

Influence of additives of amphiphilic block copolymers on the porosity of hollow ultrafiltration membranes based on polyethersulfone

N. Fateev^{1*}, M. Ivanov¹, N. Korotkova², G. Dibrov¹, N. Pavlukovich^{3,4}, and I. Storozhuk^{3,4}

¹TEKON Membrane Technologies LLC, st. 3rd Khoroshevskaya, 20, 123298 Moscow, Russia

²Macromer LLC, st. Bolshaya Nizhegorodskaya, 77, 600016 Vladimir, Russia

³A.N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences (INEOS RAS), st. Vavilova, 28, 119991 Moscow, Russia

⁴Bauman Moscow State Technical University, 2nd Baumanskaya st., 5/1, 105005 Moscow, Russia

Abstract. It has been shown that the addition of hydrophilic polyarylate-polyalkylene oxide and polyethersulfone-polyalkylene oxide block copolymers to polyethersulfone can control the porosity of the selective layer of hollow fiber ultrafiltration membranes. The selection of the optimal amount of the additive makes it possible to increase the performance of membranes in the purification of drinking water from microalgae, large mineral particles, bacteria and viruses. **Key words:** fiber membranes, polyethersulfone, porosity.

1 Introduction

Polysulfone (PSU) based on 4,4'-dioxydiphenyl-2,2-propane (bisphenol A) and 4,4'-dichlorodiphenylsulfone and polyethersulfone (PES) based on 4,4'-dioxydiphenylsulfone (bisphenol S) and 4,4'-dichlorodiphenylsulfone are structural thermoplastics with high heat resistance and mechanical properties [1–5]. At the same time, they are the most versatile and popular polymers for creating continuous (diffusion) gas separation and porous ultrafiltration membranes [6–8]. Diffusion membranes are used to implement such membrane processes as dialysis, electro dialysis, piezodialysis, pervaporation, and separation of gas mixtures [9, 10]. The use of porous membranes is more extensive, in particular, they are used in the processes of micro-, ultra-, and nanofiltration, reverse osmosis, hyperfiltration, dialysis, and electro dialysis [11–14].

The subject of this study is the synthesis of two hydrophobic-hydrophilic block copolymers of the polycondensation type and the study of the effect of their additives on the porosity of ultrafiltration PES membranes with a pore size of 0.01–0.1 μm , which are used to purify water from solid particles, dissolved macromolecules (with a molecular weight from 10,000 Da and above), bacteria and viruses, the size of which exceeds the size of the membrane pores.

* Corresponding author: fateev@tecon.ru

2 Materials and methods

Polyarylate-polyalkylene oxide (PAR-PAO) block copolymer was synthesized by the reaction of acceptor-catalytic polycondensation [15], according to the reaction equation shown on figure 1.

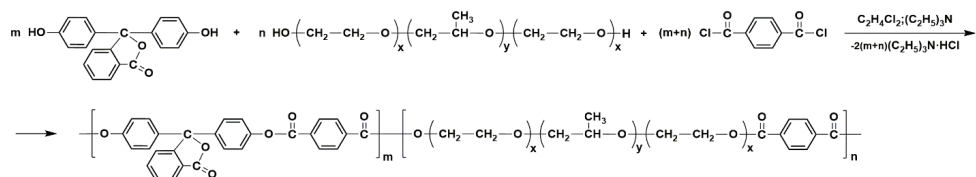


Fig. 1. PAR-PAO block copolymer synthesis reaction equation.

Phenolphthalein, terephthaloyl chloride, and low molecular weight (oligomeric) polyalkylene oxide with terminal hydroxyl groups were used as initial compounds for the synthesis of a block copolymer (BCP). Liquid hydrophilic oligomer brand "Laprol-2002" produced by "Macromer" Ltd. (Vladimir) had a molecular weight of 2000 Da, the content of units based on ethylene oxide was 70 wt%. and based on propylene oxide 30 wt%. The ratio of hydrophobic blocks of polyarylate and hydrophilic blocks of polyalkylene oxide in the multiblock block copolymer was 70:30 wt%.

A triblock polyethersulfone-polyalkylene oxide-polyethersulfone (PES-PAO-PES) block copolymer was obtained by a nucleophilic substitution reaction by reacting a two-fold excess of oligoethersulfone with phenolate groups with oligoalkylene oxide terminated with chloroalkyl groups according to the reaction equation shown on figure 2.

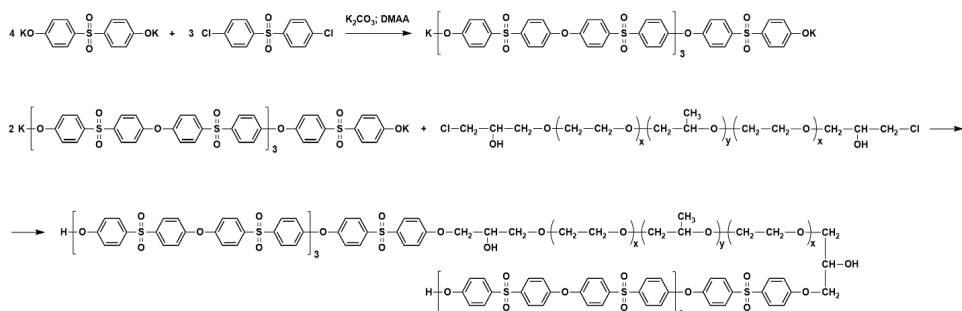


Fig. 2. PES-PAO-PES block copolymer synthesis reaction equation.

Synthesis of the block copolymer was carried out in a dimethylacetamide (DMAC) medium in two stages: first, an oligoethersulfone with a molecular weight of 1700 Da was obtained, and then a solution of oligoalkylene oxide with a molecular weight of 2000 Da in toluene was slowly introduced into the reaction mass. A liquid hydrophilic oligomer with a ratio of units based on ethylene oxide (70% wt.) and propylene oxide (30% wt.) was synthesized at Makromer LLC (Vladimir).

The structure of the synthesized amphiphilic PAR-PAO and PES-PAO-PES block copolymers was confirmed by elemental analysis, IR spectroscopy, and gel permeation chromatography. To obtain IR spectra, a Nicolet iS10 spectrometer was used, in the range 4000-650 cm⁻¹ with a germanium crystal. The molecular weights and molecular weight distribution of BSP were determined by gel permeation chromatography (GPC) using a Shimadzu Prominence LC-20 chromatograph equipped with a RID 20A refractive index detector and 100 angstrom PSS GRAM analytical columns. Dimethylformamide was used as

a solvent, the concentration of the samples was from 1.1 to 2.1 mg/ml. Calibration curves were generated using six 1 mg/mL polyacrylate standards.

3 Results and discussions

The synthesized amphiphilic block copolymers were used to modify spinning solutions to obtain ultrafiltration hollow fiber membranes based on polyethersulfone Ultrason E 6020.

Membrane technologies are increasingly being used in industrial water treatment processes. Membranes are most widely used for clarification of water, as well as for the removal of bacterial contaminants, viral particles, and colloidal suspensions of inorganic origin from it [14]. For these purposes, as a rule, ultrafiltration hollow fiber membranes are used.

Membrane contamination with organic substances is a key problem in water treatment, since hydrophobic organic molecules are easily deposited on the membrane surface or clog its pores, which leads to a sharp decrease in the productivity of the entire process. Backwashing and chemical washing cannot fully restore the productivity of the membrane process [15], which leads to a low clean water recovery and high cost of the entire process.

To solve this problem, it is necessary to adjust the selective layer of the hollow fiber membrane. So important characteristics of the membrane for a successful ultrafiltration process are: the localization of the limiting pore on the membrane surface, the absence of large pores (vacuoles) in the morphology of its walls, and the hydrophilicity of the selective layer [16].

Often the limiting pores (selective layer) are located not on the surface, but in the depth of the membrane structure. This leads to the fact that its purification in the processes of backwashing and chemical washing is difficult, requires a larger dosage of hypochlorite and other cleaning agents, and sharply increases the cost of the process [17]. Large pores are also centers of increasing contamination, drastically reducing productivity.

Another important point when using membranes in water treatment processes is the hydrophilicity of the selective layer [18]. As a rule, the polluting substances contained in water are hydrophobic organic compounds [19], which adhere to the membrane surface and are very difficult to remove.

The aim of this work is to create a hydrophilized hollow fiber membrane without vacuoles, the selective layer of which is localized on the inner surface.

The standard composition of the spinning solution in the manufacture of hollow fiber membranes includes a polymer, a solvent, and a non-solvent. It often includes other additives. Such as polyvinyl pyrrolidone (PVP) of various molecular weights, surfactants (surfactants, usually copolymers of polyethylene oxide and polypropylene oxide) and other hydrophilizing and pore-forming compounds. In this work, when forming membranes, polyethersulfone PES Ultrason E 6020 P (BASF) was used as a polymer, dimethyl sulfoxide (DMSO) as a solvent, and polyethylene glycol (PEG-200) as a non-solvent. Polyvinylpyrrolidone PVP K-90 (BASF), copolymer of polyethylene oxide and polypropylene oxide Pluronic f127 (BASF), as well as polyarylate-polyalkylene oxide (PAR-PAO) block copolymer and triblock polyethersulfone-polyalkylene oxide were used to control the morphology and hydrophilicity of the membrane. -polyethersulfone (PES-PAO-PES) block copolymer synthesized in the laboratory.

The polymer solution was prepared in a flask using an anchor type stirrer. The polymer was dissolved in dimethyl sulfoxide with constant stirring for 3 hours at a temperature of 100°C. After that, the temperature was reduced to 60°C and a hydrophilizing additive was introduced. The non-solvent was introduced fractionally, dividing into four parts. The solution was stirred until complete homogeneity. The compositions of the solutions obtained during the experiment are presented in Table 1.

Table 1. The composition of spinning solutions for the production of hollow ultrafiltration fibers.

Solution components	Solution 1	Solution 2	Solution 3	Solution 4	Solution 5	Solution 6
PES. wt %.	19%	19%	19%	19%	19%	19%
DMSO. wt %.	25%	27%	26%	26%	26.5%	26%
PEG-200. wt %.	56%	53.5%	54%	54%	52.5%	54%
Additive and its equivalent. wt %.	-	K-90 0.5%	Pluronic fl27 1%	PAR- PAO 1%	PAR- PAO 2%	PES- PAO- PES 1%

To spin the fiber, the method of co-extrusion of the polymer solution and the internal coagulant through the spinneret into the air gap was used. Then the fiber entered the precipitation bath (table 2). Further, the hollow fiber membrane passed through the washing bath and fell onto the receiving reel.

The resulting hollow fiber membrane was tested for permeability, its rupture pressure was determined, and microscopic studies and porosimetry were also carried out.

Membrane permeability was tested on fiber segments 500 mm long. To do this, deionized water was supplied inside the fiber at transmembrane pressure values of 1 bar. The initial water temperature was 20°C. The permeate was collected in a graduated cylinder. The time for filling 20 ml was noted on the stopwatch. The experiment was repeated at least 3 times until the results were repeatable. The “bubble” method was used to find the rupture pressure of the membrane. To do this, a piece of a hollow fiber membrane 1000 mm long was placed in a bath filled with water at room temperature. One end of the hollow fiber segment was sealed with a thermal gun. In the opposite direction, air was supplied from a cylinder through a reducer. The pressure was built up gradually at a rate of 0.5 bar per minute. The pressure at which defects appeared was fixed (air bubbles began to emerge from the membrane wall). For microscopic studies, a Tescan Vega Compact microscope was used. The pore size was determined not only using an electron microscope, but also by porosimetry.

Table 2. Parameters of the process of forming hollow ultrafiltration fibers.

External / internal diameter of the membrane, mm	1.3/0.8
Air gap cm	18
Temperature of the polymer solution, °C	room temperature
Precipitation bath temperature, °C	60
Precipitation bath composition	de-ionized water
Temperature of internal coagulant, °C	room temperature
Composition of the internal coagulant	DMSO 70% Water 30 %

Figure 3 shows the microstructure of the walls of hollow fiber membranes obtained from spinning solutions 1 and 2, Figure 4 shows the structure of the selective layer of membranes

obtained from all tested solutions 1-6. Table 3 shows the main characteristics of molded ultrafiltration membranes.

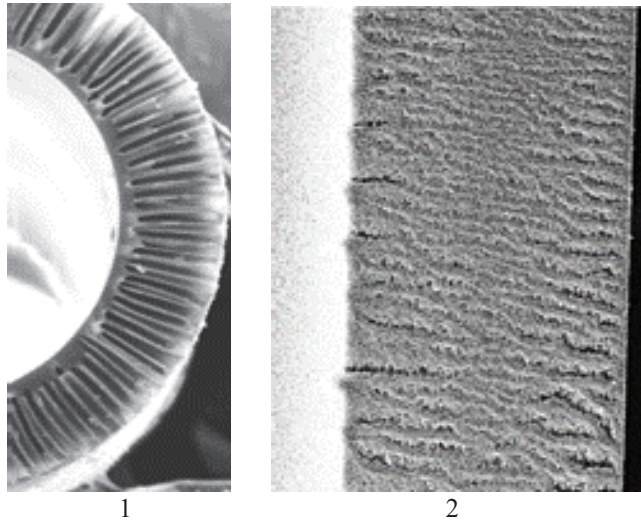


Fig. 3. Microstructure of the walls of hollow fiber membranes obtained from solutions 1 and 2.

Figure 3 shows the membrane obtained from solution 1 without functional additives contains a large number of finger-shaped voids, which leads to the formation of large visible pores (Fig. 4, Table 3) and a strong decrease in the membrane rupture pressure (Table 3). The introduction of K-90 grade PVP leads to an improvement in the microstructure of the porous sublayer of the membrane (Fig. 1), a decrease in the pore size, and a significant increase in the membrane rupture pressure (Table 3).

The disadvantage of the membrane obtained from solution 2 is the presence of spherical particles firmly adhering to the membrane surface and also found inside the formed pores (Fig. 5). The formation of microspheres from the polymer during the formation of the membrane leads to a noticeable decrease in the productivity of the membrane, compared with membranes from solutions 4-6 (Table 3). The addition of block copolymer PAR-PAO and PES-PAO-PES additives obviously reduces the likelihood of microsphere formation (solutions 4, 5 and 6) and contributes to an increase in the specific permeability of membranes.

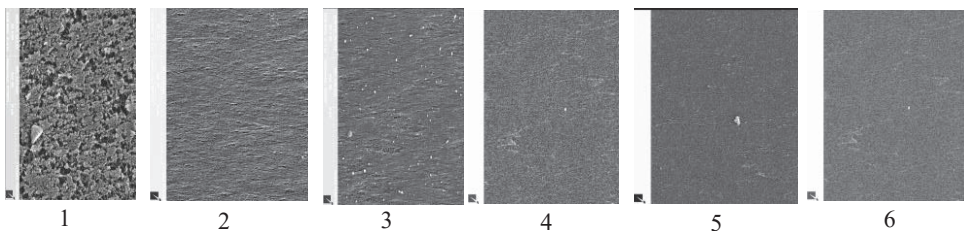
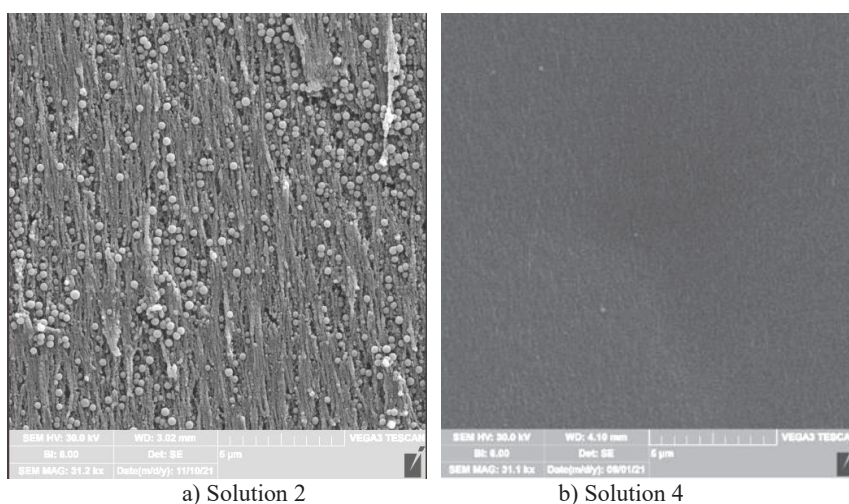


Fig. 4. Microstructure of the selective layer of hollow fiber membranes obtained from spinning solutions of compositions 1-6.

Table 3. The main characteristics of ultrafiltration membranes obtained from solutions 1-6.

Membrane characteristic	The spinning solution from which the membrane was made.					
	1	2	3	4	5	6
Visible pore size, nm	450	200	180	45	35	43
Pore size on porosimetry, nm	40	38	36	31	27	30
Specific permeability, $l/m^2 \cdot h \cdot bar$	905	1028	952	1420	1231	1350
Bursting pressure, bar	3.6	10.4	10.3	11.6	12.1	11.5

**Fig. 5.** Micrograph of the inner surface of hollow fibers obtained from solutions 2 and 4.

4 Conclusion

It is shown that the introduction of amphiphilic block copolymer additives into the spinning solution based on polyethersulfone makes it possible to control the deep morphology of the ultrafiltration membrane, and most importantly, to influence the morphology of its selective layer. The membranes obtained with the addition of PAR-PAO and PES-PAO-PES block copolymers showed high permeability values, while their structure did not include vacuoles and spherical particles, and the apparent surface porosity approximately corresponded to the values obtained by porosimetry.

From the studied series of membranes, the best results were shown by the membrane obtained from the spinning solution 4 containing 1% wt. PAR-PAO block copolymer, which is characterized by the absence of vacuoles and spherical microparticles, high burst pressure and water specific permeability equal to $1420 l/m^2 \cdot h \cdot bar$.

It is planned that work aimed at regulating the microstructure and performance of polyethersulfone membranes using synthesized PAR-PAO and PES-PAO-PES block copolymers will be continued. In addition, these block copolymers with water-soluble PAO blocks can be used in the formation of nanofiltration membranes, since they are able to regulate the zeta potential by concentrating on the membrane surface, which will ultimately lead to a decrease in membrane fouling and an increase in the time period between washings.

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