
MACROMOLECULAR COMPOUNDS AND POLYMERIC MATERIALS

Preparation and Structure of Poly(4,4'-oxydiphenylene)pyromellitimide Asymmetric Ultrafiltration Membranes

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Abstract—A process was developed for preparing asymmetric ultrafiltration poly(4,4'-oxydiphenylene)pyromellitimide membranes, involving wet forming of the membranes from the prepolymer, followed by catalytic solid-phase thermal transformation of the prepolymer into the polyimide. The influence exerted on the structure and characteristics of the membranes by the compositions of the forming solution and precipitation bath, and also by thermal imidization conditions was examined. The optimal conditions were determined for preparing asymmetric ultrafiltration poly(4,4'-oxydiphenylene)pyromellitimide membranes exhibiting the water permeability coefficient of $(10\text{--}500) \times 10^{-6} \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1} \text{ atm}^{-1}$ and molecular weight cut-off in the range $(5\text{--}100) \times 10^3 \text{ g mol}^{-1}$.

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The use of membranes for separation of aggressive media, in production of fuel cells, and in development of high-temperature membrane reactors poses stringent requirements upon the heat resistance and chemical stability of the membranes. Inorganic porous membranes fabricated from glass, metals, or ceramics meet these requirements. However, their high cost and limited range of pore sizes strongly restrict their applicability. Series-produced polymeric ultrafiltration (UF) membranes of wide nomenclature are applicable, as a rule, in a limited temperature interval (up to 100°C) and cannot be used in certain solvents and in aggressive media.

Among the most promising polymers for production of heat-resistant and chemically stable polymeric membranes are aromatic polyimides (PIs) [1]. Polyimides withstand prolonged service at 250–350°C (depending on chemical structure) and are resistant to the majority of organic solvents and to corrosive media. Asymmetric ultraporous membranes based on commercially available polyimides soluble in amide solvents are known (Matrimid 5218, Lenzing P84) [2, 3]. Such membranes withstand prolonged operation at high temperatures (up to 200°C) and are resistant to many solvents. These membranes,

however, are broken down in media containing solvents in which the polyimides used are soluble, e.g., chlorinated hydrocarbons and amides.

More heat-resistant and chemically stable polyimide filtration membranes can be developed on the basis of insoluble infusible polyimides resistant to all organic solvents including amides [4]. In this case, membranes (as well as other articles) can be formed only from a soluble prepolymer, polyamido acid (PAA). This should be followed by solid-phase transformation of PAA into PI membrane (so-called PAA imidization). This process requires harsh conditions. As a rule, it requires heating to 300–350°C. Heating is performed in steps. However, the action of high temperatures on membranes may lead to significant changes in their pore structure formed in the PAA step. Specifically this fact is apparently the major obstacle impeding the development of PI UF membranes based on insoluble and infusible polyimides and is responsible for the lack of such heat-resistant and chemically stable PI membranes on the world market.

The best studied, the cheapest, and the most commercially available insoluble and infusible polyimide is poly(4,4'-oxydiphenylene)pyromellitimide (PI PM in Russia; Kapton in the United States).

The goal of this study was the development of a procedure for preparing asymmetric ultrafiltration membranes based on PI PM. To this end, we determined the conditions of formation of asymmetric ultraporous prepolymeric membranes and developed a low-temperature catalytic procedure for their conversion to the polyimide form.

EXPERIMENTAL

To form membranes, we used solutions of poly(4,4'-oxydiphenylene)pyromellitimido acid (PAA PM) in dimethylformamide (DMF), produced by Estrakom (Russia). The intrinsic viscosity of the starting polymer was 1.5–1.7 dl g⁻¹ (DMF, 20°C). The polymer concentration in the forming solution was 10–14 wt %. Benzimidazole (BI), glycerol, and chemical imidization agents (acetic anhydride, pyridine) were used without additional purification. They were introduced into a PAA solution by the procedure described in [5]. The membranes were formed by applying a forming solution onto a glass support using a slit die with a clearance of 0.3–0.4 µm, which was followed by precipitation at room temperature. As a precipitant we used water or ethanol–water mixture (40 : 60 by weight). The formed membrane was impregnated with a high-boiling filler [5], after which it was heated to 200°C.

The completeness of the conversion of PAA to PI in the course of heat treatment was checked by IR spectroscopy. We measured the spectra of homogeneous (monolithic) films 5 µm thick [4] with a Specord M-80 spectrophotometer. The films were cast from the same prepolymeric solutions from which the porous membranes were formed, after which they were heated under the same conditions as the porous membranes.

The membrane morphology was examined with a JSM-35 scanning electron microscope (Jeol, Japan).

The selectivity (separation power) of membranes was studied by calibration with a model protein mixture [6, 7]. To this end, membrane samples 25 mm in diameter were tested in an ultrafiltration cell with laminar stirring at a rate of 200–600 min⁻¹. The pressure differential across the membrane was 1 atm and was provided by compressed nitrogen. The model mixture consisted of proteins and other substances differing in the molecular weight *M*: vitamin B₁₂ (*M* 1.34 × 10³), cytochrome C (*M* 12.50 × 10³), chymotrypsinogen (*M* 24.0 × 10³), ovalbumin (*M* 44.5 × 10³), bovine serum albumin (*M* 67.0 × 10³), and

Table 1. Influence of the compositions of the forming solution and precipitation bath on the permeability coefficient of prepolymeric membranes

Sample no.	Forming solution in DMF		Precipitation bath		$k(\text{H}_2\text{O}) \times 10^6, \text{m}^3 \text{m}^{-2} \text{s}^{-1} \text{atm}^{-1}$
	polymer	<i>c</i> , wt %	water, wt %	ethanol, wt %	
1	PAA	13	100	—	<0.01
2	PAA	11	60	40	<0.1
3	PAA/BI	11	60	40	450
4	PAA/BI	12	100	—	90
5			60	40	328
6	PAA/BI	14	60	40	80
7	PAA/BI (+20% glycerol)	12	60	40	118
8	(PAA + PI) ^a /BI	11	60	40	406

^a Partially imidized PAA containing 20 mol % imide units.

gamma globulin (*M* 160.0 × 10³). These substances in a total concentration of about 0.4 µg ml⁻¹ were dissolved in 0.05 M phosphate buffer solution (pH 6.5) with addition of 0.1 M NaCl.

Samples of the filtrate and concentrate were analyzed by high-performance exclusion chromatography. The retention coefficients ϕ were calculated by the formula $\phi = 1 - c_f/c_c$, where c_f and c_c are the component concentrations in the filtrate and concentrate, respectively, after which the retention curve of the membrane $\phi = f(M)$ was plotted, where *M* is the molecular weight of the mixture component. From the retention curve we determined the molecular-weight cut-off value corresponding to the weight of the protein 90% retained by the membrane ($\phi = 0.9$) [8].

The membrane performance was evaluated by determining the permeability coefficient for distilled water as the amount of the filtrate (m³) that passed through 1 m² of the membrane in 1 s at a pressure differential of 1 atm.

It is well known that ultrafiltration consists in separation of solutions and colloidal systems with UF membranes in a special apparatus under a pressure. UF membranes retain finely dispersed and colloidal impurities, and also macromolecules with the molecular weight from several thousand daltons and higher. The main service parameters of UF membranes are as follows: permeability coefficient for distilled water $k(\text{H}_2\text{O}) = (2\text{--}500) \times 10^{-6} \text{m}^3 \text{m}^{-2} \text{s}^{-1} \text{atm}^{-1}$ in the pressure range 0.2–3.0 atm, molecular-weight

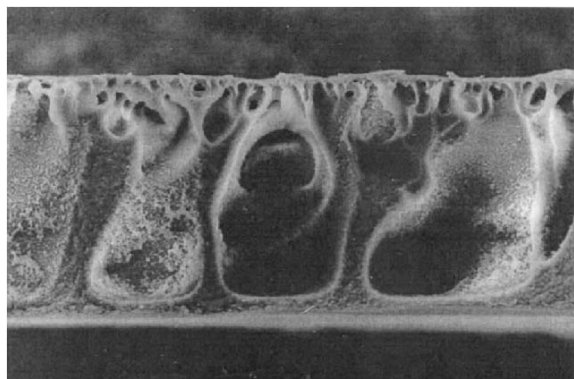


Fig. 1. Electron micrograph of the transverse section of a prepolymeric membrane prepared from a 10 wt % PAA/BI solution with addition of 20 wt % glycerol. Precipitation with ethanol–water mixture (40 : 60 by weight) at room temperature.

cut-off in the range $(5\text{--}500) \times 10^3 \text{ g mol}^{-1}$ [6, 7].

The desired UF PI PM membranes were prepared by a two-step procedure involving forming of asymmetric membranes from a solution of the prepolymer in DMF in the first step and solid-phase conversion of the prepolymer into PI in the course of heat treatment in the second step [5, 9]. Search for conditions for preparing UF PI PM membranes involved in the first step determination of conditions for forming of an asymmetric membrane consisting of a thin finely porous layer (thickness 0.1–5.0 μm) providing the selectivity and a coarsely porous support (thickness 50–150 μm) providing the mechanical strength of the membrane. The major problem in the second step was search for conditions for preserving the pore structure of the membrane in the course of the heat treatment, so as to obtain a final PI membrane suitable for ultrafiltration.

Wet forming of PAA membranes. Asymmetric polymeric membranes are often prepared by polymer coagulation on immersing into a precipitation bath, or so-called wet forming of membranes [10, 11]. For successful wet forming of membranes, it is necessary to ensure conditions for fast phase separation developing on contact of a polymer solution with the precipitation (coagulation) bath. These conditions include composition of the forming solution, prepolymer concentration, composition of the coagulation bath, and precipitation temperature. The results of studying the influence of the compositions of the forming solution and precipitation bath on the permeability coefficient for water $k(\text{H}_2\text{O})$ of prepolymer membrane samples prepared at room temperature are given in Table 1.

It is known that water is a hard precipitant for polymer solutions in DMF. Hard precipitation conditions, at which the difference between the rates of solvent diffusion from a polymer solution into the precipitant and of precipitant diffusion into a polymer solution is small, usually lead to formation of highly porous membranes characterized by high permeability [8]. However, membranes (Table 1, sample no. 1) prepared by precipitation of PAA from its solutions into water at room temperature had extremely low permeability. A decrease in the concentration of the forming solution and an increase in the precipitation temperature did not lead to an increase in the permeability. In forming from solutions of the concentration less than 10 wt %, the coagulation was considerably decelerated, and defective membranes were obtained. An increase in the forming temperature to 60°C led to only an insignificant increase in the permeability coefficient but, at the same time, was accompanied by an increase in the membrane defectiveness.

Low permeability of membranes prepared by precipitation into water is apparently associated with high hydrophilicity of PAA. To decrease the hydrophilicity, we performed chemical modification of the polymer by adding into the forming solution benzimidazole which forms complexes with hydrophilic carboxy groups of PAA [12]. Owing to lower thermodynamic quality of the modified PAA–water system, water became a harder precipitant, and the resulting membranes had a more permeable porous structure (Table 1, sample no. 4).

At the same time, the diffusion rates of the solvent and precipitant depend on the viscosity. This dependence can account for the experimentally observed fact that introduction into the coagulation bath of 40 wt % ethanol led to a considerable increase in the permeability of prepolymeric membranes (Table 1). It is known [13] that the viscosity of water–ethanol mixtures as a function of the ethanol content passes through a maximum. The viscosity of a mixture containing about 40 wt % ethanol is almost three times higher than the viscosities of the components, which are close to each other.

Thus, the use of an aqueous precipitation bath containing 40 wt % ethanol provides formation of more permeable asymmetric prepolymeric membranes based on PAA modified with BI. After thermal imidization by heating to 200°C, the membrane permeability decreases insignificantly. However, in calibration with a model mixture of proteins, these PI membranes virtually fully transmit all the components of the calibration mixture,

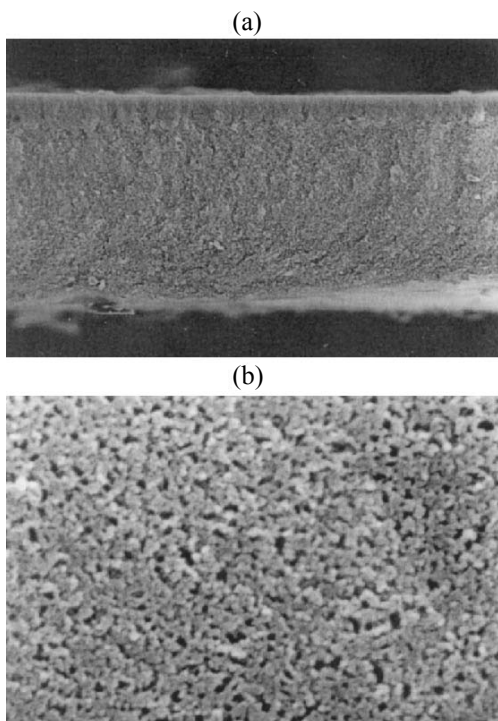


Fig. 2. Electron micrographs of (a) transverse section of the membrane and (b) lower surface of the membrane from the support size. The PI PM membrane was prepared by thermal imidization of the prepolymeric membrane preliminarily impregnated with PMS (Table 2, sample no. 4).

which is indicative of the presence of coarse pores in their selective layers, with the size that does not meet the requirements to ultrafilters.

To improve the separation power of membranes, we modified the forming procedure by adding to the forming solution various substances: tetrahydrofuran, lithium chloride, citric acid, valeric acid, and glycerol. In preparation of other types of PAA membranes,

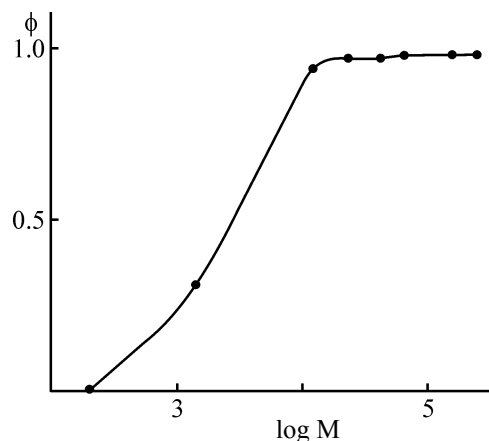


Fig. 3. Curve of retention of a protein mixture by a PI PM membrane prepared by thermal imidization of the prepolymeric membrane preliminarily impregnated with PMS (Table 2, sample no. 4). (ϕ) Retention coefficient and (M) molecular weights of components of the model protein mixture.

additions of these substances induced formation of the desired pore structure [14]. However, addition of the majority of these substances to the forming solution led to a decrease in the membrane permeability even in the step of PAA (Table 1, sample nos. 5, 7), and after thermal imidization the membranes prepared in the presence of tetrahydrofuran, lithium chloride, and the organic acids became impermeable. Only additions of glycerol favor formation of an ultraporous structure of the selective layer and development of the porous structure of the support (Fig. 1). Based on PAA/BI forming solutions containing 10–20 wt % glycerol, we prepared strong flawless prepolymeric membranes (Table 1, sample no. 7).

As an additional way to affect the pore structure of membranes, we also tested variation of the chemical composition of the prepolymer by performing controllable

Table 2. Influence of conditions of prepolymeric membrane preparation and their impregnation with PMS before heating to 200°C on the permeability coefficient of membranes

Sample no.	Forming solution in DMF		PI membrane, $k(\text{H}_2\text{O}) \times 10^6$, $\text{m}^3 \text{m}^{-2} \text{s}^{-1} \text{atm}^{-1}$	Impregnation with PMS	Prepolymeric membrane, $k(\text{H}_2\text{O}) \times 10^6$, $\text{m}^3 \text{m}^{-2} \text{s}^{-1} \text{atm}^{-1}$
	polymer	c , wt %			
1	PAA/BI	11	450	No	280
2	PAA/BI (+20% glycerol)	12	118	Yes	448
3				No	<0.1
4	(PAA + PI) ^a /BI	12	264	Yes	8.9
5				No	109
6				Yes	205

* Partially imidized PAA containing 20 mol % imide units.

partial imidization of PAA in solution under the action of dehydrating agents [5, 9] (so-called chemical imidization). If no more than 1/3 of amido acid units undergo imidization, at a polymer concentration in the forming solution of 11–13 wt %, the polymer solubility is not lost. This fact allowed preparation of membranes from partially imidized PAA with the mean degree of imidization of ≤ 20 mol % as a prepolymer. In this case, the forming solution contained, apart from the polymer, solvent, and BI, a small amount (less than 1 wt %) of pyridine and acetic acid (product of chemical imidization). The membranes formed had a more coarsely porous structure of the selective layer, as indicated by high $k(\text{H}_2\text{O})$ (Table 1, sample no. 8). In the transverse section, the membranes had an asymmetric structure with a thin dense selective layer and a coarsely porous spongy support.

Solid-phase conversion of PAA into a PI membrane.

The second important step in preparation of ultrafiltration polyimide membranes is the conversion of the prepolymer forming the initial membrane into PI under the action of heat treatment, which is performed in classical cases at 300–350°C [4]. When the prepolymeric membrane contained BI, the known catalyst of thermal imidization of PAA [12, 16, 17], cyclization into PI occurred on heating to 200°C. According to the IR spectra, the conversion of PAA to PI at this temperature was complete. This is indirectly confirmed by the fact that these PI membranes neither swelled nor dissolved in amide solvents. The membranes formed from PAA (without BI) and heated to 200°C strongly swelled and partially dissolved in these solvents.

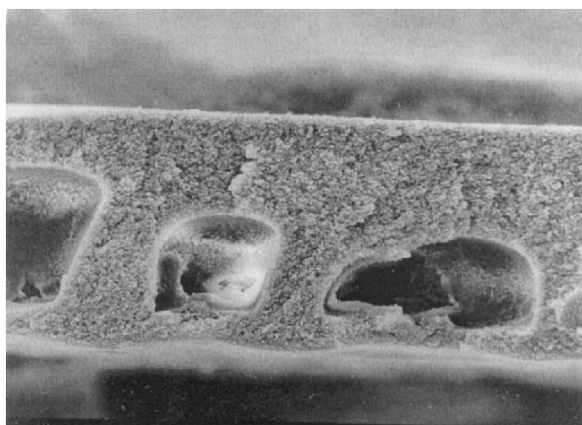


Fig. 4. Electron micrographs of the transverse section of a PI PM membrane prepared by thermal imidization of the prepolymeric membrane preliminarily impregnated with PMS (Table 2, sample no. 6).

Thus, BI in the step of forming favors formation of an asymmetric pore structure of the membrane, and in the step of imidization it acts as imidization catalyst, allowing the process temperature to be decreased.

It should be borne in mind that drying and thermal imidization of prepolymeric membranes is inevitably accompanied by contraction and collapse of pores with partial (or full) loss of the porous structure obtained in the step of wet forming. It is known [4] that high imidization temperatures cause, along with the development of cyclodehydration, also ordering of macromolecular packing, which strongly affects the morphology of the sample formed in the prepolymer step. As follows from experimental data, heating in the course of imidization is accompanied by a decrease not only in the membrane area (by up to 12%), but also in the membrane thickness (by a factor of 1.5–2). This considerable shrinkage inevitably leads to changes in the membrane pore structure and hence in its operation characteristics. The development of such processes should primarily lead to a considerable decrease in the performance (permeability) of PI membranes, compared to prepolymeric membranes.

To preserve the pore structure, the prepolymeric membranes prior to the heat treatment were filled with high-boiling fillers, e.g., glycerol, polymethylsiloxane (PMS), or paraffin oil. The best results were obtained with PMS, which is characterized by chemical inertness, weak temperature dependence of the viscosity, and very high fluidity. The characteristics of membranes prepared from forming solutions of various compositions, determined before and after the heat treatment, are given in Table 2. In each case, the prepolymeric membrane before the heat treatment was divided in two parts, one of which was impregnated with PMS [5]. It can be seen that, at such pore protection, the membrane permeability coefficient after heating to 200°C decreased to a considerably lesser extent.

Figure 2 shows the electron micrographs of the transverse section and lower surface of this PI membrane. It can be seen that the membrane has an upper thin selective layer and a spongy microporous support (Fig. 2a) with open pores in the lower layer (Fig. 2b) of size about 0.2–0.4 μm . The molecular-weight cut-off for this PI membrane, determined from the retention curve of a protein mixture (Fig. 3), is $6 \times 10^3 \text{ g mol}^{-1}$. The retention curve flattens out at $\phi(M) = 100\%$, which indicates that the membrane is flawless.

The polyimide membrane formed from a solution of partially imidized PAA (Table 2, sample no. 6) also

has a thin selective layer and a spongy structure of the support with coarse vacuoles (Fig. 4). These vacuoles are relatively remote ($>30\text{ }\mu\text{m}$) from the selective layer and therefore do not make the membrane defective. Examination of the separating power of this membrane (Table 2, sample no. 6) showed that its molecular-weight cut-off is $40 \times 10^3\text{ g mol}^{-1}$, with the retention curve dispersion close to unity.

Thus, we have determined the conditions for preparing heat-resistant and chemically stable poly(4,4'-oxydiphenylene)pyromellitimide UF membranes. The developed PI PM UF membranes with respect to their main service parameters (performance, selectivity) are level with commercially produced ultrafiltration membranes [17]. At the same time, they surpass commercial membranes in the chemical stability and heat resistance.

One of the main requirements to the supporting membrane is high resistance to solvents. The chemical stability of the PI PM membranes developed allows their use as supporting membranes onto which it is possible to apply soluble polyimides or prepolymers of insoluble polyimides as solutions in amide solvents. In the latter case, the heat resistance of the membranes developed will allow thermal imidization of the prepolymers incorporated in the composite membrane.

The preparation of PI PM UF membranes is based on specific approaches to modification of the chemical structure of the prepolymer and preservation of the pore structure of the formed membrane at high thermal imidization temperatures. Apparently, the use of these approaches, with certain variation of preparation conditions, will allow expansion of the class of PI PM filtration membranes and preparation of micro- and nanofiltration membranes.

CONCLUSIONS

(1) Conditions were determined for two-step preparation of asymmetric ultrafiltration membranes based on poly(4,4'-oxydiphenylene)pyromellitimide, involving wet forming from a prepolymer solution in the first step and solid-phase thermal conversion of the prepolymer into the insoluble form in the second step.

(2) Introduction into the forming solution of benzimidazole giving a complex with the polyamido acid leads to a decrease in

its hydrophilicity and formation of an asymmetric pore structure of the membrane in the wet precipitation step. Furthermore, benzimidazole catalyzes the subsequent imidization, allowing its temperature to be decreased to 200°C .

(3) The resulting membranes at a flow of $(10\text{--}500) \times 10^{-6}\text{ m}^3\text{ m}^{-2}\text{ s}^{-1}\text{ atm}^{-1}$ are characterized by the molecular-weight cut-off in the range $(5\text{--}100) \times 10^3\text{ g mol}^{-1}$, i.e., are typical ultrafiltration membranes.

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