PAN filtration membranes with extended solvent stability

A A Yushkin¹, M N Efimov¹, A A Vasilev¹, G P Karpacheva¹, A V Volkov¹

¹ A.V. Topchiev Institute of Petrochemical Synthesis, RAS, Moscow, Russia
Halex@ips.ac.ru

Abstract. This work focuses on preparation of PAN membranes stable in aprotic solvents. Laboratory samples of PAN with different molecular weight were synthesized by varying the polymerization conditions. Membranes were prepared by non-solvent induced phase inversion method. Membranes prepared with higher molecular weight PAN had stable separation characteristics at pressures up to 30 bar and higher retention but lower permeability than for membranes prepared from PAN with lower molecular weight. At the same time membranes from PAN with lower molecular weight had higher but unstable in time permeabilities. The retention of Bovine serum albumin (M_w=69 kDa) from water solutions reached the value up to 98%. After IR irradiation treatment membrane permeability for water were the same as for initial membranes and varied from 5 to 1500 kg/m²·h·bar. At the same time PAN membranes was stable toward aprotic solvents NMP, DMSO, DMFA, DMAA although initial polymer was soluble in such solvents.

1. Introduction
Polyacrylonitrile (PAN) has received wide acceptance as a material for the development of chemically resistant membranes used in the filtration of liquids [1,2]. PAN has high strength, good resistance to solvents, thermal and chemical stability, and low cost [2,3]. In comparison to other membrane materials like polyvinylidene fluoride, polysulfone and polyethersulfone, membranes from PAN are less prone to fouling during operation [4-8]. However, the solubility of this polymer in polar aprotic solvents and in aqueous electrolyte solutions with high ionic strength limits an application of such membranes.

Usually porous membranes from PAN are prepared by phase separation induced by non-solvent (for example, water) [2, 9-12], although other non-solvents, for example, supercritical CO₂, can be used [13]. Important parameters for the membrane preparation are the composition of the casting solution, its temperature, additives, solvent and non-solvent used. In addition, the structure of the resulting membranes depends significantly on the viscosity of the polymer solution and non-solvent.

Membrane characteristics can be improved by addition special poreforming additives, such as calcium chloride, poly(ethylene glycol), or polyvinylpyrrolidone [14, 15]. In [16], the addition of carbon nanotubes to PAN-based membranes was used for improve their filtration properties.

Another way to improve membrane characteristics is plasma treatment, grafting of different functional groups, or hydrolysis [16–23]. Modification of PAN based membranes with calcium carbonate help to obtain membranes with retention of Congo Red (M_w~700) up to 98% and water permeability 25.5 L/(m²·h·bar) [24]. It was shown that hydrolysis of PAN membranes also can increase membrane permeability [25].

Modification often used for increase membrane chemical stability for solvents. For example, cross linking of PAN by solutions of hydrazine hydrate at elevated temperature is often used for obtain membranes stable in different solvents [26-27]. Temperature treatment also can be used for cross
linking of PAN by cyclization of the nitrile groups and dehydrogenation [28]. Recently IR treatment was used to improve resistance of PAN membranes for aprotic solvents [11,12]. In the case of IR radiation treatment of PAN, the mechanism of chemical transformation does not differ from thermal modification but takes place much faster. The application of IR radiation makes it possible reduce time of processing to several minutes and also to decrease processing temperature [11,12].

The synthesis of PAN is carried out by radical polymerization of acrylonitrile in a solvent, aqueous emulsion or suspension. As initiators, azo and diazo compounds, peroxides, organoelement compounds, and oxidation-reduction systems are used. The synthesis time, temperature and gas medium in which the polymerization is carried out also have a significant effect on the molecular weight characteristics of the polymer. By varying the conditions for polymer synthesis, a wide range of molecular weight characteristics can be obtained.

This work focuses on preparation of PAN membranes stable in aprotic solvents using laboratory synthesized PAN with different molecular weight. The stability of membranes was achieved by the modification of the polymer with IR irradiation treatment after membrane preparation. Membranes were prepared by non-solvent induced phase separation method.

2. Membrane preparation and modification

Laboratory samples of PAN were synthesized by varying the polymerization conditions. The synthesis was carried out in an aqueous medium in the presence of an oxidation-reduction system from ammonium peroxodisulfate ((NH₄)₂S₂O₈) and sodium dithionite (Na₂S₂O₄) as initiators. The polymerization was carried out under the following conditions: [(NH₄)₂S₂O₈]=1.47×10⁻³ mol/l, [Na₂S₂O₄]=6.29×10⁻⁴ mol/l, [H₂SO₄]=1.9×10⁻² mol/l, and [acrylonitrile]=1.45 mol/l. The initial concentrations of ammonium peroxodisulfate and sodium dithionite varied by a factor of 0.5; 1; 1.5; 2. Water, monomer and sulfuric acid were charged into the reactor in two stages. The initiator, which is a redox system of ammonium peroxodisulfate and sodium dithionite, was charged to a reactor containing 3/4 of the required volume of water, monomer and acid, followed by a reaction for 20 or 40 minutes at 60°C. Then, the remaining 1/4 solution was loaded, after which the reaction was continued for 4 hours. The polymer was then 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 polymer samples were named after the synthesis conditions of PANab, where «a» is the coefficient of change in initiator concentration, and «b» is the duration of the first polymerization step in minutes.

The molecular mass characteristics of the obtained polymer were studied by GPC. The study was carried out on a GPC-120 chromatograph from PolymerLabs. The analysis was carried out at 50°C in DMF.

When varying the conditions for polymer synthesis, it was found that an increase of the concentration of ammonium peroxodisulfate and sodium dithionite leads to a decrease in the molecular weight of PAN (Table 1). This may be due to the fact that a large number of radicals formed as a result of the introduction of a higher concentration of ((NH₄)₂S₂O₈) and (Na₂S₂O₄) (and vice versa) leads to the initiation of chain growth on a larger number of monomer molecules. As a consequence, the probability of recombination of two radicals at the ends of short polymer chains increases, on which the growth of the polymer chain ceases. As a result of varying the concentration of initiators, samples of a polymer with different molecular weights were obtained (Table 1).

Table 1. Molecular-mass characteristics of laboratory synthesized PAN samples.

| Sample | M_w × 10^3 | M_n × 10^3 | M_w/M_n |
|--------|------------|------------|---------|
| PAN₂₀  | 57.7       | 267.2      | 4.63    |
| PAN₄₀  | 79.1       | 280.0      | 3.54    |
| PAN₁₅₄₀| 47.9       | 183.0      | 3.82    |
| PAN₂₄₀ | 41.9       | 146.5      | 3.49    |
Solutions of synthesized PAN samples in DMSO were prepared with concentration 9%. For this purpose, the PAN samples in the required proportions were dissolved in DMSO. The solution was stirred for 72 hours, after which an additional 50 minutes was treated in an ultrasonic bath. The resulting polymer solution with a thin layer (200 μm) was applied to glass and precipitated in distilled water. The time between application of the solution on the glass and immersion in water did not exceed 10 seconds. The rate of application of the polymer solution was 2.5 m/min. The resulting flat membrane was sequentially washed with distilled water, ethanol, and hexane (each time for an hour) and dried at room temperature in air.

Thermal treatment of membranes was carried out in a laboratory setup of pulsed IR radiation at temperature 130°C under a nitrogen atmosphere for 5 minutes. Halogen lamps KG-220 were used as a source of incoherent IR radiation. The radiation maximum of which falls within the range 0.9-1.2 μm. The lamps were arranged in such a way as to ensure a uniform heating of the entire sample. The membrane was fixed in a graphite cassette, which was placed in a cylindrical quartz reactor. The intensity of the IR radiation was controlled by the sample heating temperature, since sample temperature increased only due to IR radiation and not from separate heat source. Temperature was measured with a chromel-alumel thermocouple placed directly below the sample. The temperature regulation was accurate to within 0.25°C.

### 3. Membrane characteristics

A study of filtration characteristics of membranes was carried out in dead-end cells at a transmembrane pressure of 5-30 bar equipped with a magnetic stirrer to reduce the effect of concentration polarization. The active area of the membranes in the cells was 8 cm². The pressure in the system was created with the aid of an inert gas (helium). The permeate flux ($J$) was determined gravimetrically as follows:

$$J = \frac{m}{S \cdot \Delta t},$$

where $m$ is the mass of permeate (kg) that passed through the membrane with area $S$ (m²) per time $\Delta t$ (h). The membrane permeability ($P$) was defined as the ratio of flux ($J$) to the applied transmembrane pressure $\Delta p$ (bar):

$$P = \frac{J}{\Delta p} = \frac{m}{S \cdot \Delta t \cdot \Delta p}$$

To characterize the separation properties of the membrane, the retention $R$ (%) was used:

$$R = \left(1 - \frac{c_p}{c_0}\right) \cdot 100\%,$$

where $c_0$ and $c_p$ are the concentration of solute in the feed and permeate, respectively. Bovine serum albumin (BSA, MM = 69 kDa), Ovalbumin (45 kDa), Pepsin (34.5 kDa), Lysozyme (14.3 kDa) were used as model solutes. The concentration of dissolved substances in the solution was determined spectrophotometrically at a wavelength of 280 nm.

It is established that the molecular weight of the polymer has a significant effect on the characteristics of the membranes obtained. Membranes were characterized by water permeability and solutes retention at transmembrane pressure 5 bar. The highest permeability was observed for membranes obtained from the PAN$_2$40 sample which has lowest molecular weight (Figure 1). At the same time studies of the dependence of membrane retention on the molecular weight of the polymer shows that membranes prepared from polymers with a lower molecular weight have generally lower retention values (Figure 2), but difference was much lower than for permeability. Although membranes prepared from PAN$_2$40 and PAN$_{1.5}$40 have permeability much higher than from other
samples at elevated pressures 10-30 bar their permeability constantly decreased with time up to 20%
per hour. From the other hand permeabilities of PAN\textsubscript{40} and PAN\textsubscript{20} were stable during whole time of experiment even at higher pressure 30 bars.

![Figure 1. Water permeability of membranes prepared from PAN with different molecular weight at 5 bar; ■ – before IR radiation treatment; ♦ – after IR radiation treatment.](image1)

![Figure 2. Retention of solutes by membranes prepared from PAN with different molecular weight; ■ – Lysozyme (14.3 kDa); ♦ – Pepsin (34.5 kDa); ▲ – Ovalbumin (45 kDa); ● – BSA (69 kDa).](image2)

After IR irradiation treatment membrane permeability for water were slightly lower than for initial samples but difference did not exceed experimental errors. At the same time such membranes prepared from PAN\textsubscript{40} and PAN\textsubscript{20} have stable permeabilities toward aprotic solvents NMP (3-5 kg/m\textsuperscript{2}\cdot h\cdot bar), DMSO (3-5 kg/m\textsuperscript{2}\cdot h\cdot bar), DMFA (7-12 kg/m\textsuperscript{2}\cdot h\cdot bar) and DMAA (6-11 kg/m\textsuperscript{2}\cdot h\cdot bar) although initial polymer was soluble in it. For PAN\textsubscript{40} and PAN\textsubscript{1.540} stable permeabilities of aprotic solvents did not observed as well as for water with these polymers but membranes still not dissolved in these solvents. This means that membrane permeability decreases due to membrane compaction instead of polymer dissolution.

4. Conclusion
In this work laboratory samples of PAN with different molecular weight were synthesized by varying the polymerization conditions. Membranes were prepared by non-solvent induced phase inversion method. Membranes prepared with higher molecular weight had stable separation characteristics at pressures up to 30 bar and higher retention but lower permeability than for membranes prepared from PAN with lower molecular weight. The retention of Bovine serum albumin (M\textsubscript{w}=69 kDa) from water solutions reached the value up to 98%. After IR irradiation treatment membrane permeability for water were the same as for initial membranes and varied from 5 to 1500 kg/m\textsuperscript{2}\cdot h\cdot bar. At the same time PAN membranes was stable toward aprotic solvents NMP, DMSO, DMFA, DMAA although initial polymer was soluble in such solvents.

Acknowledgments
Alexey Yushkin acknowledges Russian Foundation of Basic Research (RFBR project no. 16-38-60152) for financial support.

References
[1] Kumar M, Shevate R, Hilke R, Peinemann K-V 2016 Novel adsorptive ultrafiltration membranes derived from polyvinyltetrazole-co-polyacrylonitrile for Cu(II) ions removal Chem Eng J 301 306
[2] Scharnagl N and Buschatz H 2001 Polyacrylonitrile (PAN) membranes for ultra-and
microfiltration *Desalination* **139** (1-3) 191

[3] Tran T D, Mori S, Suzuki M 2007 Plasma modification of polyacrylonitrile ultrafiltration membrane *Thin Solid Films* **515** (9) 4148

[4] Marbelia L, Mulier M, Vandamme D, Muylaert K, Szymczyk A, Vankelecom I F 2016 Polyacrylonitrile membranes for microalgae filtration: Influence of porosity, surface charge and microalgae species on membrane fouling *Algal Research* **19** 128

[5] Guillon G R, Pan Y, Li M, Hoek E M 2011 Preparation and characterization of membranes formed by nonsolvent induced phase separation: a review *Industrial & Engineering Chemistry Research* **50** (7) 3798

[6] Cornelissen E R, Van den Boomgaard T, Strathmann H 1998 Physicochemical aspects of polymer selection for ultrafiltration and microfiltration membranes *Colloids and surfaces A: Physicochemical and engineering aspects* **138** (2-3) 283

[7] Lohokare H, Bhole Y, Taralkar S, Kharul U 2011 Poly (acrylonitrile) based ultrafiltration membranes: Optimization of preparation parameters *Desalination* **282** 46

[8] Klaysom C, Hermans S, Gahlaut A, Van Craenenbroeck S, Vankelecom I F 2013 Polyamide/Polyacrylonitrile (PA/PAN) thin film composite osmosis membranes: Film optimization, characterization and performance evaluation *Journal of membrane science* **445** 25

[9] Kim I C, Yun H G, Lee K H 2002 Preparation of asymmetric polyacrylonitrile membrane with small pore size by phase inversion and post-treatment process *Journal of Membrane Science* **199** (1-2) 75

[10] Yang S and Liu Z 2003 Preparation and characterization of polyacrylonitrile ultrafiltration membranes *Journal of membrane science* **222** (1-2) 87

[11] Yushkin A A, Efimov M N, Vasil’ev A A, Ivanov V I, Bogdanova Y G, Dolzhikova V D, Karpacheva G P, Bondarenko G N, Volkov A V 2017 Effect of IR Radiation on the Properties of Polyacrylonitrile and Membranes on Its Basis *Polymer Science, Series A* **59** (6) 880

[12] Yushkin A A, Efimov M N, Vasilev A A, Bogdanova Y G, Dolzhikova V D, Karpacheva G P, Volkov A V 2017 Modification of polyacrylonitrile membranes by incoherent IR radiation *Petroleum Chemistry* **57** (4) 341

[13] Wang H, Yu J, Bai H, Li L 2016 Preparation of PAN nanofiltration membranes by supercritical-CO$_2$-induced phase separation *The Journal of Supercritical Fluids* **118** 89

[14] Linkov V M, Sanderson R D, Jacobs E P 1994 Carbon membranes from precursors containing low-carbon residual polymers *Polymer international* **35** (3) 239

[15] Kaminska G, Bohdziewicz J, Palacio L, Hernandez A, Pradanos P 2016 Polycrylonitrile membranes modified with carbon nanotubes: characterization and micropollutants removal analysis *Desalination and Water Treatment* **57** (3) 1344

[16] Fei Z D, Wan L S, Wang W M, Zhong M Q, Xu Z K 2013 Thermo-responsive polycrylonitrile membranes prepared with poly (acrylonitrile-g-isopropylacrylamide) as an additive *Journal of membrane science* **432** 42

[17] Khulbe K C, Feng C, Matsuura T 2010 The art of surface modification of synthetic polymeric membranes *Journal of Applied Polymer Science* **115** (2) 855

[18] Zhao Z P, Li J, Zhang D X, Chen C X 2004 Nanofiltration membrane prepared from polycrylonitrile ultrafiltration membrane by low-temperature plasma: I. Graft of acrylic acid in gas *Journal of Membrane Science* **232** (1-2) 1

[19] Zhao Z P, Li J, Wang D, Chen C X 2005 Nanofiltration membrane prepared from polycrylonitrile ultrafiltration membrane by low-temperature plasma: 4. Grafting of N-vinylpyrrolidone in aqueous solution *Desalination* **184** (1-3) 37

[20] Chen J, Li J, Zhao Z P, Wang D, Chen C X 2007 Nanofiltration membrane prepared from polycrylonitrile ultrafiltration membrane by low-temperature plasma: 5. Grafting of styrene in vapor phase and its application *Surface and Coatings Technology* **201** (15) 6789
[21] Ulbricht M, Oechel A, Lehmann C, Tomaschewski G, Hicke H G 1995 Gas-phase photoinduced graft polymerization of acrylic acid onto polyacrylonitrile ultrafiltration membranes Journal of applied polymer science 55 (13) 1707

[22] Zhang G, Song X, Li J, Ji S, Liu Z 2010 Single-side hydrolysis of hollow fiber polyacrylonitrile membrane by an interfacial hydrolysis of a solvent-impregnated membrane Journal of Membrane Science 350 (1-2) 211

[23] Wang J, Yue Z, Ince J S, Economy J 2006 Preparation of nanofiltration membranes from polyacrylonitrile ultrafiltration membranes Journal of membrane science 286 (1-2) 333

[24] Chen X N, Wan L S, Wu Q Y, Zhi S H, Xu Z K 2013 Mineralized polyacrylonitrile-based ultrafiltration membranes with improved water flux and rejection towards dye Journal of membrane science 441 112

[25] Bao W, Xu Z, Yang H 2009 Electrokinetic and permeation characterization of hydrolyzed polyacrylonitrile (PAN) hollow fiber ultrafiltration membrane Science in China Series B: Chemistry 52 (5) 683

[26] Kasperchik V P, Yaskevich A L, Bil’dyukevich A V 2005 Membranes, Series Kriticheskie Tekhnologii 28 (4) 35

[27] Pérez-Manríquez L, Aburabi’e J, Neelakanda P, Peinemann K V 2015 Cross-linked PAN-based thin-film composite membranes for non-aqueous nanofiltration Reactive and Functional Polymers 86 243

[28] Tsai H A, Chen Y L, Lee K R, Lai J Y 2012 Preparation of heat-treated PAN hollow fiber membranes for pervaporation of NMP/H2O mixtures Separation and purification technology 100 97