Asymmetric hollow-fiber filtration membranes based on insoluble polyimide (R-BAPB): Influence of coagulation bath on porous structure

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Abstract. The insoluble polyimides are the most promising group of polymer materials for fabrication of solvent stable filtration membranes suitable for operation at elevated temperatures. In order to synthesize asymmetric membranes from insoluble polyimide, it is proposed to fabricate the membranes from a pre-polymer solution (polyamide acid – PAA) by non-solvent induced phase separation method followed by imidization to form non-soluble porous polyimide membrane. The thermoplastic crystallizable polyimide R-BAPB, which is resistant to a number of known organic solvents, was chosen as a membrane material. For the first time, hollow fiber membranes based on imidized PAA (R-BAPB) with a controlled distribution of pores on the inner side of the hollow fiber were formed. It has been established that the use of "hard" non-solvents, such as water or aqueous-organic solutions, is preferable for the formation of a porous structure in the membranes based on PAA (R-BAPB). Synthesized PAA membranes were used to prepare porous membranes based on the thermoplastic polyimide R-BAPB by thermal imidization. Imidization process was confirmed by an increase in the glass transition temperature of the material to 220 °C (corresponds to the glass transition temperature of polyimide (R-BAPB)) and is accompanied by a significant increase in its elastic modulus. The results of the measurements of the transport properties of polyimide membranes for gases and liquids indicate that microfiltration transport pores are present in the membranes.

1. Introduction
The design of new polymer membranes for the filtration of aggressive organic solutions is an important part of membrane technology. However, the lack of the necessary balance between permeability/selectivity on one hand and the chemical and mechanical resistance of these materials to external influence on the other slows down the commercialization of most polymer membranes.

Aromatic polyimides (PI) are materials with high mechanical strength and chemical stability due to the rigid structure of the backbone chain and the strong interaction between adjacent macromolecules [1-5]. However, high rigidity of the backbone chain and strong interchain interactions often lead to poor solubility of PI, which complicates their processing [6-8]. To solve this problem, PI structure is often modified to increase chain flexibility and/or weaken interactions between macromolecules, which makes PI soluble in organic solvents [9]. The use of membranes made of polymers with soluble
behavior under harsh operating conditions (for example, in the nanofiltration of organic solvents, desulfurization of natural gas, etc.) is associated with certain difficulties, such as plasticization, swelling or dissolution of the membrane material. To increase the stability of PI, impregnation of nanoparticles (metal–organic frameworks [10], TiO2 [11] and polyhedral oligomeric silsesquioxane [12]) or post-processing (crosslinking, annealing, or applying protective coatings [1]) are necessary.

Membranes with stable separation characteristics under harsh operating conditions can be produced from polymers with high resistance to various organic solvents and chemical reagents [7]. PIs synthesized from dianhydrides with rigid framework such as 1,2,4,5-benzenetetracarboxylic acid dianhydride, benzenone-3,3′,4,4′-tetracarboxylic dianhydride, etc. are generally insoluble in most organic solvents and appear to be promising materials for manufacturing of the solvent-resistant membranes [2]. But because of the complexity of processing of such insoluble PIs, scientific literature mentions membranes based on these materials much rarely than membranes based on soluble PIs.

W. Schumann and H. Strathmann first patented the process of formation of ultrafiltration and reverse osmosis flat membranes based on insoluble PI in 1975 [13]. The process was carried out as follows: first, asymmetric membranes were formed from soluble prepolymers, like polyamido acids (PAA), and then stable in organic solvents PI membranes were made by thermal or chemical imidization. Subsequently, the preparation and separation characteristics of asymmetric membranes based on insoluble PIs were described in a number of patents and articles [14-25]. Six sources [13, 14, 20-22, 24] investigated flat membranes based on PAA; hollow fiber membranes were the subject of other works. An attempt to systematically study the conditions of hollow fiber PI membranes formation was undertaken in [26]. The authors chose poly-4,4’-oxydiphenylene pyromellitimide (PMDA-ODA) as a membrane material, since this material is one of the most well-studied insoluble polyimides. The PMDA-ODA PAA solution is commercially available and has stable characteristics, which is an important condition for the reproducible preparation of dope solutions with given viscosity values [27].

Literature analysis shows that the overwhelming majority of papers on PAA based membranes, both patents [17, 18] and articles [25, 28], are devoted to the fabrication of gas separation membranes with dense selective layer. Hollow fiber and flat membranes for filtration of organic solutions are produced by soluble PI crosslinking, for example, with polyethyleneimine [29, 30] or hexanediamine [31]. Ultrafiltration [32] and nanofiltration [33, 34] asymmetric membranes that are stable in organic solutions can be produced from PAA with subsequent imidization. However, there are no data in the literature on the investigation of fabrication of porous hollow fiber membranes based on PAA with subsequent imidization. The preparation and study of membranes that are stable in organic solvents is significant both from the fundamental science and practical application in the field of petrochemistry points of view.

A two-stage method of fabrication was proposed and samples of porous thermo- and chemical-resistant PI filtration membranes were studied in this work. For the first time, a PAA polymer synthesized at the IMC RAS with the general formula R-BAPB based on resorcinol dianhydride R (1,3-bis(3,3′,4,4′-dicarboxyphenoxy)benzene) and tetra-nuclear diamine BAPB (4,4′-bis(4-aminophenoxy)biphenyl) was used as a membrane-forming polymer [35-37].

2. Experimental
The preparation of a PAA solution for the fabrication of membranes was carried out in accordance with the procedure described in [38]. PAA was synthesized by polycondensation reaction of 1,3-bis(3,3′,4,4′-dicarboxyphenoxy)benzene (dianhydride R) and 4,4′-bis(4-aminophenoxy)biphenyl (diamine BAPB) in N-methylpyrrolidone (NMP). During the synthesis, the equimolar ratio of the reactants was strictly controlled. PAA was formed by stirring for 4 hours in an inert atmosphere of argon at room temperature. The initial concentration of PAA in the solution of NMP was 20 wt.%. The PAA was diluted to 18 wt.% before filtration. The resulting PAA solutions were filtered and degassed at room temperature in a vacuum oven for 12 hours. The dope solution of PAA in the N-MP was kept at 40 °C for 30 minutes before formation to achieve optimal solution viscosity.
Hollow fiber membranes were prepared by nonsolvent induced phase separation (NIPS) via free-fall spinning method [39–41]. The casting solution and the coagulant were supplied to the spinneret by compressed air with flow controlled by a manometer. The same coagulant was used both inside and outside of the hollow fiber. The membranes were formed at a low speed of about several centimeters of fiber per hour due to the low speed of the phase separation process and curing of the fiber. The time between the appearing of the solution from the spinneret to solidifying the fiber was from tens of minutes to several hours, depending on the strength of the coagulant. A wide range of liquids was used as a coagulant: distilled water, methanol, ethanol, isopropanol, and also a mixture of ethanol and ethylene glycol (50:50 wt.%). The formed hollow fiber membranes were processed and dried to remove solvent residues from the pores. This process consisted of membranes washing sequentially in a polar (ethanol) and then nonpolar (hexane) solvent, followed by drying in air. This technique was used to exclude capillary contraction of the narrowest pores that occurs when water is removed by simple drying [39]. Imidization was carried out in convection heat chambers (Binder) in the following temperature conditions: 1 h at 100 °C, then 1 h at 200 °C, then 1 h at 300 °C [38]. Next, the membrane was cooled to room temperature during the day.

The structure and morphology of PAA membranes was studied by scanning electron microscopy (SEM) using a Tabletop TM 3030 Plus electron microscope (Hitachi, USA). To analyze the structure of the membrane, it was transversely cleaved in liquid nitrogen. Before placing the samples inside the microscope chamber, a thin conducting layer of gold was sputtered onto their surface. The accelerating voltage was 3-5 kV.

The porosity of the hollow fiber membranes was evaluated by processing SEM micrographs using the Gwyddion software (ver 2.54).

The process of phase separation of the PAA in NMP solution upon contact with the coagulant and the formation of the asymmetric structure of the boundary layer was studied using a Micromed R-1 optical microscope and a video camera.

The transport properties of imidized PI membranes were studied by gas permeation tests for a number of gases (nitrogen, oxygen, carbon dioxide) and hydraulic permeation test with water. The gas permeability was measured by the volumetric method with the following parameters: room temperature, pressure above the membrane (gauge) was 50 – 350 kPa, vacuum below the membrane (0.1-1 kPa). The determination of hydraulic permeance was carried out on a special setup in a dead end mode at room temperature with a transmembrane pressure of 1 to 20 atm. The membranes active area was 0.15-3.4 × 10⁻⁴ m². The volume of the initial solution was 800 ml, and permeate flow was determined by the gravimetric method. During the measurement, the dependence of the permeate flow on the applied transmembrane pressure was recorded, and it was close to a linear for all investigated membranes, i.e., Darcy’s law was held true for these membranes. The permeability of the membrane was determined by the slope of the permeate flow from the pressure. Distilled water was used as a model fluid to assess the filtration properties of the membrane.

The mechanical properties of the synthesized samples were studied using the dynamic mechanical analyzer DMA/SDTA861e (Mettler Toledo, Switzerland). The samples were tensile tested at a frequency of 1 Hz, a load amplitude of 0.5 N and a strain amplitude of 50 μm in the temperature range 25-300 °C with a heating rate of 3 °C/min.

3. Results and Discussions

Figure 1 features micrographs of PAA hollow fiber cross-sections of PAA formed with various coagulants. An analysis of the morphology of cross-sections shows that for all alcohol-based coagulants, a cellular-like pore structure of the membrane with a low degree of asymmetry is observed (Figure 1). This indicates that the limiting stage in the membrane formation is the mass transfer rate between the polymer solution and the coagulant. In this case, a dense polymer layer with thickness of several micrometers is formed on the membrane surface. This is also confirmed by the long polymer solidification time (up to 30 minutes). Since the process of phase separation in the membrane is relatively slow, larger pores with fairly thick solid walls form. This is reflected not only in the porous
structure of the membrane, but also in its geometry. A long process of solidification of the membrane leads to its deformation, which is the reason for the irregularities in the axis alignment of the membranes. The non-concentricity of the fibers is observed in transition from water (strong coagulant) to alcohols (weak coagulant) (Figure 1). This is especially noticeable in the case of a membrane formed in isopropanol, for which not only the alignment is violated, but also the regular shape of the inner and outer surfaces.

When water was used as a coagulant, a pronounced asymmetric structure is observed in the SEM images near the deposition surface. The pore size in the surface layer is a fraction of a micrometer, and the thickness of the selective layer is 0.1-0.2 microns. This structure corresponds to the typical morphology of asymmetric membranes.

![SEM images of PAA membranes formed by precipitation in various coagulants, prior to their imidization.](image)

**Figure 1.** The porous structure of PAA membranes formed by precipitation in various coagulants, prior to their imidization.
Table 1 presents the dependence between the porosity of the synthesized membranes and the coagulant. It can be seen that as the coagulant becomes weaker, the porosity of the membrane decreases. This is due to the fact that the curing time of the polymer increases when using weaker coagulants, which leads to the formation of a denser membrane structure.

Table 1. The effect of coagulant on the porosity of the synthesized hollow fiber membranes.

| Solvent             | Porosity of the hollow fiber membrane, % |
|---------------------|------------------------------------------|
| Water               | 60                                       |
| Methanol            | 55                                       |
| Ethanol             | 53                                       |
| Isopropanol         | 50                                       |
| Ethanol/ethylene glycol | 43                             |

The phase separation process was examined by means of optical microscopy (Figure 2), and it was shown that with water as a coagulant, the phase separation of the polymer solution occurs with the formation of a three-layer asymmetric structure consisting of a) a thin surface layer; b) an ordered layer with finger-like pores oriented normally to the solution-precipitating interface (the layer thickness is 2-3 times greater than the thickness of the surface layer); c) an even thicker support layer with a finely porous sponge-like structure, where macro cavities (vacuoles) are also observed, clearly expanding deep into the formed polymer film (see Figure 2). Such porous structure and the presence of vacuoles, which starts to form at the beginning of the precipitation process, provide transport of the coagulant into the bulk of the polymer solution for continued phase separation. For example, the thickness of the formed porous polymer layer at the interface increased from 200 μm (2 minutes after the contact with the coagulant) to 800 μm (30 minutes after the contact with the coagulant) due to an increase in the thickness of the spongy layer. Note that the thicknesses of the two near-surface layers almost do not change with time.
Figure 2. Optical microscopy data on the phase separation of an 18 wt.% PAA solution in NMP after 2 (left) and 30 (right) minutes of contact with the coagulant. Scale bar is 100 mkm.

Fundamentally different behavior is observed in the phase separation process with the change of the coagulant from water to alcohols. The process of phase separation usually proceeds more slowly in the weak coagulant and is accompanied by the formation of a more “loose” porous layer because of a greater penetration of the coagulant into the polymer solution [42]. When precipitated in alcohols, PAA (R-BAPB) forms a dense boundary layer (skin-layer), which prevents further diffusion of the coagulant and the formation of a porous structure. For instance, during precipitation in isopropanol, a very thin dense layer (~40 microns) is formed, and its thickness decreases by a factor of 2-3 in half an hour. Repeated experiments confirmed this pattern, which suggests that the formed dense (barrier) layer prevents the penetration of the coagulant into the bulk of the polymer solution. In the case of isopropanol and ethanol/ethylene glycol mixture, the porous layer from the polymer solution side partially dissolves over time.

In the methanol and ethanol cases, a two-layer polymer structure is observed, which consists of a surface layer and a layer with a spongy structure. At the same time, the polymer precipitation occurs more irregularly and the interphase boundary is unstable, which can be explained by the absence of an intermediate reinforcing layer with finger-shaped pores, in contrast with the water precipitation bath. Initially, a dense polymer layer is formed at the PAA solution-coagulant boundary, but further phase separation is accompanied by its thinning and “loosening”. The formation of isolated microdrops in the
second spongy layer is noticeable, with their concentration decreasing deeper into the solution and away from the boundary. During the precipitation of PAA (R-BAPB) in methanol, the thickness of the surface layer slightly decreases with time (from 100 to 70 μm), while further phase separation is accompanied by an increase in the thickness of the "loose" spongy layer (from 20 to 500 μm) and the formation of isolated microdrops, as is the case with ethanol. However, in methanol, precipitation occurs with the formation of a more dense and uniform porous structure. When ethanol/ethylene glycol mixture is used as a coagulant, a thin polymer film with a thickness of about 30 μm is formed at the phase boundary, and the structure of the film takes on a more pronounced asymmetric character due to its "loosening" and partial dissolution on the polymer solution side (similarly to isopropanol).

It should be noted that the study of the deposition process in various liquids was carried out in a thin gap, and the volumes of the polymer solution and coagulant were comparable. Of course, the investigation of the precipitation process with an “infinite” layer of polymer solution cannot provide an entire picture of the formation of an asymmetric membrane. In the case of forming hollow fiber membranes, the ratio of polymer solution/coagulant is comparable during precipitation from the inner surface of the fiber. But when precipitating from the outer surface of the fiber, the volume of the polymer solution is negligible in comparison with the volume of the coagulant. However, this method allows you to compare the prospects of different coagulants for choosing the optimal combination of polymer-solvent-coagulant.

The synthesized PAA membranes underwent a process of thermal imidization to give them stability at elevated temperatures and the exposure to aggressive solutions. At the end of the heat treatment, the membranes became light brown in color and noticeably shrank in size. To assess the shrinkage of the samples, the geometric dimensions and mass of the membranes were measured before and after imidization. It was shown that all samples lose 19-22% of the initial mass, while shrinkage reaches 35-37%. The thickness of the membranes is reduced by 10-20%. It was shown that after imidization, the porous structure of the membranes was preserved, but the pores decreased in size.

Despite the presence of an open porous membrane structure according to SEM data, almost all imidized membranes showed low gas (less than 10 l/m²•h•atm) and water permeances (less than 2 l/m²•h•atm), and the absence of the selectivity (see table 2). The membrane produced with isopropanol had the highest permeance (up to 80 l/m²•h•atm for gases and up to 8 l/m²•h•atm in water). The absence of gas selectivity suggests that microfiltration pores are present in the membranes. To prepare ultrafiltration and nanofiltration membranes, an additional selection of the solvent–coagulant system and a modification of the imidization step to allow preservation of the finely porous structure of the selective membrane layer, are required.

| Penetrant | Water | MeOH | EtOH | iPrOH | EtOH/EG |
|-----------|-------|------|------|-------|---------|
| N₂        | 3.55  | 2.08 | 2.07 | 80.9  | 3.18    |
| O₂        | 4.02  | 1.55 | 1.55 | 65.7  | 3.07    |
| CO₂       | 4.05  | 1.55 | 1.55 | 77.4  | 3.05    |
| Water     | 0.21  | 1.03 | 1.06 | 7.37  | 1.15    |

The study of the mechanical properties of PAA and PI (R-BAPB) based membranes (see Figure 3) showed that after imidization, the elastic storage modulus of the material increases significantly. For example, at 23 °C the storage modulus is 1260 MPa for the PAA membrane, and 3450 MPa for the PI membrane. This is because during imidization additional five-membered rings appear in the polymer backbone, which increases the rigidity of the polymer molecules, allows it to crystallize, and thereby limits its ability for relaxation and mechanical deformation [43]. The tangent of the loss angle of imidized membranes has a maximum at about 220 °C, which corresponds to the glass transition temperature of PI.
4. Conclusions
1. For the first time, hollow fiber membranes based on imidized PAA (R-BAPB) with a controlled distribution of pores on the inner side of the hollow fiber were formed.
2. It is more preferable to use strong coagulants, such as water or aqueous–organic solutions for the formation of a porous structure in membranes based on PAA (R-BAPB).
3. Elastic storage modulus of the material increases significantly during heat treatment of the membrane. Glass transition of the heat-treated membranes is about 220 °C, which confirms the fabrication of membranes based on R-BAPB polyimide.
4. Novel R-BAPB polyimide based membranes are microfiltration membranes. To produce ultrafiltration and nanofiltration membranes, an additional selection of the solvent–coagulant system and a modification of the imidization technique to allow preservation of the finely porous structure of the selective membrane layer, are required.
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