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Polyimide Ultrafiltration Membranes with High Thermal Stability and Chemical Durability

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Abstract: Asymmetric ultrafiltration membranes based on poly[(4,4′-oxydiphenylene)pyromelliteimide] were produced by wet technique from prepolymer casting solution, followed by solid-phase conversion of the prepolymer membranes into polyimide insoluble form at 200°C. It was demonstrated that by adding benzimidazole to the casting solution and filling of prepolymer membrane pores with inert high-boiling oil prior to thermal treatment allow us to prepare asymmetric porous polyimide membranes. The main characteristics of the membranes obtained (permeability coefficients and molecular weight cut-off) match those typical to ultrafiltration membranes. It was found that the developed asymmetric ultrafiltration polyimide membranes have excellent thermal and chemical resistance. The membranes retain rigidity above Tg (360°C) and are chemically stable at temperatures up to 400°C. The developed membranes are resistant against swelling and dissolving in aggressive and organic media including amide solvents.

Keywords: Chemical durability, membrane, poly[(4,4′-oxydiphenylene) pyromelliteimide], thermal stability, ultrafiltration

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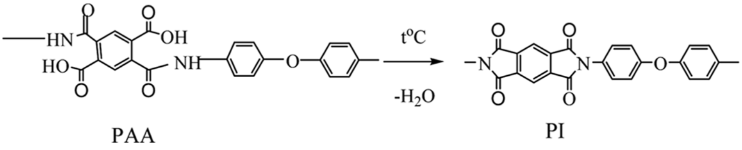
INTRODUCTION

Polymer membranes for modern applications in electronic, biological, and chemical industries have to exhibit not only high permeability, selectivity, and mechanical properties but also thermal stability and chemical durability. The development of such membranes requires proper selection of polymer materials and technique of membrane preparation. Thermal and chemical stabilities of a polymer are interrelated characteristics. Many factors contributing to increase of glass transition temperature, melting point, and the crystallinity degree of a polymer lead also to the rise of the chemical stability of the polymer. Thermal and chemical stabilities of membranes involve thermal resistance, hydrolytic stability in a wide pH range, resistance to solvents, and to chlorination. However, as a rule, the higher the thermal and chemical stabilities of a polymer, the lower its processability.

Aromatic polyimides exhibit exclusive thermal and chemical stabilities, high strength and deformability of films, excellent transport properties that makes polyimides the promising materials for membranes of different applications (1,2). At present, asymmetric membranes for ultrafiltration and gas separation based on soluble polyimides (Matrimid 5218, Lenzing P84, etc) are known (3–5). They are durable at the temperature up to 260°C and are resistant to many solvents. Unfortunately, these membranes undergo destruction in chlorohydrocarbons and amide solvents. More recently soluble polyimides such as Lenzing P84 have been used as the basis for crosslinked materials that are stable in various amide solvents and dimethylsulfoxide (6,7). However, this durability against amide solvents is achieved at the cost of thermal stability while already at 150°C the materials lose crosslinking and undergo partial destruction of imide cycles (6).

More thermally and chemically stable polyimide filtration membranes can be developed on the base of insoluble and infusible polyimides that are resistant to all organic solvents including amide solvents (8–10). The most studied, inexpensive, and commercially available among infusible polyimides is poly[(4,4′-oxydiphenylene)pyromelliteimide] (PI) prepared from pyromellitic dianhydride and 4,4′-oxydianiline. Membranes based on this PI can be molded only from its soluble prepolymer – polyamic acid (PAA), and after that the membrane must be heated for solid phase conversion of PAA into insoluble PI by imidization.



To realize the imidization, harsh conditions are needed. As a rule, it is high temperature up to 300–400°C which is achieved by stepwise heating. However, when using high temperature treatment it is difficult to retain the porous structure of membranes obtained at the previous stage. This is probably the main hindrance for the development of PI ultrafiltration (UF) membranes based on insoluble and infusible polyimides. Apparently, this is also the reason for the absence of these thermally and chemically stable polyimide UF membranes at the world market.

It is known that the addition of heterocyclic azoles (imidazole, benzimidazole) to PAA casting solution allows for lowering the imidization temperature from 300–400°C down to 150–200°C (11,12). This approach proved to be successful for the preparation of thin gas separating rigid-chain polyimide layer in composite membranes with poly(phenylene oxide) support in (13–15). Imidazole and its derivatives were also used for the preparation of nanofiltration polyimide membranes (16,17). Use of benzimidazole for obtaining porous UF membranes of poly[(4,4′-oxydiphenylene)pyromelliteimide] was briefly described in our recent work (18). Benzimidazole plays a dualistic role: it

(i) ensures formation of porous structure during wet casting stage, and
(ii) by lowering the cyclization temperature allows for retaining of this structure on the imidization stage.

In this work we demonstrate that a combination of benzimidazole and inert high-boiling polymethylsiloxane oil as pore-filling agent is beneficial for obtaining and retaining of porous structure. Special attention is paid to thermal and chemical stability of ultrafiltration poly[(4,4′-oxydiphenylene)pyromelliteimide] membranes obtained by this method.

EXPERIMENTAL

Materials

N,N′-dimethylformamide (DMF), benzimidazole (BI), glycerol purchased from Aldrich and polymethylsiloxane oil (PMS) purchased from Vekton Co (Russia) were used as received. The poly[(4,4′-oxydiphenylene)pyromelliteamic acid) (PAA) was purchased from Estrokom Co. (Russia) in the form of 16–18% solution in DMF. The intrinsic viscosity of initial PAA was 1.5–1.7 dl/g (DMF, 20°C).

Membrane Preparation

Casting PAA solution in DMF, containing BI and glycerol was used for membrane formation as in (18,19). The polymer concentration in casting solution was 11–14 wt%. The content of BI in casting solution was two moles of BI per one mole-unit of PAA, to comply with the stoichiometric ratio of BI molecules to amic acid groups of PAA.

To prepared membranes, the polymer solution was poured onto a glass plate. Then the plate was immersed into a precipitation bath with ethanol/water mixture containing 40 wt% ethanol, at room temperature. The obtained membranes were impregnated by inert high-boiling PMS oil and then heated up to 200°C for conversion of PAA into insoluble PI membranes. The degree of the conversion was controlled by IR spectroscopy using films with the thickness of 5 μm. «Vertex-70» (Bruker) was used to record the spectra. These films were obtained by evaporation of the same casting solutions on the glass plate and by heating at the same regime as porous membranes.

Characterization

The membrane morphology was studied using scanning electron microscope JSM-35 (Jeol, Japan). Liophilically dried samples were chipped in liquid nitrogen, cathodically covered with gold, and then were scanned with the microscope.

Ultrafiltration experiments were carried out in a dead-end stirred cell type FM-01, the membrane diameter was 25 mm, the initial filtration volume was 10 ml, the transmembrane pressure was 0.1 MPa. Membrane retention curves, characterizing separation efficiency, were determined by the calibration method with the use of model mixtures of proteins of different molecular weights according to the technique described elsewhere (16,17). The model mixtures used for analysis of UF membranes consisted of vitamin B12 (M $1.34 \cdot 10^3$ g/mol), and the following proteins: cytochrome C (M $12.50 \cdot 10^3$ g/mol), chymotrypsinogen (M $24.00 \cdot 10^3$ g/mol), ovalbumin (M $44.50 \cdot 10^3$ g/mol), bovine serum albumin (M $67.00 \cdot 10^3$ g/mol), γ-globulin (M $160.00 \cdot 10^3$ g/mol), M stands for the molecular weight. The retention coefficient (R) was found by the equation:

$$R = 1 - C_p/C_c,$$

where C_p is the protein concentration in penetrate and C_c is the protein concentration in the feed, accordingly (22).

Thermogravimetric analysis (TGA) was performed in the self-generating atmosphere at a heating rate 5°/min using the laboratory-made thermobalance.

The mechanical tests were carried out in the uniaxial stretching mode using the universal mechanical test system UTS 10 (Germany). The stripe-like specimens of the dimensions $2 \times 20\,\text{mm}$ were cut off by the surgical knife.

The glass transition temperatures (T_g) of membranes were determined by the thermo-mechanical method at the UMIV-3 (Russia) test system. At these tests the strip-like film specimens ($15 \times 2\,\text{mm}$) were heated at the speed of 5 deg/min under the action of constant loading of 0.5 MPa.

RESULTS AND DISCUSSION

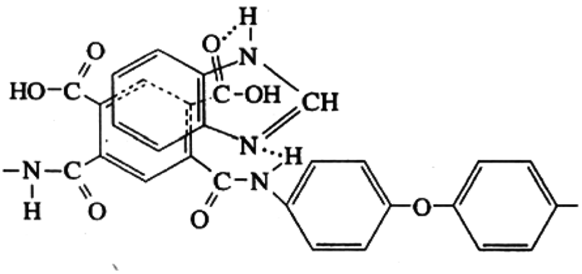
Membrane Formation

Target UF PI membranes were obtained in accordance with a two-stage procedure described elsewhere (18,19). The first stage was aimed at the wet formation of asymmetric prepolymer membranes. The conditions of this stage were optimized by variation of the chemical composition of the casting solution and of the precipitation bath. The solid phase conversion of PAA into insoluble PI membranes was performed at the second (imidization) stage by thermal treatment. Considerable decrease of the imidization temperature from 350° to 200°C was attained by use of the catalyst benzimidazole (BI) that was added in the casting solution.

The BI catalytic role is in the acceleration of the cyclization process which, in turn, allows for decreasing the maximum temperature and the temperature range of the dehydration. BI forms a complex with PAA as had been proved by mass-spectrometry thermal analysis and X-rays analysis in (11,12). BI partly displaces the solvated solvent (DMF) and prevents the interchain donor-acceptor interaction of macromolecules. The binding of BI to PAA takes place at three sites in PAA unit:

(i) carboxylic group,
(ii) carboxiamide group, and
(iii) benzene ring.

It was shown (11) that the second BI molecule per one mole-unit of PAA is required for ended complexation, via analogous bonds on the reverse side of the benzene ring.



During the preparation of asymmetric PI membranes, BI exerts significant influence not only on the temperature conditions of the second stage, but also on the process of wet formation of PAA membranes at the first stage. Table 1 lists the results of studying the effect of the casting solution composition on water permeability through PAA and PI membranes, characterized by k_0 that is the permeability coefficient of water.

Table 1 shows that a membrane produced from PAA casting solution exhibits quite low permeability $<0.1 \cdot 10^{-6}\,\mathrm{m/s \cdot bar}$ that is in 2–3 orders of magnitude lower than the typical values of permeability coefficients of ultrafiltration membranes. According to SEM analysis, the membrane has a sponge-like isotropic structure with a dense top layer. The reason for such structure formation is the hydrophilicity of PAA leading to soft conditions of polymer precipitation. Being a soft precipitator the aqueous solution of ethanol suppresses the formation of a highly permeable asymmetric structure with a thin selective layer.

It was found that BI additives in casting solution decrease the hydrophilicity of PAA by blocking its carboxylic groups as a result of complexation of BI with PAA molecules (18). In this way, conditions of polymer precipitation became more rigid facilitating the formation of an asymmetric porous structure.

Table 1. The effect of the casting solution composition on the membrane permeability

Sample no.	Casting solution composition (in DMF)	$k_0 \cdot 10^6$, m/s · bar PAA membrane	$k_0 \cdot 10^6$, m/s · bar PI membrane
0	12% PAA	<0.1	–
1	12% PAA:BI	154	120
2	14% PAA:BI	80	3.7
3	14% PAA:BI + 20% glycerol[a]	220	12

[a] The glycerol content is expressed as wt% vs. PAA.

Additional increase of membrane permeability was achieved by use of various pore forming agents—tetrahydrofuran, lithium chloride, citric acid, valeric acid, and glycerol. The best results were obtained with glycerol that exhibits good compatibility with BI.

The second important stage is solid-phase conversion of membrane polymer from PAA to PI. The conversion occurs by heating up to 200°C due to the presence of BI in membrane. According to IR spectra, full conversion of PAA to PI was achieved (Fig. 1). The presence of typical PI bands at 1780, 1720, 1380, and 720 cm^{-1} and the absence of typical PAA bands (1) confirm this fact. Thus, BI facilitates the formation of an asymmetric structure of the PAA membrane and, furthermore, BI acts as an imidization catalyst that allows for decreasing the temperature of the process.

It should be noted that during drying and thermal imidization of the PAA membranes the pores may collapse with partial (or complete) loss of porous structure obtained at the stage of wet formation. It is known (1) that a high temperature of imidization, besides the chemical process of cyclodehydration, promotes processes of ordering of macromolecular packing. The latter process may significantly alter the morphology and the productivity of the membranes. To retain the porous structure, the PAA membrane pores were filled with inert high-boiling oil PMS (19) prior to thermal treatment.

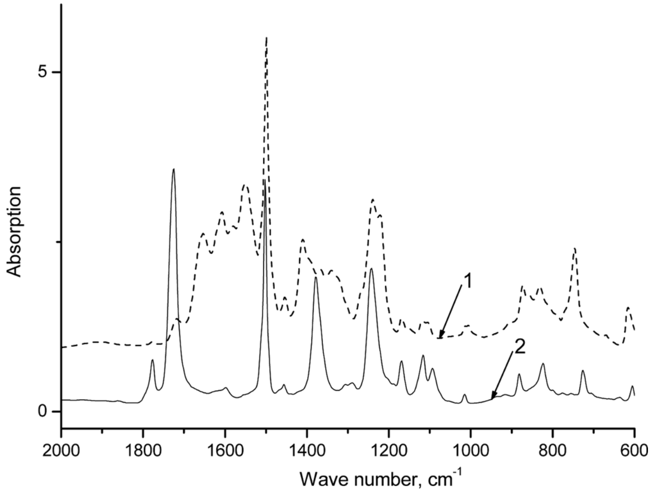


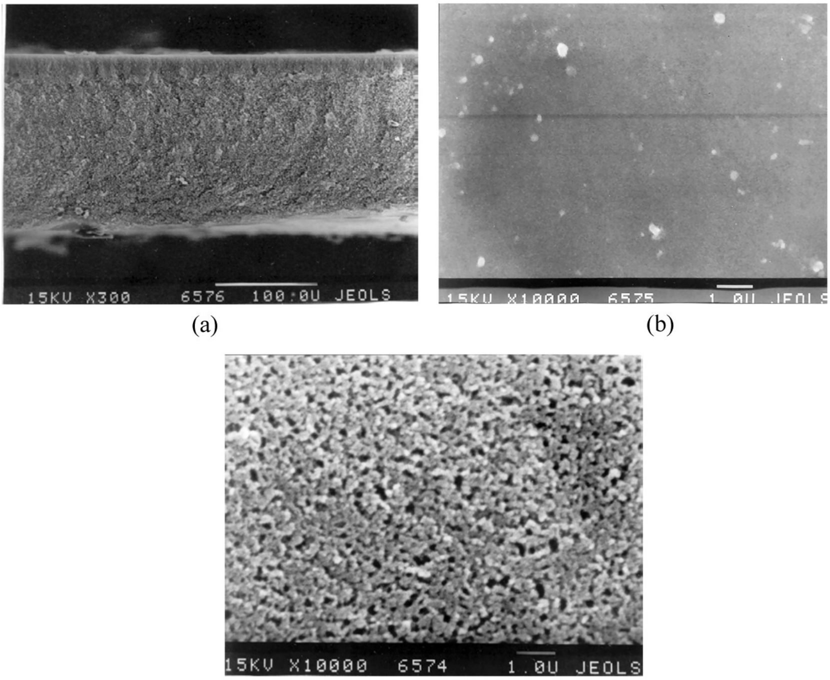
Figure 1. FTIR spectra of the polymer film before (1) and after (2) the thermal imidization.

The above method was used for the preparation of the UF PI membranes. The pore size was tuned by varying the concentration of casting solutions.

Membrane Characterization

The membrane morphology was studied by SEM. Figure 2 demonstrates typical micrographs of the cross section, the top, and the bottom surfaces of the PI membrane. The membrane exhibits an anisotropic structure consisting of a thin selective layer on top and a thick microporous substrate; the size of the substrate pores is 0.2–0.4 μm.

The mechanical tests showed that the PI membranes are strong and elastic. For example, the sample (Table 1, No. 3) demonstrated the Young's modulus value as high as 1.25 ± 0.07 GPa, the ultimate strength



(a) (b)

(c)

Figure 2. Micrographs of (a) the cross section, (b) top, and (c) bottom surfaces of PI membrane (Table 1, No. 3).

51 ± 3 MPa, and the ultimate deformation 40 ± 4%. The other membranes studied in our work exhibit high enough mechanical properties too.

The calibration of membranes was made by using a model mixture of proteins with different molecular weights in filtration tests. The dependence of the protein retention on their molecular weight (Fig. 3) allows for determining the molecular weight cut-off (M_L) of the membrane. The value of M_L is equal to the molecular weight of a protein rejected by the membrane for not less than 90%. It was found that PI membranes with the permeability coefficients in the range $(10 \div 200) \cdot 10^{-6}$ m/s bar are characterized by M_L in the range $(10\text{–}100) \cdot 10^3$ g/mol, being therefore typical ultrafiltration membranes.

To estimate the competitiveness of the obtained membranes, their flux and retention characteristics were plotted on a classification diagram containing the same data of various commercially available ultrafiltration membranes (Fig. 4) described in (20). Our PI membranes labeled with stars are located in the top part of the diagram, suggesting rather well their production parameters in comparison with known membranes. The AB axis characterizes l_s/f_o the reduced thickness of the selective layer, where l_s is the thickness and f_o is the porosity of the selective layer. For the obtained PI membranes the reduced thickness equals to 10–30 μm, being consistent with the selective layer thickness of ~1 μm.

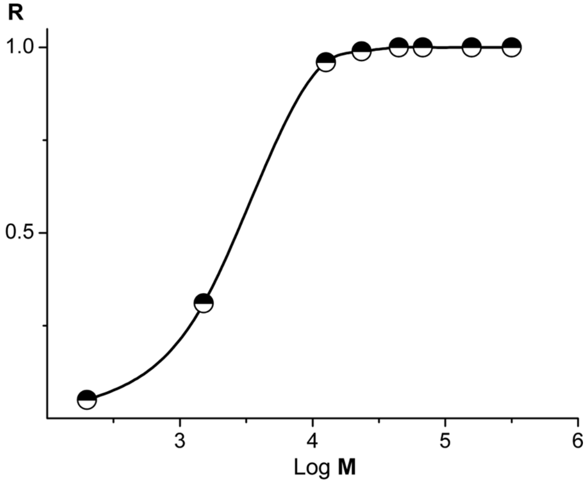


Figure 3. Dependence of proteins retention on their molecular weight for PI membrane (Table 1, No. 3). R is retention coefficient, M is molecular weight of the protein.

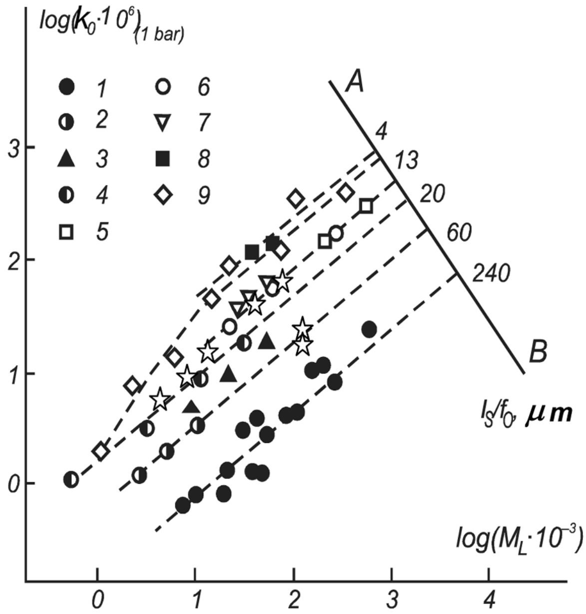


Figure 4. Classification diagram of ultrafiltration membranes by the reduced thickness of the selective layer: 1 – Sartorius SM 115–117, and Vladipore UAM, 2 – Biopore A2–10, 3 – DDS-5,600, –800, 4 –Diaflo UM, 5 – Biopore A-20-500, 6 – Diaflo XM, 7 – Dorr-Oliver XP, 8 – Diaflo PM, 9 – Gelman Omega. Stars are data on PI membranes.

Thermal Stability

The ability of any material to stable work at high temperatures is determined by two factors. Thermally stimulated chemical reactions, on the one hand, lead to thermal decomposition of the material. On the other hand, phase transitions, namely, glass transition and the melting process lead to the failure of the mechanical stiffness of the material. For semi-flexible PI films such as those studied in this work, the well-defined glass transition takes place at temperature as high as ~360°C (1) which is about 100°C less than the temperature of the thermal destruction onset.

To clarify the situation with the thermal stability of the PI membranes, both the glass transition temperature (T_g) and thermal destruction characteristics (TGA curves and thermal stability indices) were obtained. Figure 5 shows TGA curves of three PI membranes prepared under different conditions (Table 1, No. 1–3). The curves demonstrate two different groups of thermally stimulated processes which take place in the membranes studied. Moderated weight losses in

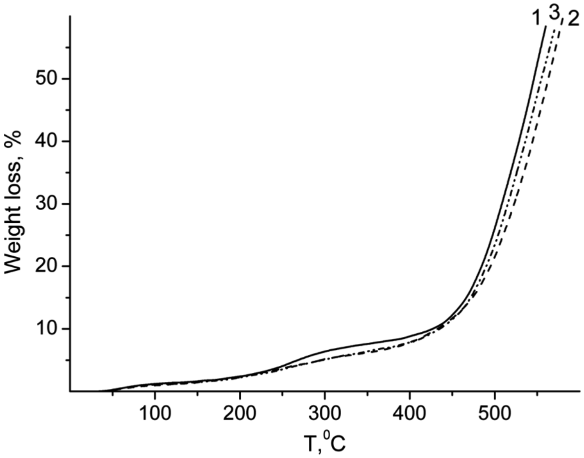


Figure 5. TGA curves for PI membranes prepared as No. 1, 2, and 3 in Table 1.

the temperature range 200–300°C originate in the removal from the membrane of residual low molecular weight components (predominantly the residual solvent). Thermal destruction of polymer takes place at the temperature above 400°C.

As far as we can see in Fig. 5 the TGA curves obtained for different membranes are very similar. This suggests similarity of the membranes structure and a high degree of PAA conversion into thermally stable PI form accomplished under the curing conditions used in this work.

The TGA data were used to calculate the indices of the thermal stability; τ_1, τ_5, and τ_{10} are the temperature values at which polymer sample losses 1, 5, and 10 wt% of its initial weight under the thermal destruction processes. Table 2 shows that PI membranes prepared as No. 1, 2, and 3 in Table 1 exhibit similar indices of thermal stability.

It should be noted that the thermal stability of ultrafiltration membranes under study is slightly lower than that of PI dense films. This

Table 2. Indices of the thermal stability of PI membranes prepared as No. 1, 2, and 3 in Table 1 and that of PI dense film

Sample no.	τ_1, °C	τ_5, °C	τ_{10}, °C
1	413	456	477
2	403	450	481
3	404	452	478
PI film	448	517	536

difference may be ascribed to the developed porous structure of the membranes. The intensity of weight losses under heating of the polymer sample is determined both by the speed of the appropriate chemical reactions and by the physical process of diffusion of volatile products of these reaction through the sample to its surface. Naturally in the case of the thermal destruction of the porous membrane the second stage of the weight losses process can be practically neglected and the intensity of the weight losses is determined only by the speed of the first chemical stage of this process.

At the same time, the results obtained suggest that the PI membranes are thermally stable at temperatures up to 400°C.

The unusual results were obtained at the thermo-mechanical tests of the membranes Fig. 6. The T_g values of the membrane tested was found to be practically equal to that of the PI dense film (~365°C). But the extent of the rise of polymer chains mobility above the glass transition, observed in these membrane structures, is substantially less than that in the PI dense film. Really, the slopes of the thermo-mechanical curves of membranes at temperatures above T_g are 4 to 5 times less than that of the thermo-mechanical curve of dense film.

This means that heating of the PI membrane above T_g does not lead to a dramatic fall of their stiffness and, in principal, does not mean the loss of the material capacity for work. So, for these materials the real temperature range, in which they can be practically used, is limited not by the glass transition process but by the chemical reactions of the thermal destruction.

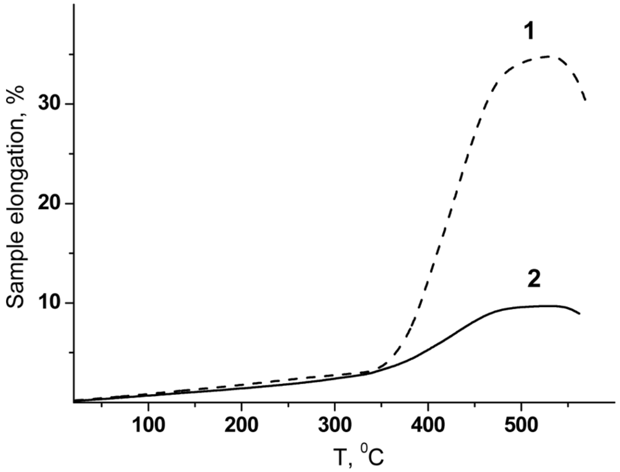


Figure 6. Thermo-mechanical curves of (1) PI dense film and (2) PI membrane.

Chemical Durability

Chemical stability or resistance of polymers is not a well-defined property because it strongly depends on the exploitation conditions, under which the polymers can alter their physico-chemical properties. McCarthy used a quite general definition: "The chemical resistance of a polymeric material is its ability to withstand chemical attack with minimal change in appearance, dimensions, mechanical properties, and weight over a period of time" (23).

Currently, standard tests of determining polymer chemical resistance are lacking; this fact can be explained by a large variety of polymer properties. To determine the chemical resistance of membranes prepared from commercially available polymers, their resistance against solving and swelling in different media is usually estimated. Table 3 lists literature data for membranes made of polysulfone, polyacrylonitrile, soluble polyimide (24–27), and the results obtained for PI membranes under study.

Table 3 shows that in terms of chemical stability the PI membranes obtained in the present work are superior to the main types of polymer membranes currently used. The resistance of PI membranes against solving and swelling in amide solvents should be especially noted. As can be seen from Table 3, none of the known ultrafiltration polymer membranes show such stability. It was found that diluted inorganic acids like hydrochloric and nitric acid have no effect upon the PI membranes,

Table 3. Polymer membrane stability in solvents of different types

Solvents	Polysulfone	Polyethersulfone	Polyacrylonitrile	Polyimide soluble	PI (present work)
Alcohols	+	+	+/−	+	+
Aliphatic hydrocarbons	+	+	+	+	+
Aromatic hydrocarbons	−	+	+	−	+
Ethers	−	−	+	−	+
Esters	−	−	+	+	+
Ketenes	−	−	+	+	+
Aliphatic acids	+	+	+	−	+
Amide solvents	−	−	−	−	+
Halogenated hydrocarbons	−	−	+	−	+

Sign (+) labels stable polymers (no visible solving and swelling), while (−) labels unstable polymers.

and besides, they dissolve in concentrated fuming acids. PI membranes like homogeneous films are relatively low-resistant in alkaline media. When immersed into 1–2 M aqueous KOH at room temperature, membranes became colorless in 1 hour, and destruct after 5 hours.

The rigidity of the porous structure of the membranes and their resistance to different solvents were estimated by the filtration of various solvents through the membranes. The viscosities (η, $10^3\,\mathrm{Pa \cdot s}$) of the liquids used in this experiment were follows: hexane (0.30), water (1.0), ethanol (1.13), and *iso*-propanol (2.43). Therefore the flux through membrane for these liquids was also different, in accordance with the Hagen-Poiseuille equation (28). It was found that the permeability coefficient was inversely proportional to the liquid viscosity; pointing at negligible swelling of our membranes in these liquids. Membrane stability in various liquids was estimated by the values of the permeability coefficient normalized to the water viscosity (k_{nor}) that was calculated by equation:

$$k_{nor} = k\eta/\eta_0$$

where k is the permeability coefficient of the liquid with the viscosity η, and η_0 is the water viscosity.

The dependence of the permeability coefficient and the permeability coefficient normalized to the water viscosity on the liquid viscosity is shown in Fig. 7 for PI membrane prepared as (Table 1, No. 3). Although the permeability coefficient decreases with the viscosity of the liquid, the normalized permeability coefficient is virtually independent on the viscosity, i.e., on the nature of the liquid.

A similar pattern of the dependence of the permeability coefficient on viscosity, as well as the independence of the respective normalized value was obtained for all the membranes studied according to this scheme (Table 4). The values of the normalized permeability coefficient of hexane, water, ethanol, and *iso*-propanol are comparable with each other. This fact quantitatively confirms that PI membranes do not swell in these liquids and the porous structure remains unchanged.

PI membranes are meant for use in aggressive chemical media at elevated temperatures. Therefore, joint action of these two factors on the properties of the membranes obtained was studied. The influence of thermal treatment in various chemical media on the stability of PI membranes is shown in Fig. 8. Heating in aggressive medium (acetic acid at 100°C) did not affect the membrane permeability significantly. Membranes heated in "neutral" organic solvents such as *n*-butanol and heptane near their boiling point held their appearance and permeability virtually unchanged. Membranes heated at 100°C in DMF also hold their

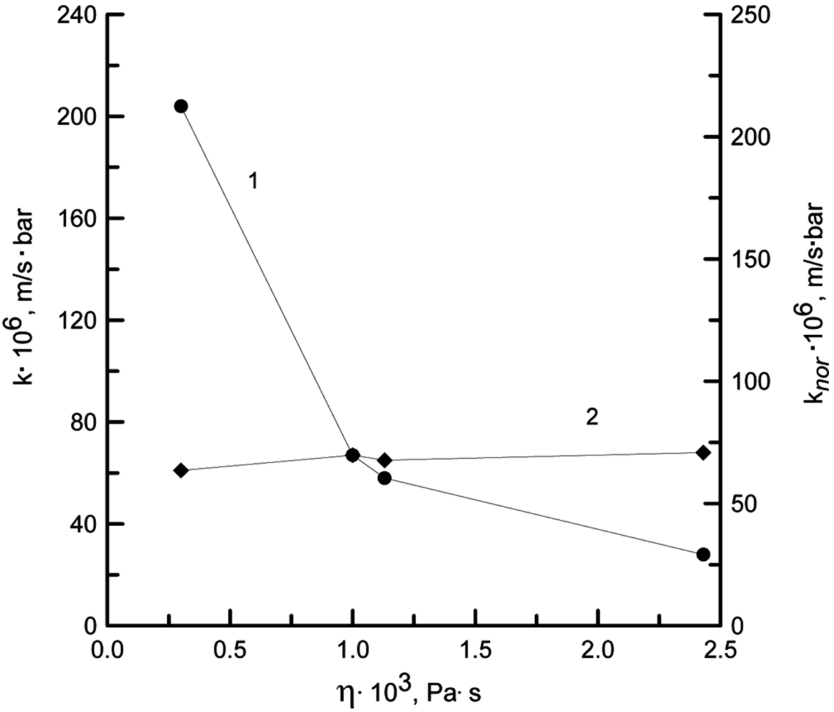


Figure 7. Dependence of (1) the permeability coefficient (k) and (2) the normalized permeability coefficient (k_{nor}) on the liquid viscosity for PI membrane.

appearance although their permeability slightly decreased. Tests in PMS oil allowed heating at higher temperature 250°C, leading to the permeability decrease on ~20%.

Table 4. Permeability coefficients and normalized permeability coefficients for PI membranes prepared from casting solutions with different PAA concentration (C_{PAA})

	$k \cdot 10^6$, m/s · bar				$k_{nor} \cdot 10^6$, m/s · bar			
C_{PAA}, wt%	Hexane	Water	Ethanol	*i*-PrOH	Hexane	Water	Ethanol	*i*-PrOH
11*	1800	528	465	225	540	528	525	547
12*	689	217	204	92	206	217	230	223
12	204	67	58	28	61	67	65	68
14	99	32	28	13	30	32	31	32

*Casting solution contains 20 wt% of glycerol.

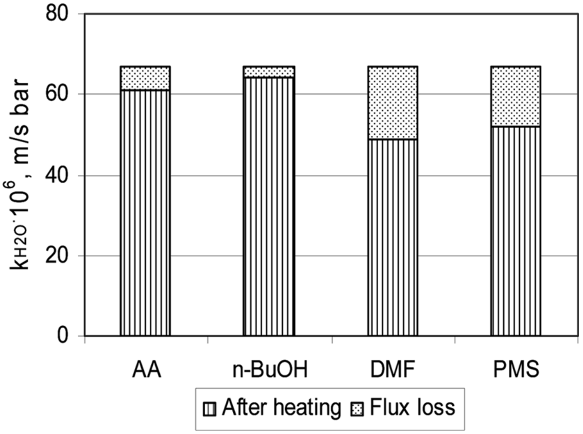


Figure 8. The effect of thermal treatment on the permeability coefficient of water (k_{H_2O}) for PI membranes. Heating at 100°C for 2 hours in: acetic acid (AA), *n*-butanol (*n*-BuOH), DMF. Heating at 250°C for 2 hours in PMS oil. Initial k_{H_2O} was $67 \cdot 10^{-6}\,\mathrm{m/s \cdot bar}$.

The results of the research demonstrate a sufficiently high level of thermal and chemical resistance of the developed PI membranes. These membranes can be used at temperature up to 400°C in a wide variety of solvents. The fields of their application may be high temperature filtration (purification of lubricating viscous oils, aggressive liquids, lignin, etc.), separation, purification, and concentration of polymeric solutions in organic synthesis, in an aggressive chemical environment, and also in high temperature membrane reactors (high temperature catalysis, reaction in gaseous phase such as methane reforming, one-stage production of oxygen). The membranes obtained may be used as a support for new composite membranes prepared by the casting of a second polymer layer from a solution in an aggressive solvent.

CONCLUSIONS

1. A two-stage method of asymmetric ultrafiltration PI membranes preparation was developed, which includes wet formation from prepolymer casting solution at the first stage and solid-phase conversion of the prepolymer PAA membrane in PI insoluble form at the second stage.
2. BI, that forms complexes with PAA, when added to casting solution leads to decrease of PAA hydrophilicity and facilitates the formation of the asymmetric structure of the membrane at the stage of wet

precipitation. Furthermore, BI acts as imidization catalyst, and this allows for decreasing the temperature of the process down to 200°C.

3. Membrane calibration using a model mixture of proteins shows that PI membranes with the permeability coefficients in the range $(10 \div 200) \cdot 10^{-6}\,\mathrm{m/s}$ bar are characterized by M_L in the range $(10\text{–}100) \cdot 10^3\,\mathrm{g/mol}$.
4. It was found that PI ultrafiltration membranes retain thermal stability at temperatures up to 400°C. This is comparable with the thermal stability of homogeneous PI films.
5. The developed PI ultrafiltration membranes are resistant to swelling and dissolving in aggressive and organic media including amide solvents. Thermal treatment in various chemical media has only an insignificant effect on the permeability of PI membranes.

REFERENCES

1. Bessonov, M.I.; Koton, M.M.; Kudryavtsev, V.V.; Laius, L.A. (1987) *Polyimides: Thermally Stable Polymers*; Plenum Press: New York.
2. Ohya, H.; Kudryavtsev, V.V.; Semenova, S.I. (1996) *Polyimide Membranes*; Gordon and Breach Publishers: Tokyo, Japan.
3. Anderson, B.P. (1990) Ultrafiltration Polyimide Membrane and its Use for Recovery of Dewaxing Aid. U.S. Patent 4,963,303, October 12, 1990.
4. White, L.S. (2002) Transport properties of a polyimide solvent resistant nanofiltration membrane. *J. Membrane Sci.*, *205*: 191.
5. Shishatskiy, S.; Nistor, C.; Popa, M.; Nunes, S.P.; Peinemann, K.-V. (2006) Comparison of asymmetric and thin-film composite membranes having Matrimid 5218 selective layer. *Desalination*, *199*: 193.
6. See-Toh, Y.H.; Lim, F.M.; Livingston, A.G. (2007) Polymeric membranes for nanofiltration in polar aprotic solvents. *J. Membrane Sci.*, *301*: 3.
7. See-Toh, Y.H.; Silva, M.; Livingston, A.G. (2008) Controlling molecular weight cut-off curves for highly solvent stable organic solvent nanofiltration (OSN) membrane. *J. Membrane Sci.*, *324*: 220.
8. Makino, H.; Kusuki, Y.; Yoshida, H.; Nakamura, A. (1983) Process for preparing aromatic polyimide semipermeable membranes. U.S. Patent 4,378,324, March 29, 1983.
9. Semenova, S.I.; Ohya, H.; Higashijima, T.; Negishi, Y. (1992) Effect of viscosity of coagulant on asymmetric polyimide (PMDA-4,4′-ODA) membrane preparation. *Membrane*, *17* (3): 193.
10. Ohya, H.; Okazaki, I.; Aihara, M.; Tanisho, S.; Negishi, Y. (1997) Study on molecular cut-off performance of asymmetric aromatic polyimide membrane. *J. Membrane Sci.*, *123*: 143.
11. Sazanov, Yu.N.; Stepanov, N.G.; Shibaev, L.A. (1988) Influence of organic compounds on cyclization, degradation and carbonization process of poly (pyromellitimides). *Acta Polymerica*, *39* (7): 422.

12. Shibaev, L.A.; Sazanov, Yu.N.; Stepanov, N.G. (1988) Nonisothermal kinetics of solid-phase cyclodehydratation of polyamic acids. *Polymer Sci.* (*Russia*), *30* (ser. A): 934.
13. Polotskaya, G.A.; Kostereva, T.A.; Elyashevich, G.K. (1998) Gas transport properties and structural order of poly(4,4′-oxydiphenylene pyromelliteimide) in composite membranes. *Separation & Purification Technology*, *14*: 13.
14. Polotskaya, G.A.; Sklizkova, V.P.; Kozhurnikova, N.D.; Elyashevich, G.K.; Kudryavtsev, V.V. (2000) Formation and analysis of polyimide layer in composite membranes. *J. Appl. Polymer Sci.*, *75*: 1026.
15. Marek, M.; Houska, M.; Schauer, J.; Hynek, V.; Sipek, M. (1996) Ultra-thin polyimide film as a gas separation layer for composite membranes. *Polymer*, *37*: 2577.
16. Ding, Y.; Bikson, B.; Nelson, J.K.; Macheras, J.T. (2004) Polyimide Amic Acid Salts and Polyimide Membranes Formed Therefrom. U.S. Patent 6,716,270, April 6, 2004.
17. Echido, Y.; Miki, N.; Tomioka, I. (1997) Preparation of poly[*bis*(trialkylammonium) 4,4′-oxydiphenylenepyromelliteamide] films: a useful polyimide precursor film. *J. Polym. Sci.: Part A: Polym. Chem.*, *35*: 2493.
18. Polotsky, A.; Cherkasova, V.; Potokin, I.; Polotskaya, G.; Meleshko, T. (2006) Chemically and thermally resistant polyimide ultrafiltration membranes prepared from polyamic acid. *Desalination*, *200* (1–3): 341.
19. Polotskaya, G.A.; Meleshko, T.K.; Polotsky, A.E.; Cherkasov, A.N. (2008) Ultrafiltration Thermo-, Heat-, and Chemically Durable Polyimide Membrane and Method of its Preparation. R.F. Patent 2335335, October 20, 2008.
20. Cherkasov, A.N. (2005) A rapid analysis of ultrafiltration membrane structure. *Sep. Sci. Technol.*, *40*: 2775.
21. Cherkasov, A.N. (2002) Express analysis of structure of ultrafiltration membranes in process of their development. *Membranes* (*Russia*), *14*: 3.
22. Mulder, M.H.V. (2000) Phase inversion membranes. In: *Membrane Preparation*, Mulder, M.H.V., ed.; Academic Press: New York, p. 3331.
23. McCarthy, R.A. (1985) Chemically resistant polymers. In: *Encyclopedia of Polymer Science and Engeneering*, Mark, H.F.; Bikales, N.M.; Overberger, C.G.; Mengels, G., eds., J.Wiley: New York, 3: 412.
24. Bo, D.; Kun, Z. (1991) Preparation and properties of polyimide ultrafiltration membranes. *J. Membrane Sci.*, *60*: 63.
25. Miller, W.K., McGray, S.B., Friesen, D.T. (1998) Solvent-Resistant Microporous Polyimide Membranes. U.S. Patent 5,725,769, March 14, 1998.
26. Kesting, R.E. (1971) *Synthetic Polymeric Membranes*; McGraw Hill: New York.
27. Critchley, J.P.; Knight, G.J.; Wright, W.W. (1983) *Heat Resistant Polymers*; Plenum Press: New York.
28. Cherkasov, A.N., Pasechnik, V.A. (1991) *Membranes and Sorbents in Biotechnology*; Chemistry: Leningrad, R.F.