides (PAIs) [1–3]. Polymers of this class are characterized by a high degree of structural ordering on the supramolecular level. They have fixed values of the free volume and its elements, with the element size comparable with the kinetic diameters of molecules of substances being separated [4, 5]. Polyamido imides attract particular attention as a promising class of polymers for membranes [6, 7], because they are soluble in such commonly used organic solvents as dimethylacetamide, dimethylformamide, and *N*-methylpyrrolidone. Syntheses of polyamido imides of various chemical structures have been described [8, 9]. Many polymers of this class were reported to be high-performance mem-brane materials [6–10]. However, PAI membranes for wide-scale applications still are not commercially available on the world market. Their commercial produc-tion is apparently hindered by the lack of efficient procedures for preparing polyamido imides in suf-ficient amounts and with the required set of physico-mechanical properties for forming membranes.

It is well known that the permeability of rigid-chain polymers to the majority of gases and liquids is extremely low [11]. Therefore, practically used membranes based on this type of polymers are formed as morphologically complex structures, in particular, with asymmetric pore-size distribution. A characteristic feature of such structures is the presence of a thin defect-free surface layer (skin layer) and a porous sublayer with coarse through pores, which minimizes the membrane resistance to mass transfer. Asymmetric membranes are prepared by the phase inversion method in the polymer–solvent–precipitant system.

The major requirement to polymers for phase-inversion membranes is their capability to form a continuous "gel" [12] whose structure determines the membrane morphology [13]. For this purpose, the polymer solution should be so viscous as to preserve integrity in the course of sol–gel transition when a porous structure is formed. To meet this requirement, the polymer should have high molecular weight (MW) (or high weight of stable molecular associates present in the forming solution) and a narrow molecular-weight distribution (MWD).

Preparation of polyamido imides with the required molecular-weight characteristics was a difficult problem for a long time. All the known procedures for preparing such polymers yielded products with low molecular weights, and films prepared from such PAIs were brittle [9, 14]. A procedure developed at the

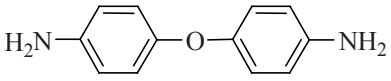
Institute of Macromolecular Compounds, Russian Academy of Sciences, for synthesizing polyamido imides by low-temperature polycondensation in solution allowed preparation of PAIs in required amounts and with the required MWD and physicochemical characteristics. Using a PAI synthesized by this procedure from dicarboxyphenylphthalimide dichloride and 4,4'-diaminodiphenyl ether (PAI-1), we prepared high-performance asymmetric and composite membranes for separation of gases and liquids [15, 16]. However, the selectivity of an asymmetric diffusion membrane of PAI-1 in separation of an O_2/N_2 mixture appeared to be lower than that of the same polymer in a homogeneous independent film (selectivity coefficient 1.8 and 5.1, respectively), whereas the performance of the membrane in separation of a number of liquid mixtures was high [17]. For example, in separation of a methanol/cyclohexane azeotropic mixture, the separation factor for methanol was 164, at a permeate flow through the membrane of 2.3 kg m^{-2} h^{-1} [18]. The effect is determined by the difference in the molecular size of the substances being separated and in their affinity to the membrane material, by morphological features of the membrane, and by probable presence in the skin layer region of microvoids comparable in size with the gas molecules, decreasing the efficiency of the gas separation [4, 17].

A different pattern was observed in studies of composite diffusion membranes formed by application of nonporous layers of other polymeric materials onto surfaces of phase-inversion membranes of PAI-1 [18, 19]. Membranes of this type showed high separation characteristics different from those of diffusion layer polymers [17–19]. The most efficient model allowing description of the transport properties of composite PAI membranes taking into account characteristics of all the constituent polymers is the Henis–Tripodi resistance model [20]. More precisely, purposeful construction of a composite membrane was attempted on the basis of data on the transport properties of polymers and of layers with a complex morpholology, formed from these polymers. Thus, not only the chemical structure of a polyamido imide but also the morphology of a microporous membrane based on it, primarily in the skin layer region, was taken into account.

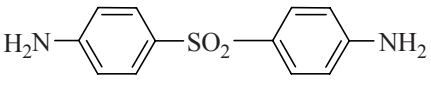
The goal of this study is preparation of polyamido imides from dicarboxyphenylphthalimide dichloride and diamines with diphenyl sulfone fragments and examination of physicochemical, in particular transport, properties of nonporous films and of microporous and composite membranes based on them. Passing from PAI-1 to polymers containing diphenyl sulfone fragments in the backbone will affect not only pervaporation (separation of liquids) but also service characteristics of the membranes. Our goal is closely associated with the problem of forming asymmetric and composite membranes of materials stable under the conditions of critical technologies, in particular, in organic solvents and in some cases at elevated temperatures.

EXPERIMENTAL

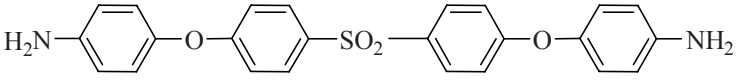
As materials for preparing asymmetric membranes we used aromatic polyamido imides synthesized by low-temperature polycondensation from dicarboxyphenylphthalimide dichloride and the following diamines:



PAI-1



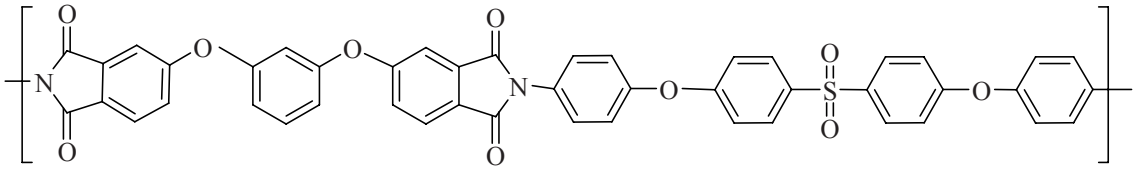
PAI-2



PAI-3

Polymers PAI-1–PAI-3 were synthesized in *N*-methyl-2-pyrrolidone (N-MP) by the procedure described in [21–23].

As material for forming nonporous diffusion layers, we used polyether imide (PI) of the following structure:



The reduced viscosity η_{red} was determined from the outflow time of N-MP and 0.5 wt % solutions of PAI-1–PAI-3 in N-MP by the formula

$$\text{Hred} = (t_s/t_{\text{N-MP}} - 1)/c,$$

where t_s is the solution outflow time; $t_{\text{N-MP}}$, N-MП outflow time; and c, solution concentration (g dl^{-1}).

Continuous nonporous polymer films were formed by casting onto glass surface 10 wt % solutions of PAI-1–PAI-3 in N-MP, which was followed by solvent removal by heating to 150°C.

Mechanical tests of nonporous films were performed with strips 40 μm thick and 15–20 mm long, with the working part width of 1 mm, on a UTS-10 universal installation (UTStestsysteme, Germany) in the uniaxial extension mode. Extension was performed at a constant rate of 10 mm min^{-1}. In the course of tests we measured the elastic modulus E, plastic limit σ_p, strength σ_t, and breaking elongation ε_b. The temperatures of glass transition and other transitions (T_1 etc.) were determined by the thermomechanical method with a UMMIV-3 device in the course of sample heating at a rate of 5 deg min^{-1}. The stretching load was 0.5 MPa.

The equilibrium swelling coefficients of polymer films α (%) in water, ethanol, and cyclohexane were measured at room temperature and calculated by the formula

$$\alpha = \frac{m_2 - m_1}{m_2} \times 100\%,$$

where m_1 and m_2 are the weights of the dry and equilibrium-swollen films, respectively (g).

Asymmetric membranes were prepared by wet forming in the system PAI–solvent (N-MP)–nonsolvent (water) under similar conditions of the phase-inversion process. Exposure in the bath lasted in each case until the moment of membrane detachment from the glass surface. The membrane detached from the glass plate was washed with water and dried in air at room temperature.

The membrane morphology was studied by scanning electron microscopy (SEM) on a JSM-35C device (JEOL, Japan). The surface of low-temperature brittle chips of membranes was coated with 20-nm-thick gold films by thermal vacuum sputtering.

Composite membranes were prepared by casting a solution of a coating polymer onto the working surface of the support under the conditions given in [15, 17].

The permeability of asymmetric membranes P (kg m^{-2} h^{-1}) to water, ethanol, and water–ethanol mixtures (48% ethanol) was measured at 20°C and pressure differential Δp on the membrane of 1, 2, or 3 atm on an ultrafiltration cell with a membrane area of 3.14×10^{-4} m^2. The permeability factor P (kg m^{-2} h^{-1} atm^{-1}) was calculated by the formula

$$P = m/St\Delta p,$$

where m is the weight of the substance that passed through the membrane (kg); S, area of the membrane sample (m^2); and t, outflow time (h).

Pervaporation characteristics of membranes were determined for a series of solvents and their mixtures (water, ethanol, cyclohexane) at 20°C on a pervaporation installation with a working area of the membrane of 7.1 cm^2. Knowing the working area of the membrane and the amount of the permeate that passed through the membrane, we estimated the permeate flow Π (kg m^{-2} h^{-1}).

The conditions for PAI synthesis were chosen so as to obtain polyamido amides meeting the following requirements: (1) molecular weights exceeding 50000 Da and physicomechanical characteristics allowing preparation of self-supporting nonporous films less than 20 μm thick and of asymmetric microporous films (phase-inversion membranes); (2) close viscosities of solutions of equal concentrations, so as to form membranes with similar morphology and structure.

Table 1. Physicomechanical properties of nonporous PAI films[a]

Sample no.	Polymer	η_{red}	E, GPa	σ_t, MPa	ε_t, %	T, °C
1	PAI-1	1.7	3.79	129	36	T_1=140; T_2=256
2	PAI-2	1.6	3.35	116	48	T_1=355
3	PAI-3	1.7	3.02	105	98	T_1=200; T_2=395

[a] (η_{red}) Reduced viscosity of 0.5 wt % solution of PAI in N-MP and (T) transition temperature according to thermomechanical analysis.

The characteristics of nonporous self-supporting films of PAI-1–PAI-3, 40-μm thick (sample nos. 1–3) are given in Table 1. In the thermomechanical curve of sample no. 2, a sharp transition to the ductility growth is observed at 355°C. Sample no. 3 is characterized by the presence of two regions of ductility growth at T_1 = 200 and T_2 = 395°C. Thus, PAIs containing diphenyl sulfone fragments are characterized by transitions at higher temperatures than PAI-1 (Table 1). PAI-1 and PAI-2 films failed in the course of neck propagation through the sample. In the coarse of extension of PAI-3 films, the neck propagated to the whole working length of the sample (up to 55–65% strain), with the subsequent transition to the region of deformation strengthening in which the force required for further extension of the sample noticeably increased. In going from PAI-1 to PAI-3, E and σ_t somewhat decreased.

Analysis of the physicomechanical characteristics of PAI-1–PAI-3 films led to a conclusion that these polymeric materials can be used for preparing by wet forming asymmetric microporous films as membranes suitable for use at elevated pressures and temperatures.

The reduced viscosities of 0.5% solutions of PAI-1–PAI-3 in N-MP are essentially equal, which allows solutions of these polymers of equal concentration to be used for preparing membranes of similar morphology.

Under equal conditions of the phase-inversion processes, we prepared asymmetric microporous membranes by wet forming from 10 wt % solutions of PAI in N-MP. Figure 1 shows electron micrographs of low-temperature chips of samples whose transport properties under the conditions of a baromembrane process are illustrated by Table 2. According to the SEM data, the membrane morphology is characterized by the finger-like structure of macropores cutting the whole cross section and narrowing toward the upper surface. The macropore walls have a network morphology with a pore size of 50–100 nm.

In going from PAI-1 to more hydrophilic (see equilibrium swelling coefficients in water, Table 2) polymers PAI-2 and PAI-3 containing SO_2 groups, the general morphology of the membranes remains essentially unchanged. Nevertheless, the asymmetric porous structure of PAI-2 membrane differs in the shape and size of coarse finger-like pores in internal layers. This membrane is distinguished by the presence of more round-shaped pores of smaller size, cutting the cross section, along with finger-like pores characteristic of PAI-1 and PAI-3. These differences in the morphology of coarse pores in the membranes can be attributed to the fact that for PAI-2 water is a milder precipitant than for PAI-1. Indeed, PAI-2 contains a hydrophilic SO_2 group in the molecular unit. However, PAI-3 also contains one SO_2 group per molecular unit, but no changes in the shape of coarse pores in internal layers of the membrane are observed. This apparent contradiction can be readily accounted for by the difference in the weights of molecular units of the

Table 2. Transport properties of PAI films at 3 atm. Time of keeping in water (ethanol) 15 h

Sample no.	Polymer	μ, rel. units	α, %		P (water), kg m^{-2} h^{-1} atm^{-1}		P (ethanol),[a] kg m^{-2} h^{-1} atm^{-1}	
			water	ethanol	membrane after drying	membrane after keeping in water	membrane after drying	membrane after keeping in ethanol
4	PAI-1	475	5.45	2.30	1.4	0.0	10.1	9.7
5	PAI-2	707	9.08	6.11	3.7	0.2	16.4	24.8
6	PAI-3	523	8.75	4.27	5.1	0.0	7.2	2.6

[a] 96 wt % aqueous ethanol.

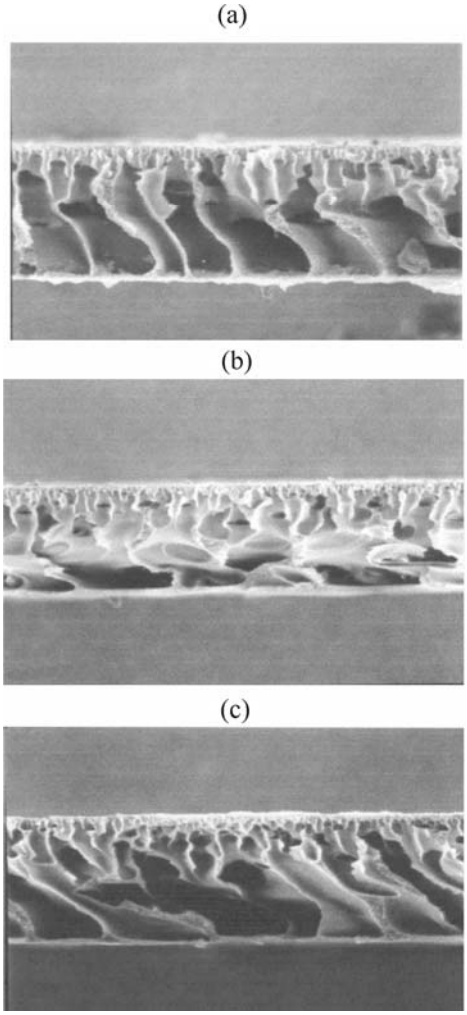


Fig. 1. SEM micrographs of low-temperature chips of membranes based on (a) PAI-1, (b) PAI-2, and (c) PAI-3.

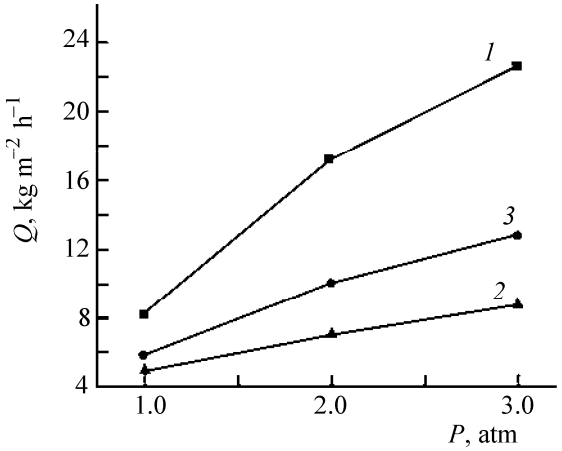


Fig. 2. Partial water flow Q in passing of 48 wt % aqueous ethanol through microporous PAI films as a function of pressure P: (*1*) PAI-1, (*2*) PAI-2, and (*3*) PAI-3.

polymers or, more precisely, in the gravimetric concentrations of sulfone groups. As the size and weight of the molecular unit in PAI-3 are considerably larger than in PAI-2 (see Experimental and Table 2) and the number of sulfone groups per molecular unit is the same, PAI-2 is a more hydrophilic polymer, and among the examined PAIs it shows the highest affinity for the precipitant (water).

The transport properties of asymmetric microporous membranes of the above-described morphology are given in Table 2. Table 2 demonstrates the effect of morphology and post-treatment on the transport properties of sample nos. 4–6, among which sample no. 6 prepared from the more hydrophilic PAI-2 exhibits particular properties. The morphological features of this membrane are reflected in relaxation of pores in its skin layer, leading to a decrease in their size on keeping in aqueous solution and to an increase, on keeping in 96 wt % ethanol.

Despite the "capability" of the examined membranes to change the morphology of fine pores on keeping in aqueous ethanol, which is reflected in their permeability to alcohol and water, their structures are stable at elevated pressures. Figure 2 shows the pressure dependences of the partial water flows in passing of 48% aqueous ethanol through asymmetric PAI membranes. As the pressure differential across the membrane is increased to 3 atm, the flows in all the cases monotonically increase and hence the pore structures of the membranes do not undergo significant deformations.

From the asymmetric membranes obtained, we prepared composite membranes with nonporous coating layers of an aromatic polyether imide, PI. The choice of the polymer for the coating layer was governed by its capability to transfer with high selectivity polar liquids such as water and aliphatic alcohols, with a low permeability to low-polarity components (methyl *tert*-butyl ether, cyclohexane) [18]. The polyether imide was preliminarily characterized under the conditions of a pervaporation experiment. The transport properties of its nonporous film toward water, ethanol, and cyclohexane are given in Table 3.

Table 3 shows that the permeability of PI is very low. This fact is well consistent with its high separation characteristics. Low permeability in combination with high selectivity in separation of liquids of different polarities is the main factor making

Table 3. Pervaporation properties of nonporous PAI films at 20°C

Sample no.	Polymer	l,[a] μm	$\Pi\times10^2$, kg m^{-2} h^{-1}		
			water	ethanol	cyclo-hexane
7	PAI-1	18	1.79	2.11	4.22
8	PAI-2	16	18.00	4.30	1.3
9	PAI-3	17	6.90	4.70	3.80
10	PI	18	0.59	0.63	0.06

[a] (l) Film thickness.

PI suitable as a coating polymer, i.e., for forming a thin nonporous layer of a composite membrane. In addition, the coating polymer was chosen as a compound similar in the chemical structure (presence of diphenyl sulfone fragments in the diamine moiety) to polyamido imides of porous asymmetric layers. The thermal and hydrolytic stability of this polymer [24] are also favorable factors. The solubility of PI in such low-boiling solvents as chloroform allows formation of thin defect-free coatings of this polymer on the surfaces of PAI porous layers for which chloroform is not a solvent. Thus, we prepared multilayer composite membranes in which all layers were formed from chemically and thermally stable aromatic polyimides containing diphenyl sulfone fragments.

The transport properties of the membranes were evaluated for ethanol–cyclohexane mixtures of various compositions. The goal of a pervaporation experiment was to reveal trends in separation of liquid mixtures on composite membranes of this type and to elucidate the role of microporous supports in the process. It is significant that all the membranes under consideration were formed in all the steps under equal conditions. The membranes have nonporous layers on the surfaces of skin layers of microporous PAI films, which are prepared by casting of PI from its 2 wt % solution in chloroform. Before applying the coating polymer, microporous PAI membranes were dried with tension under the conditions used previously [25] for preparing from PAI-1 structures in which the mean diameter of pores in skin layers was 5 nm. Despite the fact that the pore structure of asymmetric PAI-1–PAI-3 membranes can vary depending on the post-treatment procedure and time (Table 2), for all the three types of samples prepared under similar conditions the water and ethanol flows are of the same order of magnitude. Thus, under similar conditions of wet forming we prepared microporous membranes in which differences in the pore size in skin layers cannot lead to significant differences in the morphology on the PI/PAI phase boundary in composite membranes. Because for forming the nonporous coating layer we used a rigid-chain polymer with a high molecular weight and a high glass transition point, flowing of PI into pores of skin layers of asymmetric PAI membranes is impossible.

It was shown previously that PAI-1 and PI are highly selective in pervaporation separation of methanol–methyl *tert*-butyl ether and methanol–cyclohexane mixtures [17, 18, 26]. We expected that the PI/PAI-1 composite membrane should have similar characteristics. It was unclear how efficient this membrane would be in separation of a more difficultly separable ethanol–cyclohexane mixture and whether the separation efficiency can be affected by using membranes containing microporous layers of PAI-2 and PAI-3.

Figure 3 shows the dependences of the ethanol concentration in the permeate (Fig. 3b) and of the total flow through the membrane (Fig. 3a) on the mixture concentration in pervaporation of ethanol–cyclohexane mixtures at 20°C. Apparently, all the three types of membranes are efficient in separation of such mixtures with the aim to isolate the polar component. The PI/PAI-1 membrane is more permeable (up to 5.5 kg m^{-2} h^{-1}) and less selective (Fig. 3a) than the membranes based on PAI-2 and PAI-3. This fact contradicts the known assumption [27] that the permeability of composite membranes is determined by the morphology of the microporous support layer. If this were true, the highest flows would be expected with PAI-2. Surprisingly, the flows through PI/PAI-2 and PI/PAI-3 are approximately equal, whereas the separation properties of these membranes differ essentially. The best separation is ensured by the membrane based on the most hydrophilic polymer, PAI-2, having the highest swelling coefficient in ethanol in the series PAI-1, PAI-3, PAI-2 (Table 2). This result indicates that both polymers in each of the membranes play an active role in the pervaporation process of selective transport of substances being separated. Apparently, a joint diffusion layer of a complex morphology, favoring redistribution of flows of liquids being separated, is formed in the membrane in the place of contact of the two polymers (PAI in the skin layer with nanosized pores and PI in the coating nonporous layer).

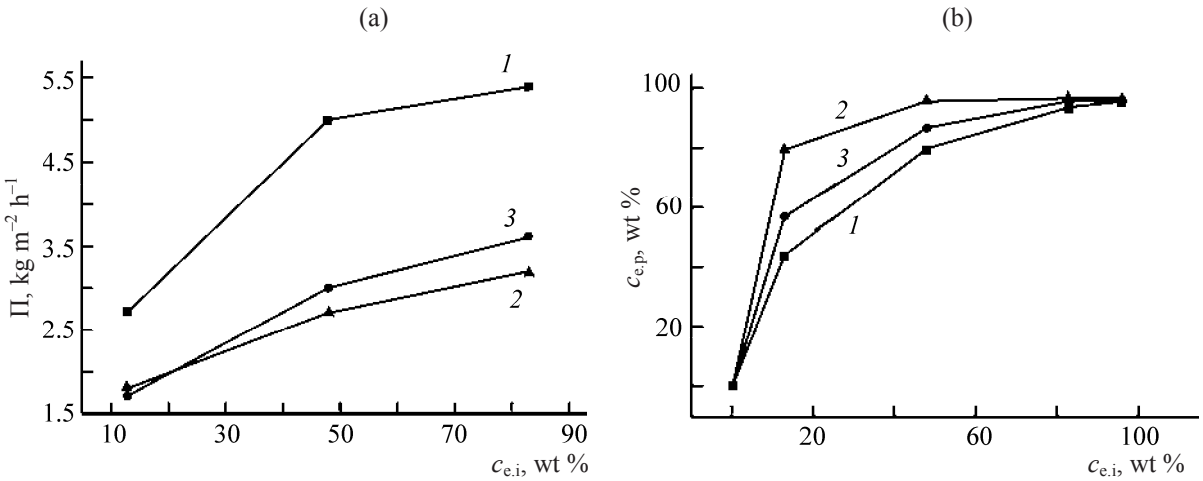


Fig. 3. (a) Total flow through the membrane Π and (b) ethanol concentration in the permeate $c_{e.p}$ as functions of the ethanol concentration $c_{e.i}$ in the initial mixture in pervaporation separation of ethanol–cyclohexane mixtures at 20°C.

CONCLUSIONS

(1) New membrane-forming polymers containing imide, sulfone, and amide groups in the backbone were studied. Asymmetric microporous and diffusion composite membranes based on these polymers were prepared.

(2) Multilayer composite membranes in which all the layers consist of chemically and thermally stable aromatic polyimides with diphenyl sulfone fragments in polymer chains were prepared.

(3) Analysis of the pervaporation properties of the composite membranes prepared showed that the membranes are highly efficient in isolation of alcohols from their mixtures with less polar organic liquids. The permeability of these membranes to ethanol exceeds 2.5 kg m^{-2} h^{-1}, which corresponds to the ethanol concentration in the permeate exceeding 95 wt %.

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REFERENCES

1. Clausi, D.T. and Koros, W.J., *J. Membrane Sci*., 2000, vol. 167, p. 79.
2. Kapantaidakis, G.C., Koops, G.H., and Wessling, M., *Desalination,* 2002, vol. 145, p. 353.
3. Koros, W.J. and Woods, D.G., *J. Membrane Sci*., 2001, vol. 181, p. 157.
4. Toshiki, A., *Prog. Polym. Sci*., 1999, vol. 24, p. 951.
5. Ohya, H., Kudryavtsev, V.V., and Semenova, S.I., *Polyimide Membranes—Application, Fabrication and Properties*, Tokyo: Gordon and Breach, 1996.
6. Ziegler, S., Theis, J., and Fritsch, D., *J. Membrane Sci*., 2001, vol. 187, nos. 1–2, p. 71.
7. Huang, S.-H., Hu, C.-C., Lee, K.-R., et al., *Eur. Polym. J*., 2006, vol. 42, no. 1, p. 140.
8. Fritsch, D. and Peinemann, K.-V., *J. Membrane Sci*., 1995, vol. 99, no. 1, p. 29.
9. Fritsch, D. and Avella, N., *Macromol. Chem. Phys*., 1996, vol. 197, no. 2, p. 701.
10. Hofman, D., Ulbrich, J., Fritsch, D., and Paul, D., *Polymer*, 1996, vol. 37, no. 21, p. 4773.
11. Mulder, M., *Basic Principles of Membrane Technology*, Dordrecht: Kluwer, 1991.
12. Laninovic, V., *Vysokomol. Soedin., Ser. A*, 2005, vol. 47, no. 7, p. 1196.
13. Kesting, R.E., *Synthetic Polymeric Membranes*, New York: Wiley, 1985.
14. Tröger, L., Hunnefeld, H., Nunes, S., et al., *Z. Phys. D: At., Mol. Clusters*, 1997, vol. 40, nos. 1–4, p. 81.
15. RF Patent 2211725.
16. Kononova, S.V., Kuznetsov, Yu.P., Romashkova, K.A., and Kudryavtsev, V.V., *Vysokomol. Soedin., Ser. A*, 2006, vol. 48, no. 9, p. 1647.
17. Kononova, S.V., *Multilayer Gas-Separation and Pervaporation Membranes Based on Aromatic Poly-amido Imides, Cand. Sci. Dissertation,* St. Petersburg, 2005.
18. Kuznetsov, Yu.P., Kononova, S.V., Kruchinina, E.V., et al., *Zh. Prikl. Khim*., 2001, vol. 74, no. 8, p. 1302.

19. Kononova, S.V., Kuznetsov, Yu.P., Sukhanova, T.E., et al., *Vysokomol. Soedin., Ser. A*, 1993, vol. 35, no. 2, p. 216.
20. Henis, J.M.S. and Tripodi, M.K., *J. Membrane Sci*., 1981, vol. 8, p. 233.
21. Gusinskaya, V.A., Koton, M.M., Batrakova, T.V., and Romashkova, K.A., *Vysokomol. Soedin., Ser. A,* 1976, vol. 18, no. 12, p. 2681.
22. Sidorovich, A.V., Svetlichnyi, V.M., Baklagina, Yu.G., et al., *Vysokomol. Soedin., Ser. A,* 1989, vol. 31, no. 12, p. 2597.
23. Gusinskaya, V.A., Churganova, S.S., Koton, M.M., et al., *Zh. Prikl. Khim*., 1984, vol. 57, no. 8, p. 1819.
24. Bessonov, M.I., Koton, M.M., Kudryavtsev, V.V., and Laius, L.A., *Poliimidy – klass termostoikikh polimerov* (Polyimides: A Class of Heat-Resistant Polymers), Leningrad: Nauka, 1983.
25. Kononova, S.V., Kuznetsov, Yu.P., Shchukarev, A.V., et al., *Zh. Prikl. Khim*., 2003, vol. 76, no. 5, p. 820.
26. RF Patent 2126291.