

THE EFFECT OF PLURONIC COMPOSITION ON THE STRUCTURE AND PERFORMANCE OF THIN FILM COMPOSITE POLYPHENYL SULFONE/POLYAMIDE MEMBRANES FOR NANOFILTRATION

¹Katsiaryna Burts, ¹Tatiana Plisko, ¹Anastasia Penkova, ²Alexandr Bilydukevich

¹St. Petersburg State University, St. Petersburg, Russia

E-mail: katyaburt@gmail.com, plisko.v.tatiana@gmail.com, a.penkova@spbu.ru

²Institute of Physical Organic Chemistry, National Academy of Sciences of Belarus, Minsk, Belarus

E-mail: uf@ifoch.bas-net.by

Introduction

The novel thin film composite polyphenylsulfone (PPSU)/polyamide (PA) nanofiltration membranes were developed. Due to the high chemical and thermo stability, as well as oxidation, polymers of polysulfone group are very perspective as ultrafiltration membrane materials. However, rather high surface hydrophobicity limits their application. There are a lot of techniques for modification of such polymers and increase of their hydrophilicity. One of the most effective is the addition of hydrophilic additive into the casting solution. Block copolymers of polyethylene glycol (PEG) and polypropylene glycol (PPG) are promising modifying additives for polymer matrices due to their amphiphilic nature. There are various trademarks of PEG and PPG block copolymers which differ in their molecular weight, hydrophilic-lipophilic balance, and molecular architecture. It is known that the addition of polymeric additives to the casting solution significantly affects membrane's structure and performance, and allows the adjustment of porosity, pore size, roughness, and hydrophilicity of the membrane selective layer. The formation of the selective layer by interfacial polymerization (IP) is highly dependent on the properties of the substrate membrane. Pore size, porosity, hydrophilicity, wettability, and affinity to amine monomer of the membrane substrate are known to influence the velocity of amine monomer release from membrane substrate to reaction interface. It influences thickness and structure of the polyamide (PA) selective layer formed via IP. Increasing the surface hydrophilicity can lead to a more uniform distribution of the amine while the formation of a polyamide layer obtained by interfacial polymerization. This may result in formation of denser and thinner polyamide layer with high salt retention.

Experiments

In this work ultrafiltration membrane-supports were prepared from polyphenylsulfone (PPSU, Ultrason P3010, $M_w = 48,000 \text{ g mol}^{-1}$) and N-methyl-2-pyrrolidone as a solvent. Triblock copolymers which consist of hydrophilic PEG and hydrophobic PPG (Pluronic[®]) (Table 1) were added into the casting solution to increase hydrophilicity and adjust pore structure of polymer membranes. Copolymers used in this work are characterized by different molecular weights and content of PEG blocks. Porous membranes were obtained from 20 wt% PPSU solutions in N-methyl-2-pyrrolidone with the addition of 3 or 7 wt% of PEG-PPG-PEG block copolymer using a non-woven reinforcing polyester substrate by the phase inversion method. Distilled water was used as a coagulation bath.

Table 1: Types of Pluronic[®] copolymers and their characteristics

Type of copolymer	Molecular weight, g mol^{-1}	Content of PEG blocks, %
L61	2 000	10
L62	2 500	20
L65	3 500	50

Nanofiltration membranes were obtained by formation of a thin selective layer by interfacial polymerization of piperazine and trimesoyl chloride on the surface of a porous membrane-substrate based on PPSU with the addition of a PEG-PPG-PEG triblock copolymers. The performance of PPSU/Pluronic/polyamide (PA) nanofiltration membranes were studied in nanofiltration of model salt aqueous solutions ($2 \text{ g} \cdot \text{L}^{-1}$ of MgCl_2 , CaCl_2 , Na_2SO_4 , MgSO_4).

Results and Discussion

At the first stage, the effect of the content of PEG units in the block copolymer on the structure of the selective layer, hydrophilic-hydrophobic properties, and transport properties of porous PPSU membrane-supports was studied. The developed membrane-supports were subsequently used to obtain thin film composite membranes for nanofiltration. It was found that an increase in the content of PEG content in the triblock copolymer led to the formation of a more porous structure of the membrane selective layer. Moreover, increase in concentration of Pluronic in the casting solution also caused the rise in the pore size as well as the amount of pores. According to AFM studies increase in content of PEG units from 10–20% to 50% yielded the sharp increase in the surface roughness parameters of the selective layer of PPSU ultrafiltration membranes when triblock copolymer content was 3 wt% in the casting solution. An increase in the triblock copolymer concentration from 3 to 7 wt% regardless of PEG unit content also led to the enhancement of the surface roughness of the selective layer probably due to higher porosity and larger pore size. It should be noted that the surface roughness parameters of PPSU membranes with 7 wt% of triblock copolymer also slightly increased with the rise of the content of PEG units. The increase in hydrophilicity of the PPSU/Pluronic membrane surface with both rise in copolymer concentration and higher content of PEG units was confirmed by water contact angle measurements.

It was found that an increase in the content of PEG units in the triblock copolymer, as well as an increase in its concentration in the casting solution from 3 to 7 wt%, resulted in the increase in pure water flux of ultrafiltration membrane-substrate (Figure 1a). The flux of membranes with the addition of 7 wt% triblock copolymer significantly exceeded the flux of membranes with 3 wt%. The rejection coefficient of polyvinylpyrrolidone with $M_n=40,000 \text{ g} \cdot \text{mol}^{-1}$ (PVP K-30) with the addition of 3 wt% PEG-PPG-PEG triblock copolymer practically does not change with an increase in the content of PEG units and slightly decreases at 7 wt%. Moreover, the rejection coefficient was shown to be lower for membranes with 7 wt% copolymer in the casting solution compared to the membranes prepared using PPSU solutions with 3 wt% of copolymers due to the increase in the pore size of the selective layer.

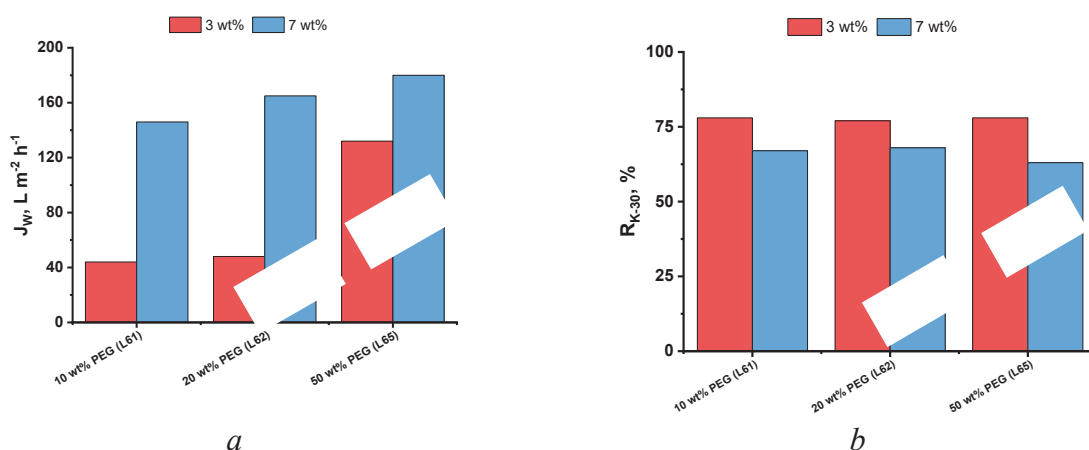


Figure 1. Dependence of water flux (a) and rejection coefficient of PVP K-30 (b) of PPSU ultrafiltration membranes on the content of PEG units in the PEG-PPG-PEG triblock copolymer used as an additive to the casting solution.

On the second stage, the polyamide layer was formed on the surface of PPSU/Pluronic ultrafiltration membranes *via* IP. It was shown that the surface of the selective layer of nanofiltration membranes consists of globular formations of polyamide, which is a typical structure of the selective layer obtained by the method of IP. With an increase in the content of PEG units in the triblock copolymer, a narrowing of the size distribution of polyamide globules is observed, the surface becomes more uniform, and the size of globular formations decreases. It was revealed that with an increase in the content of PEG units in the triblock copolymer, the formation

of a thinner and more uniform selective layer is observed (Figure 2). It was especially pronounced for membranes prepared from casting solutions with 7% PEG-PPG-PEG triblock copolymer.

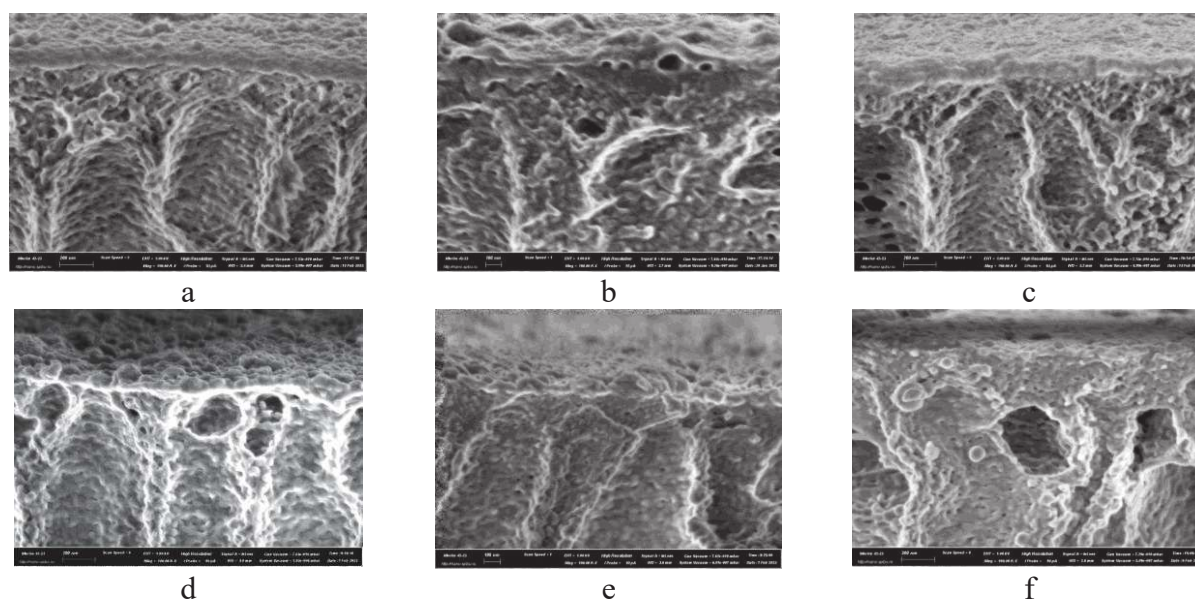


Figure 2. SEM microphotographs of the cross-sections of nanofiltration membranes based on PPSU with the addition of 3% (a-c) and 7% (d-f) PEG-PPG-PEG block copolymer to the casting solution, type of block copolymer: a, d - L61; b, e - L62; c, f - L63.

It has been shown that the water flux increased with an increase in the content of PEG units in the block copolymer for nanofiltration membranes prepared with both 3 and 7 wt% PEG-PPG-PEG in the casting solution (Figure 3a). The rejection coefficient for MgSO_4 practically did not change with an increase in the content of PEG units at 3 wt% of the additive, but slightly decreased at 7 wt%. For all other studied salts (MgCl_2 , CaCl_2 , Na_2SO_4), the rejection coefficient decreased with an increase in the content of PEG units in the triblock copolymer and an increase in the triblock copolymer concentration in the casting solution from 3 to 7 wt% (Figure 3b).

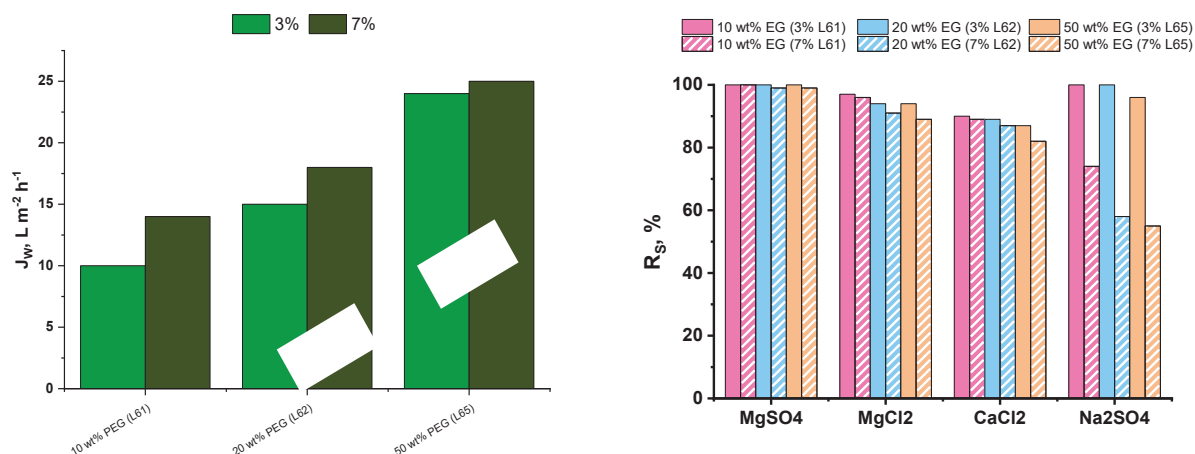


Figure 3. Dependence of the water flux (a) and the salt rejection coefficient (b) of nanofiltration composite PPSU/Pluronic/PA membranes on the content of PEG units in the PEG-PPG-PEG triblock copolymer. Nanofiltration conditions: $\Delta P = 5$ atm, stirring, room temperature.

It was found that for sodium sulfate, a very strong decrease in the retention coefficient was observed with an increase in the concentration of the block copolymer in the casting solution.

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