Characterization of porous polyacrylonitrile membranes by liquid-liquid displacement technique

A V Balynin¹, A A Yushkin¹, M N Efimov¹, D G Muratov¹ and A V Volkov¹

¹A.V. Topchiev Institute of Petrochemical Synthesis, RAS, 119071, Moscow, Russia
E-mail: Halex@ips.ac.ru

Abstract. In this work, series of PAN membranes were prepared by the combined VIPS/NIPS method using different solvents. These membranes were investigated by using liquid-liquid displacement method for membrane pore size distribution and membrane permeance measurements. Wide range of pores size (30-60 nm) and membrane permeance up to 400 L/m²·h·bar were achieved depending on the casting conditions. It was shown that longer exposure in water vapor leads to higher pore size and at the same time makes membrane less permeable due to low asymmetry of porous structure.

1. Introduction

Today membrane processes became a common approach for the separation of various mixtures in the industry due to a number of advantages, including improved energy efficiency, greater flexibility in operation and reduced footprint [1]. Wide variety of membrane processes from traditional like nanofiltration [2] or electrodialysis [3], to more specific like solvent swing adsorption [4] are actively investigated with polymeric membranes.

Polyacrylonitrile (PAN) is one of the most widely used materials for fabrication of micro- and ultrafiltration membranes for aqueous applications [5] and as a porous support for solvent resistant nanofiltration [6] due to its good mechanical and film forming properties as well as stability in many types of organic solvents [7]. Compared with other membranes materials such as poly(vinylidene fluoride), polysulfone, and poly(ether sulfone), PAN-based membranes are more hydrophilic and are less prone to fouling [8]. PAN is extensively used in such fields as biomedicine, microbiology, textile industry, and water purification [8-9]. It is also used as precursor for carbon fibers and membranes preparation [10].

Depending on the preparation conditions and casting solution composition, PAN membranes have fingerlike or spongy porous structure with pore size in UF range. There are few different techniques of membrane preparation based on phase inversion [11]. The non-solvent induced phase separation (NIPS) is the most widely used method for the fabrication of PAN membranes. According to this method, the membranes are fabricated from a viscous polymer solution and then immersed into non-solvent. The vapor induced phase separation (VIPS) technique considered as an alternative to NIPS. It includes the exposure of casted polymeric solution film to non-solvent vapors. The non-solvent gets to polymer solution from a vapor phase and induces phase separation in the membrane.

In this work, series of PAN membranes were prepared by combined VIPS/NIPS method from a wide range of casting conditions. These membranes were investigated by utilizing liquid-liquid displacement method for membrane pore size distribution and membrane permeance measurements.
2. Materials and methods

Dimethyl sulfoxide (DMSO, >99%) was purchased from Acros Organics, Belgium. N-methyl-2-pyrrolidone (NMP, >99%), dimethyl formamide (DMF, >99%), dimethylacetamide (DMAc, >99%) were acquired from Khimmed, Russia.

Laboratory samples of PAN were synthesized with various polymerization conditions. The synthesis was carried out in an aqueous medium in the presence of reduction–oxidation system with ammonium peroxydisulfate \((\text{(NH}_4\text{)}_2\text{S}_2\text{O}_8)\) and sodium dithionite \((\text{Na}_2\text{S}_2\text{O}_4)\) as initiator. The polymerization was performed under the following conditions: \([\text{(NH}_4\text{)}_2\text{S}_2\text{O}_8]=2.94\times10^{-3}\text{ mol/l}, [\text{Na}_2\text{S}_2\text{O}_4]=12.58\times10^{-4}\text{ mol/l, } [\text{H}_2\text{SO}_4]=1.9\times10^{-2}\text{ mol/l, and [acrylonitrile]}=1.45\text{ mol/l. Water, monomer and sulfuric acid were charged into the reactor in two stages. The initiator, which is a redox system of ammonium peroxydisulfate and sodium dithionite, was charged to a reactor containing 3/4 of the required volume of water, monomer and acid, followed by a reaction at 60°C for 20 or 40 minutes. Then, the remaining 1/4 solution was loaded, after what the reaction was continued for 4 hours. The polymer was filtered, washed sequentially in a solution of potassium carbonate in water and methanol to remove sulfuric acid, and then dried in a vacuum to constant weight. The molecular weight characteristics of the synthesized PAN polymer were studied by GPC \((M_n=41900, M_w=146500, M_w/M_n=3.49)\). The study was carried out on a GPC-120 chromatograph from PolymerLabs. The analysis was carried out at 50°C in DMF.

The casting solution was prepared by addition of PAN in solvent followed by stirring at ambient conditions for 72 h to obtain a homogeneous solution. PAN concentration in DMSO, NMP, DMF was 15 wt.%. The polymeric solution was placed in the ultrasonic bath for 30 min to ensure the complete dissolution and the removal of air bubbles.

The polymer solution with thickness of 200 μm was casted on a glass plate with a casting speed of 2.5 m/min. The casting was carried out at temperature of 22°C and humidity of 20%. The cast film was placed in a closed box with a constant humidity 75% and then immersed in the bath with distilled water for complete phase separation. Exposure time in water vapors was 0, 5, 10, 15, 20 min. The membrane was washed with a fresh portion of distilled water and placed in another portion of distilled water overnight to wash out the rest of solvent. The prepared membranes had a thickness in the range of 100 to 150 μm. Formed membranes were stored in distilled water till direct investigation of filtration properties.

The mean pore size and pore size distribution of the membranes was determined using a liquid-liquid displacement based porometer POROLIQTM 1000ML (POROMETER, Belgium). A measurement started with a complete saturation of the sample with a wetting liquid. Water saturated isobutanol (aprox. 15/85 W/I) was used as a wetting liquid. Membrane samples were immersed into a wetting liquid for at least 2 hours at 20°C to ensure complete filling of pores. Isobutanol saturated water (aprox. 92/8 W/I) was used as a displacement liquid. Interfacial surface tension for pair of these liquids is 2 mN/m.

The displacement of a wetting liquid was carried out via the aqueous-rich phase with stepwise increase in pressure. For every applied pressure, permeate flux was measured after initial stabilization time (at least 180 sec) when flux was constant during at least 60 sec. The permeate flux \((J)\) was determined as follows:

\[ J = \frac{V}{S\Delta t}, \]

where \(V\) is the permeated volume (ml) that passed through the membrane with area \(S\) (m²) per time \(\Delta t\) (min).

The membrane permeance \((P)\) was calculated as follows:

\[ P = \frac{J}{\Delta p} = \frac{V}{S\Delta t\Delta p}, \]

where \(\Delta p\) – transmembrane pressure (bar).

By stepwise increase in transmembrane pressure, S-shape dependence of liquid flux was obtained. For every applied pressure, relative flow was calculated from ratio of current permeance to maximum
permeance, achieved when all pores were opened. Diameter of open pore was calculated from applied pressure according to the Young-Laplace equation:

$$D = \frac{4 \cdot \gamma \cdot \cos \theta}{\Delta p}$$

(3)

where $\Delta p$ is the applied pressure, $\gamma$ is the interfacial tension, $\theta$ is the contact angle between membrane and wetting liquid and $D$ is the equivalent pore diameter. Approximation of pores being circular in cross-section was used for simplicity of calculation. In case of PAN membranes prepared via phase inversion method, pore shape usually not far from circular, so this approximation is useful for most of pores. This method allows the calculation of transport pores diameter only in their bottleneck.

Mean pore diameter was used for comparison of different membranes. Mean pore diameter was calculated based on transmembrane pressure when measured permeance was 50% from maximum permeance achieved in the experiment.

3. Results

PAN-membranes were prepared by the vapor induced phase separation technique with variable vapor exposure time (from 0 to 20 minutes) from 15% PAN solutions in different solvents. The membrane permeance was on the same level for membranes exposed to vapor with relative humidity 75% for 5 min and for membranes prepared without vapor exposure (Fig. 1). The permeance of the membranes was 221 L/(m$^2$·h·bar) for membranes prepared from DMSO, 228 L/(m$^2$·h·bar) in case of DMF, and 470 L/(m$^2$·h·bar) for NMP. Permeance of membranes prepared from DMSO and NMP was 2-3 times lower at exposure time 10 min and higher. Further increase in the exposure time of the film in water vapor leads to a sharp decrease in permeance. In the case of NMP, this decrease is observed in the range of 5-10 minutes, for DMSO – 10-15 minutes and for DMF – 15-20 minutes.

![Figure 1. Membrane permeance for membranes prepared with different vapor exposure time.](image1)

![Figure 2. Mean pore diameter for membranes prepared with different vapor exposure time.](image2)

The mean pore diameter of the membranes varied from 30 nm for membranes, prepared from NMP without vapor exposition, to 60 nm for membranes prepared from a solution in DMF with exposure time 20 min (Fig. 2). Membranes had bimodal pore size distribution (Fig. 3). In all cases, bigger pore size mode in the distribution was larger. In case of DMSO, smaller peak in pore size distribution diminished.
Figure 3. Pore size distribution for PAN membranes prepared from different solvents. Solid line corresponds to the integral transmembrane flux; dashed line corresponds to the differential flux through pores with corresponding size.

Observed dependences for membrane permeance show obvious decrease in permeance, and pore size distribution does not explain the difference in membrane permeance. The reason for apparent difference in membrane permeance is difference in structure of pores. Membranes prepared with low exposure time demonstrated a high asymmetry of the porous structure with finger-like pores and dense selective layer (Fig. 4). Membranes prepared via VIPS method with an exposure time 20 minutes have a spongy porous structure, but still have a dense selective layer with fine pores (Fig. 4).

Figure 4. SEM images of membrane prepared from 15% PAN solution in different solvent with 0 min and 20 min vapor exposure at relative humidity 75%.

Analysis of SEM of the cross section of the membranes showed that the membranes prepared by deposition in water had finger-like pores and a thin upper selective layer. Membranes manufactured with an exposure time of 20 minutes in vapor have a spongy, porous structure with a low degree of asymmetry. The low asymmetry of the porous structure means that the sorption stage on the surface between the vapor and the polymer solution is slower than the diffusion of water inside the membrane. Thus, it is established that the observed sharp change in the filtration performance of the membranes occurs as a result of changes in the structure of the membrane pores.

At short exposure times in vapors, water sorption is low and, when submerged in liquid water, the pore structure formation mechanism does not differ much from the pore formation mechanism of precipitation when membranes are directly submerged in water. When the exposure time increases, water sorption increases and spongy structure begins to form, which replaces the finger-shaped pores. Further increase in the exposure time, when the water content in the membrane reaches a critical value,
leads to a fundamental change in the mechanism of formation of the membrane pore structure. In this case, the rate of precipitation due to vapor entering the membrane is less than the rate of vapor diffusion inside the membrane, therefore the deposition process occurs throughout the entire volume. At the same time, the process of phase inversion proceeds more slowly, and the centers of new phase formation have more time for growth. As a result, larger pores are formed with a small degree of asymmetry. Changing solvent to another does not affect the mechanism of phase separation, but it does affect the time before phase separation begins.

4. Conclusions
In this work, series of PAN membranes were prepared by the combined VIPS/NIPS method using different solvents. These membranes were investigated by using liquid-liquid displacement method for membrane pore size distribution and membrane permeance measurements. Wide range of pores size (30-60 nm) and membrane permeance up to 400 L/m²•h•bar were achieved depending on the casting conditions. It was shown that longer exposure in water vapor leads to higher pore size and at the same time makes membrane less permeable due to low asymmetry of porous structure.

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