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# Fabrication of Hydrophobic PET Track-Etched Membranes using 2,2,3,3,4,4,4-Heptafluorobutyl Methacrylate for Water Desalination by Membrane Distillation

The world is currently facing a drinking water problem. Human activity, climate change and pollution of existing water bodies are exacerbating the problem. The scientists around the world are currently trying to purify water using effective and inexpensive methods. One such method is membrane distillation. Membrane distillation is a versatile thermally driven membrane separation process. This method of water purification has the potential to remove salts and other non-volatile components. The work is concerned with the desalination of salt solutions by membrane distillation using ion-track membranes based on polyethylene terephthalate (PET). PET ion-track membranes (PET TMs) were modified by photoinitiated graft polymerization of 2,2,3,3,4,4,4-heptafluorobutyl methacrylate (HFBMA) to make them hydrophobic. Optimal polymerization conditions (monomer concentration, reaction time) were determined, which led to an increase of water CA from 51 to 105°. The obtained membranes were used to purify the solution from NaCl. The effect of salt concentration as well as membrane properties on performance and degree of purification was studied. The results show that large pore size PET TMs modified with HFBMA has the potential to desalinate water in an efficient manner.

*Keywords*: Ion-track membranes, membrane distillation, UV-initiated grafting, poly(ethylene terephthalate), water desalination, fluorine-containing compounds.

## *Introduction*

Water plays a vital role in sustaining life on Earth. Although most of the planet is made up of water, but water scarcity is a major concern for the world's population [1]. Fresh water, which is essential for the survival of plants and mammals, including humans, accounts for only 3 % of the hydrosphere. The rest is salt water, which is not suitable for human consumption [2]. Population growth, rapid industrial development, urbanization and climate change are all increasing the demand for water and exacerbating the problem of pollution of available water bodies. All of these factors contribute significantly to the global water deficit. The search for effective and affordable methods of desalination is urgent [3].

A significant part of the Earth is made up of salt water. There is an urgent need to desalinate this water by removing salts and minerals [4]. There are currently several methods of water treatment reverse osmosis, nanofiltration, thermal distillation and membrane distillation (MD) and more [5, 6]. Among all these methods, membrane distillation has several advantages, including operation at low temperatures and hydrostatic pressures, high water recovery, high salt rejection (especially those with a salinity between 70 and 300 g salt per kg solution), less sensitivity to membrane fouling, and the potential for pollutant removal and usage of renewable energy resources. MD has realized several types [7] and successfully applied in many fields, such as purification of sea water, industrial and mining effluents from heavy metals, dyes, radioactive waste, acid solutions [8–12].

As mentioned above, the main characteristics of MD membranes are porosity and hydrophobicity. As materials with high suitability for MD applications, polymeric, inorganic and ceramic membranes have attracted much attention [13]. Polymeric membranes can be easily modified. They have low thermal conductivity, typically in the range of 0.1–0.5 $Wm^{-1}\cdot K^{-1}$. In general, MD membranes can be produced by track etching, sintering, phase inversion, electrospinning, etc. In addition, several types of membranes are produced by a combination of the abovementioned methods. MD requires membranes with specific characteristics such as high LEP, optimal thermal conductivity, stability, non-fouling properties, superior permeability as well as high purification degree [14].

Ion-track membranes (TMs) have these characteristics. TMs have ~~a~~ unique properties and structure that includes microscopic channels through which vapour transport occurs [15, 16]. These membranes provide high separation efficiency, which is particularly important in desalination processes [17]. Various ion-track membranes (TMs), including PVDF, PE, PDMS, PP, PTFE and PET have been used for membrane distillation [18].

In our previous studies [9, 19], PET TMs were modified with styrene and fluorosilane to small pore size by photoinitiated graft polymerization. MD has successfully used these membranes for both water desalination and the decontamination of low-level liquid radioactive waste. This article presents the preparation of large pore size hydrophobic PET TMs by grafting 2,2,3,3,4,4,4-heptafluorobutyl methacrylate (HFBMA) and their use for water desalination. The unique properties of fluorine containing compounds explain the choice of this monomer. They have low surface energy, their chemical backbone formed by stable carbon-fluorine bonds (~485 kJ $mol^{-1}$), and the particular electronic structure of fluorine, is characterized by high electronegativity, low polarizability and a small van del Waals radius (1.32 Å). As a result, there are weak dispersion interactions on the surface of fluorocarbons, and the wettability and surface tension of fluoropolymers are very low [20].

## *Experimental*

*Reagents*

2,2,3,3,4,4,4-heptafluorobutyl methacrylate (HFBMA) (97 %), N,N-dimethylformamide (99,9 %) (DMF), benzophenone (BP) (97 %), NaCl, ethanol (98 %), 2-propanol (99,8 %). All monomers were passed through a chromatographic column to remove the inhibitor. All NaCl solutions were prepared in deionized water (18.2 MΩ).

*PET TMs Preparation and Graft Polymerization of HFBMA*

The PET TMs were obtained by irradiating Hostaphan® brand PET films (Mitsubishi polyester film, Germany) with a thickness of 12 μm using Kr ions at an energy of 1.75 MeV/nucleon and an ion fluence of $1\times10^6$ ions/cm². This was conducted using the DC-60 ion accelerator (Astana Branch of the Institute of Nuclear Physics of the Republic of Kazakhstan). Irradiated PET film was etched in 2.2 M NaOH solution at 85 °C at 6–20 min. After chemical etching, the samples were washed in acetic acid and deionized water. Membranes were obtained with pore density of $1\times10^6$ pores/$cm^2$ and different pore sizes depending of etching time.

The samples were then immersed in the initiator (5 % BP in DMF) for 24 h, washed in ethanol and dried in air. The amount of BP adsorbed on the surface of PET TeMs was determined by UV-vis-spectroscopy at 253 nm [21]. According to the calibration curve, the concentration of BP was 580 μmol/g. This value was kept constant. After PET TMs were placed in a solution of HFBMA in 2-propanol. HFBMA concentrations ranged from 1–10 %. The reaction mixture was flushed with Ar to remove the dissolved oxygen. Graft polymerization was carried out using OSRAM Ultra Vitalux E27 (UVA: 315–400 nm, 13.6 W; UVB: 280–315 nm, 3.0 W) for 30–60 min. After reaction the samples were washed in 2-propanol and water and dried.

*Methods of Characterization of the PET TeMs*

Chemical changes before and after modification were measured by Fourier Transform Infrared (FTIR) spectrometer (InfraLUM FT-08) with ATR accessory (GradiATR, PIKE). Spectra were recorded in the range of 400–4000 $cm^{-1}$, with 20 scans and a resolution of 2 $cm^{-1}$ at room temperature.

The morphology and elemental composition of the membrane surface was analyzed using a Hitachi TM 3030 with a Bruker XFlash MIN SVE EDX instrument at 15 kV acceleration voltage. The EDX spectrum is selected in 120 seconds. The sample is coated with a layer of gold prior to analysis. The results are presented as an average based on three data points.

CA was assessed by the static drop method and measured at five locations on the sample at room temperature.

*Direct Contact Membrane Distillation*

Direct Contact Membrane Distillation (DCMD) has been applied for water desalination. Figure 1 shows a scheme of the DCMD.

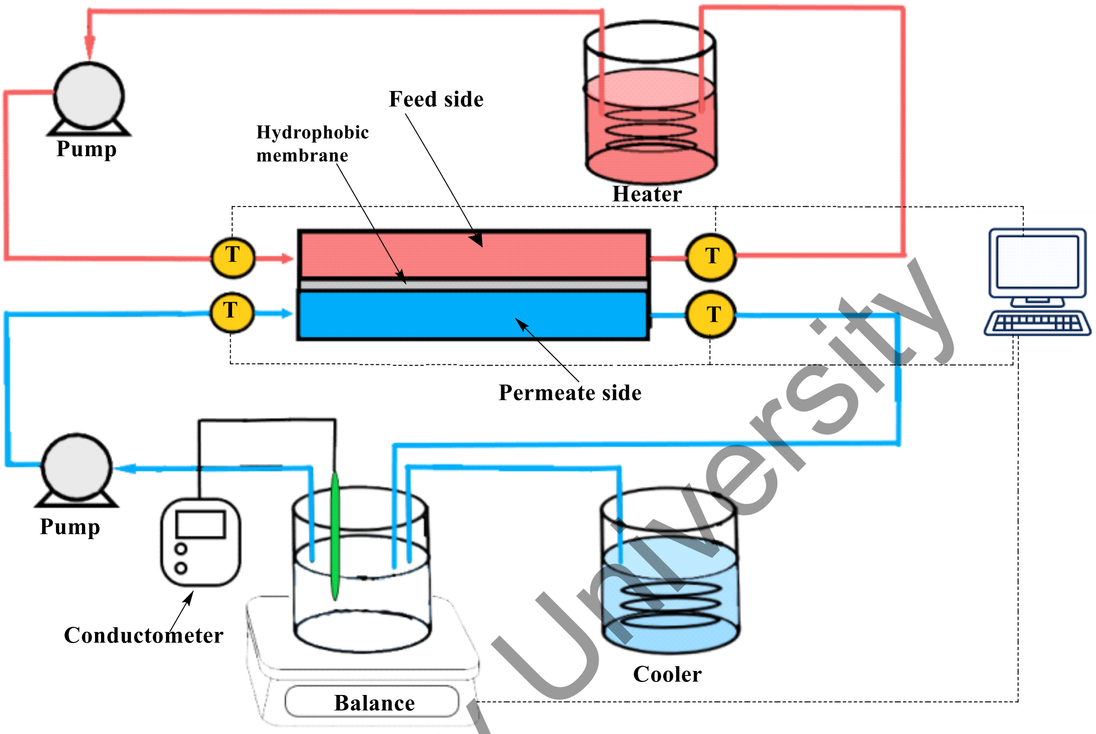


Figure 1. DCMD scheme

Type–T thermocouples were used to control the temperature at the inlets and outlets of the membrane cell, temperature differential was maintained at 70 °C. Peristaltic pumps were used to control permeate (13.5 ± 0.3 L/h) and feed flow (27.3 ± 0.3 L/h). Every 30 seconds, the collected liquid was weighed (± 0.01 g). The degree of purification was controlled by conductimetry measurements. The performance and degree of purification were computed based on the equations set out in [9].

### *Results and Discussion*

The modification of PET TMs surfaces were functionalized according to the scheme presented in Figure 2. During the process of chemical etching, the hydrolysis of ester groups in the PET film led to the breakdown of its backbone. As a result, carboxylic and hydroxyl groups at the chain ends, providing reactive sites for monomer attachment during polymerization.

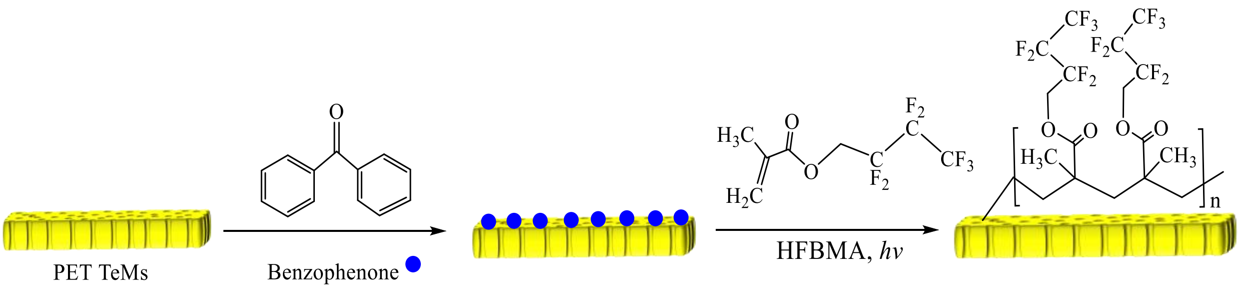


Figure 2. Graft polymerization of HFBMA

The polymerization process was influenced by monomer concentration, polymerization time and distance from the UV-source. The effect of the distance from the UV-lamp on the polymerization process was studied. When the distance exceeded 7 cm, polymerization did not occur, as no characteristic peaks were observed in the FTIR-spectra. As the distance decreased, the solvent was rapidly volatilized. Consequently, 7 cm was identified as the optimal distance.

Qualitative analysis of the obtained PET TMs samples was conducted using FTIR spectroscopy. Figure 3 depicts the FTIR spectroscopy results of the PET TMs before and after grafting. Before graft polymerization, the FTIR spectra exhibit the fluctuations, which are consistent with the data in work [19]. After modification with monomer concentration of 7 and 10 % in the FTIR spectra show the presence of peaks at 910 cm$^{-1}$ belonging to the C-F$_2$ group and 1190 cm$^{-1}$ belonging to the C-F group [22, 23].

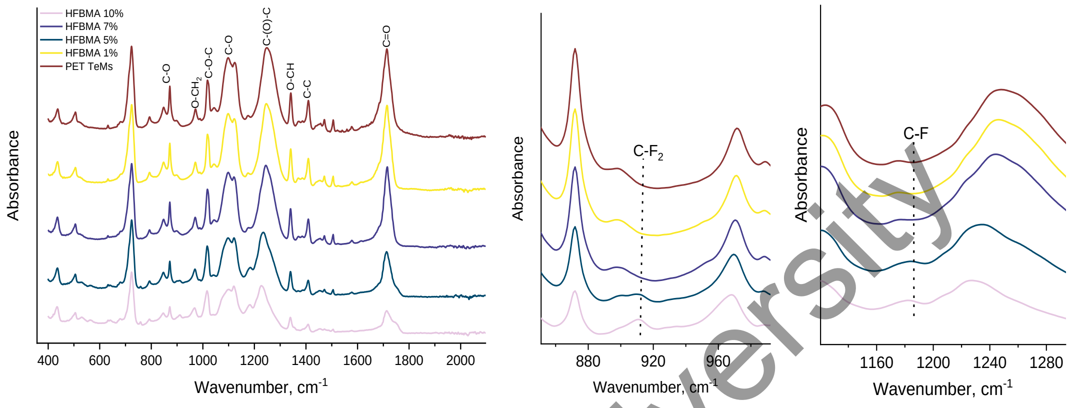
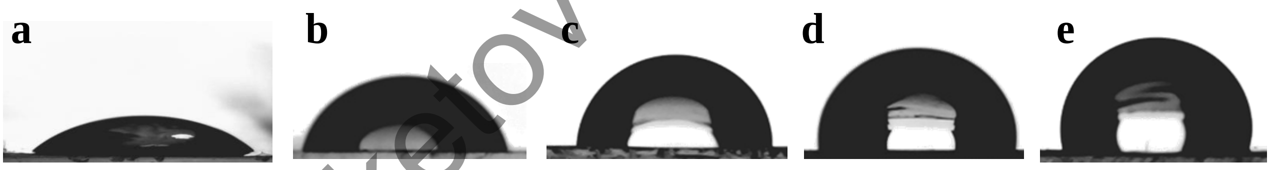


Figure 3. FTIR spectra of initial and modified PET TMs at different monomer concentration

The water repellent effects of the PET TMs were evaluated by measuring CA for each grafted sample (Fig. 4). The chemical composition and surface roughness have a significant effect on the CA.



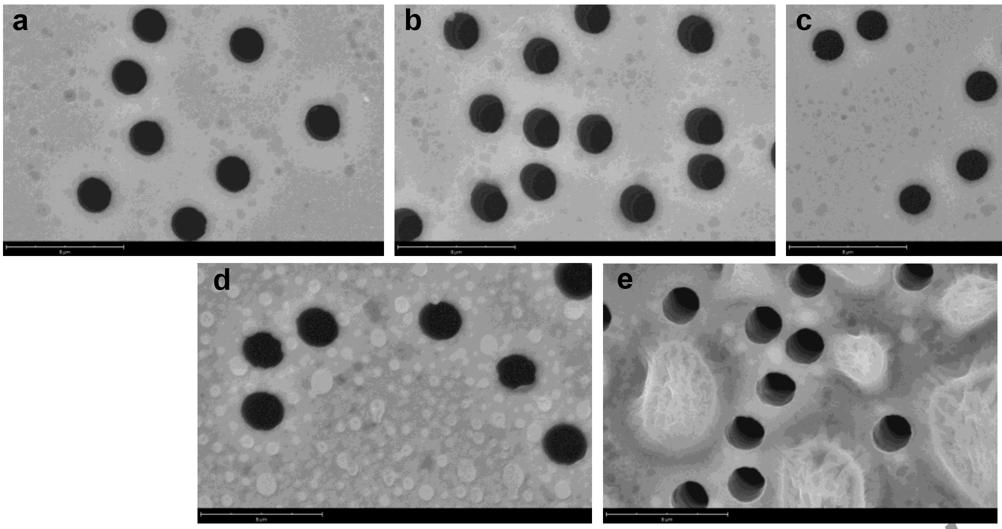
51°±3 73º±3 84º±5 85º±3 105º±2

Figure 4. CA for initial PET TMs (*a*) and grafted PET TMs for 60 min
at different concentrations (1 % (*b*), 5 % (*c*), 7 % (*d*) and 10 % (*e*))

As shown in Figure 4, the membrane surface becomes hydrophobic with increasing monomer concentration. The CA for the sample at a HFBMA concentration of 10 % averaged 105º±2º, and the water droplet did not spread for a long time. As the monomer concentration decreased, the water droplet spread faster and seeped through the membrane. The presence of HFBMA on the surface leads to increased surface roughness of PET TeMs, which we can observe using SEM (Fig. 5).

SEM images show that the PET TMs surface is uniform at 1 % and 7 % monomer concentration. The pores are open and not clogged with monomer, pore diameter decreases by 10–40 nm. At a HFBMA concentration of 10 %, a thick polymer layer forms, and the pores of the TM are not clogged with polymer. The pore diameter decreases by ~100 nm. The surface exhibits an uneven distribution of the polymer layer, characterized by polymer “islands” in certain regions that display high resistance to solvents. These islands increase roughness and form a hydrophobic layer.

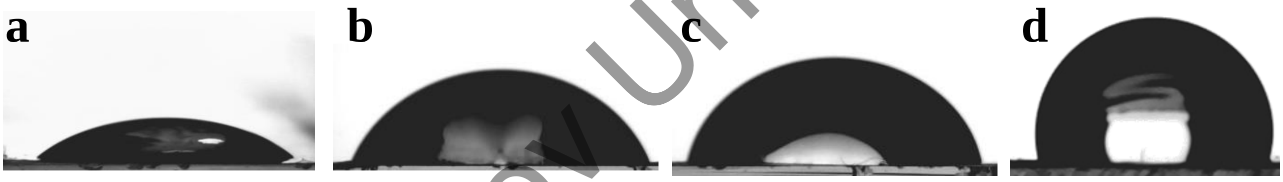
Having obtained these results, the effect of grafting time on the photoinitiated graft polymerization process was studied. 10 % monomer was chosen as the optimum monomer concentration. Following the modification, the emergence of peaks at 910 cm$^{-1}$ (C-F$_2$ ring) and 1190 cm$^{-1}$ (C-F ring) was detected on the FTIR spectra in various reaction time. With increasing polymerization time and monomer concentration, formation of homopolymer was observed, which filled the pores of the TMs.



*a* — initial PET TMs; *b* — 1 % HFBMA; *c* — 7 % HFBMA; *d* — 10 % HFBMA (side 1); *e* — 10% HFBMA (side 2)

Figure 5. SEM microphotographs of PET TMs

As the grafting time increases, the CA changes from 59º±2º at 30 minutes to 105º±2º at 60 minutes. Figure 6 depicts the CA images of both unmodified and modified PET TMs over the time span from 30 to 60 min. The TMs surface becomes hydrophobic and a drop of water at a reaction time of 60 min does not spread for a long time. Conversely, at shorter polymerization times, the surface remains water-insoluble, and the drop spreads rapidly and penetrates through the membrane's pores.



51°±3 59°±2 76°±3 105°±3

*a* — initial PET TeMs; *b* — 30 min; *c* — 45 min; *d* — 60 min

Figure 6. Effect of polymerization time on CA

The elemental composition was studied using EDX. According to the EDX analysis, the concentration of fluorine increases with both the reaction time and the monomer concentration. The maximum fluorine concentration is recorded in the sample where the monomer concentration is 10 %, and the polymerization time is 60 minutes.

The burst strength was evaluated at a pressure that would damage a circular sample of 1 cm$^2$ surface. Burst strength for initial PET TMs was more than >0.449 MPa. For modified membranes with pore size of 640 nm, burst strength is 0.425 MPa, for 960 nm = 0.438 MPa and for 1290 nm more than >0.449 MPa (Table).

Table

**Elemental analysis, CA and pore size were obtained for PET TMs under different grafting parameters**

| № sample | Grafting time, min | HFBMA concentration, % | CA, °±3° | Pore diameter (from SEM analysis), nm | Concentration of F, % |
|---|---|---|---|---|---|
| 1 | 0 | – | 51 | 2473±121 | – |
| 2 | 30 | 10 | 59 | 2471±94 | 0.89±0.46 |
| 3 | 45 | 10 | 76 | 2425±64 | 1.018±0.25 |
| 4 | 60 | 10 | 105 | 2399±91 | 13.00±1.85 |
| 5 | 60 | 7 | 85 | 2419±95 | 0.44±0.15 |
| 6 | 60 | 1 | 73 | 2463±149 | 0.3±0.1 |

Thus, according to the results of the experiment, the optimal conditions for graft polymerization of HFBMA are the distance from the UV-lamp 7 cm, HFBMA concentration 10 % and reaction time 60 min. The formation of a polymer layer on the surface of PET TMs was demonstrated by EDX, FTIR spectroscopy, SEM images and CA.

Obtained hydrophobic PET TMs at optimal grafted parameters were used for water desalination process by membrane distillation. Membranes with different pore sizes (640, 960, 1290 and 2400 nm) were taken for the process. In order to simulate practical conditions, salt concentrations were gradually increased from 7.5 to 30 g/L. After each experiment, the membranes were washed in warm water for 12 hours to remove salt residues. However, these membranes did not remove salt from the water because of LEP value is not high enough. The results of water desalination using modified membranes are shown in Figure 7.

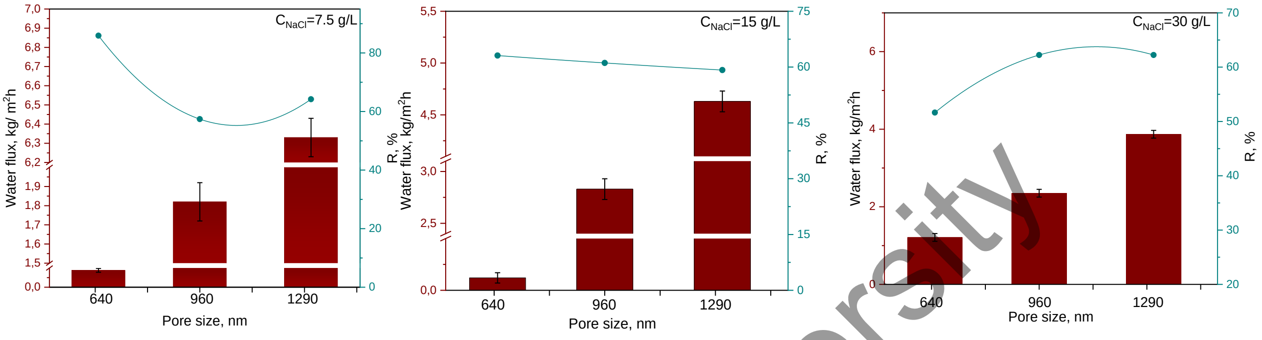


Figure 7. Effects of pore diameter on MD performance at different NaCl concentrations

The data illustrated in the graphs indicate the effect of varying NaCl concentration on water flux and degree of salt rejection. A decrease in water flux is evident with an increase in pore diameter from 600 to 1200 nm. Furthermore, a reduction in water flow is observed with the rise in NaCl concentration from 7.5 to 30 g/L. Increasing the size of pores in the membrane enhances the available space for water passage, leading to a higher rate of water flow through the membrane. This is achieved by reducing hydraulic resistance and augmenting the membrane's surface area for water passage. In addition, in highly concentrated solutions there is a decrease in water activity and a change in viscosity which affect the water flux [24, 25]. The pore diameter has a strong effect on the salt rejection, as can be seen in Figure 8. TMs with pore sizes of 640, 960 and 1290 nm have a salt rejection of 85.9 %, 63.5 % and 59.2 % respectively. This phenomenon is due to the non-uniformity of the grafted layer and thus insufficient hydrophobicity of the membrane. As a result, salts that were originally intended to be retained by the membrane begin to penetrate through it, reducing the salt rejection [9].

## *Conclusions*

In this study, a water-repellent membrane was developed by polymerization of HFBMA onto porous PET TMs for desalination via DCMD. The optimal parameters for the photoinitiated graft polymerization of HFBMA were determined as a UV lamp distance of 7 cm, a monomer concentration of 10 %, and a polymerization time of 60 min. The PET TMs obtained were analyzed using FTIR spectroscopy, SEM and CA measurements. The polymer layer deposited increased surface roughness, resulting in hydrophobic properties with a water contact angle of 105°±3°. This hydrophobic coating conferred physicochemical stability and anti-wetting properties to the fabricated PET TMs, making them suitable for membrane distillation. PET TMs with larger pore diameters exhibited a lower degree of salt rejection but demonstrated high water flux due to an increased likelihood of liquid permeation. The most significant correlation between water flux and salt rejection was observed for PET TMs with a pore diameter of 650 nm.

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All authors contributed to the preparation of the manuscript. All authors approved the final version of the manuscript. CRediT: **Aigerim Khairatovna Shakayeva** investigation, writing original draft, data curation, visualization; **Arman Bakhytzhanovich Yeszhanov** data curation, formal analysis, investigation; **Ainash Turlybekovna. Zhumazhanova** investigation, data curation; **Ilya Vladimirovich Korolkov** — supervision, writing — review & editing, project administration; **Maxim Vladimirovich Zdorovets** — funding acquisition, data curation.

## *Conflicts of Interest*

The authors declare that they had no known competing financial interests or personal relationships that might appear to influence the work reported in this article.

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