

Effect of PEG additives on properties and morphologies of polyetherimide membranes prepared by phase inversion

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Abstract This study investigated the effect of poly(ethylene glycol) (PEG) additive as a pore-former on the structure formation of membranes and their permeation properties connected with the changes in thermodynamic and kinetic properties in the phase inversion process. The membranes were prepared by using polyetherimide/*N*-methyl-2-pyrrolidone/PEG (PEI/NMP/PEG) casting solution and water coagulant. The resulting membranes, prepared by changing the ratio of PEG to PEI, were characterized by scanning electron microscope (SEM) observations, measurements of water flux and γ -globin rejection. The thermodynamic and kinetic properties of the membrane-forming system were studied through viscosity. The pore radius distribution curves were especially obtained by differential scanning calorimetry (DSC). Furthermore, the membranes were characterized for pure water flux and rejection of solute and by SEM observation. The filtration results agreed well with the SEM observations. As expected, PEG with a fixed molecular weight (PEG 600) acted as a pore forming agent, and membrane porosity increased as the PEG content of the casting solution increased.

Keywords phase inversion, polyetherimide, poly(ethylene glycol), additive

1 Introduction

Phase inversion has been found to be a versatile technique for asymmetric membrane preparation because the casting solution and the formation conditions can be varied widely to get the desired membrane structures by changing the main factors, such as the composition of the polymer solution (additives, etc.), the solvent evaporation temperature, and

the evaporation time, as well as the nature and temperature of the coagulation media [1–5]. The addition of additive as a third component to a casting solution has been one of the important techniques used in membrane preparation, and the role of additive has been reported as a pore-forming agent that enhances permeation properties [6–8]. Principally, such additives can be either organic or inorganic, as long as they are of lower volatility than the solvent and of proper solubility for the gelatin medium. Thus, the commonly used additives are methyl cellulose, glycerine, poly-(vinyl pyrrolidone)(PVP), poly(ethylene glycol) (PEG), water, LiCl, and ZnCl₂ [6–9]. It may be more reasonable to explain the organic and inorganic additive effect on the membrane formation using the thermodynamic and kinetic terms of the system such as coagulation value, viscosity, precipitation type, precipitation rate, diffusion coefficient, etc. However, studies with such a viewpoint have been rarely reported because there exist complexities in the theoretical description and quantitative analysis of the thermodynamics and precipitation kinetics of these multi-component systems [10–14].

Adding additives, such as PEG, was proposed to increase the hydrophilic property of the membrane [15–17] and the diffusive transport properties of solute through the ultrafiltration membrane. The latest research has shown that PEG additives in cellulose acetate ultrafiltration membrane influenced the membrane characteristic in terms of pore size, permeate flux and the protein rejection rates [18].

Although there has been work reported using PEG as additives, such work involved mostly polymeric systems such cellulose acetate (CA), polysulfone (PSf), polyethersulfone (PES) and polyetherimide (PEI) except for the use of PEG 600 for PEI membranes. There is yet no report regarding the effect of pore size distribution on the performance of ultrafiltration (UF) membranes. PEI has been used as membrane material due to its excellent chemical resistance, good thermal stability and mechanical properties, so it is more suitable for liquid separation and

can be used in water treatment. In this study, the effect of PEG600 additive on viscosity, pure water permeation, solute separation, flux and membrane morphology were investigated and are discussed in detail. The concentration influence of PEG additive was also studied on PEI ultrafiltration membrane performance by changing the concentration of additive from 0 wt-% to 8 wt-% in the casting solution. In addition, the PEI membranes with PEG additive were characterized by using differential scanning calorimetry (DSC) where the pore radius distribution curves were obtained.

2 Experimental

2.1 Materials

PEI (Ultem®-1000), as shown in Fig. 1, was purchased from General Electric (USA). All other chemicals used in the experiments were of reagent grade and were used without any further purification. N-methyl pyrrolidone (NMP) was used as a solvent, butyrolactone (GBL) was used as the non-solvent, and PEG with a molecular weight 600 was used as the nonsolvent additive. These chemicals were obtained from Beijing Yili Fine Chemicals Co. Ltd., Beijing, China.

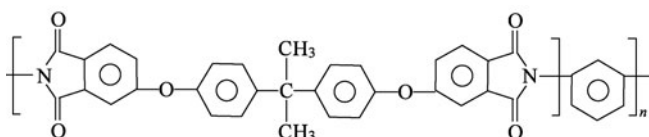


Fig. 1 The chemical structure of PEI polymer

2.2 Membrane preparation

The preparation method was the same as that of the phase inversion method employed in earlier work [19]. The casting environment relative humidity and temperature were maintained to prepare membranes with better physical properties such as homogeneity, thickness and morphology. Fixed weight percent of PEI was dissolved at 80°C, with stirring, in different mixtures of NMP and the additive. The weight ratio of the additive to NMP was changed from 0/80 to 8/72. To remove air bubbles, the homogeneous casting solution was kept at room temperature for 24 h under vacuum. After being degassed, the casting solution was cast on a polyester non-woven fabric with a scraper having 150 μm thickness, and verified with a micrometer having precision of 0.2 μm. The nascent membrane was dried for 10s at (25±1)°C. Then the solvent present in the cast membrane was gently immersed into the gelation bath for at least 2 hours for complete precipitation and formation of membranes. The membranes were removed from the gelation bath and washed thoroughly with DI water to

remove NMP and surfactant. The membranes were subsequently stored in 0.1% of formalin solution to prevent microbial growth. The casting and gelation conditions were kept constant throughout, since the thermodynamic conditions would largely affect the morphology and performance of the resulting membranes.

2.3 Scanning electron microscope (SEM) observations

The cross-sections of the morphology of membranes were observed using SEM. For this purpose, the membrane samples were dried and then fractured cryogenically in liquid nitrogen before mounting on sample stubs. The membranes were mounted on a brass plate using double-sided adhesion tape in a lateral position. The samples were then sputtered with a thin layer of gold using a sputtering apparatus. After gold sputtering, the cross-sectional morphologies of the asymmetric membranes were observed with JSM 6301F SEM (Japanese).

2.4 Determination of viscosity

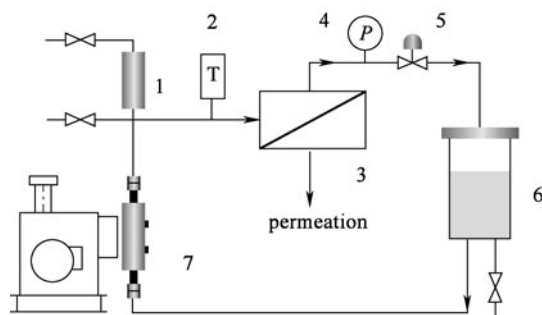
Viscosity of the casting solution can severely hinder the exchange rate of solvent and nonsolvent during the phase inversion process, and therefore, it can be used as an important parameter to influence the precipitation kinetics and thus, the formation of resulting membrane morphology. The casting solution viscosity was measured using a Brookfield DV-II + CP (Brookfield, USA) viscometer in a 25°C water bath.

2.5 Pore size determination

The freezing temperature of water held in a porous membrane was determined by DSC measurements, i.e., thermoporometry. The DSC apparatus was a Seiko DSC 6200 differential scanning calorimeter equipped with a liquid nitrogen-cooling accessory and calibrated with indium. A sample of about 10–20 mg was put in an aluminum pan and one drop of deionized water was added to maintain the sample in an excess of water. Thereafter, the pan was sealed and cooled down to –15°C at a rate of 1°C/min, which is slow enough to maintain thermodynamic equilibrium. From DSC thermograms and related equations [20], the pore radius distribution curves were obtained.

2.6 Pure water permeation experiments

The pure water flux and solute rejection tests, as shown in Fig. 2, were conducted with a cross-flow membrane module, which can offer an active membrane area of 22.4 cm², and was made of stainless steel that could endure a pressure difference of 1.0 MPa. Deionized (DI) water was used to measure the pure water flux of the membrane. The prepared membranes were cut into desired size needed



1 cushioning; 2 electric thermometer; 3 membrane model;
4 pressure gauge; 5 valve of adjusting pressure; 6 feed tank;
7 controlled volume pump

Fig. 2 Schematic flow diagram of membrane evaluating equipment

for fixing them up in the ultrafiltration kit, and initially pressurized with distilled water at 0.5 MPa for 6 h. The flux generally declined initially and attained steady state after 4–5 h of compaction in order to stabilize the membranes. Then the water flux was repeatedly measured by collection of the filtrate for given periods until a stable value of the permeation flux (J_w) was observed. Water flux was calculated with the following Eq. (1):

$$J_w = \frac{W}{A \cdot \Delta t}, \quad (1)$$

where W is the total volume of the permeate penetrating through the membrane during the experiment, A is the membrane area, and Δt is the operation time.

2.7 Separation experiments

Molecular weight cut off (MWCO) is a pore characteristic of membranes and is related to rejection for a given molecular weight of a solute. The molecular weight has a linear relationship with the pore radius or pore size of a membrane. In general, the MWCO of a membrane is determined by the identification of an inert solute, which has the lowest molecular weight and has a solute rejection of 80%–100% in steady state UF experiments. Therefore, the solute rejection rate was measured with the γ -globin (average molecular weight 157000 g/mol) as the retentate. All the protein solutions were prepared individually at a concentration of 0.1 wt-% using DI water. The permeate protein concentration was estimated using an UV-Visible spectrophotometer (Unic, Model UV-2102). The solute rejection (R) was determined using Eq. (2)

$$R = 1 - \frac{C_p}{C_f}, \quad (2)$$

where C_p and C_f are the retentate concentration in the permeate and in the feed, respectively.

3 Results and discussion

3.1 SEM photographs of PEI membranes

The SEM photographs of cross-sectional images of the PEI ultrafiltration membrane without additive and with PEG additive are shown in Fig. 3. It can be observed from Fig. 3(a) that the PEI ultrafiltration membrane without additive had a finger like structure and a thick asymmetric layer. Figures 3(b) and 3(c) show that the macrovoids increased in size and the asymmetric layer thickness decreased when PEG600 was added to the casting solution. Pure water permeation is strongly dependent on the top layer and sub layer of the membranes. This probably explained the low pure water permeation and flux rate for the PEI ultrafiltration membrane containing PEG600 as additive. The thin asymmetric layer probably explained the excellent improvement in the rejection rate, but the thick spongy structure created resistance, thus resulting in rather low flux rates.

As can be seen in Fig. 3(c), the size and shape of macrovoids are different from Figs. 3(a) and (b) when PEI content reached 23 wt-%. As can be seen in Fig. 3(c), the size of macrovoids gradually changed in structure from a finger like shape to elongated microvoids. Addition of PEG600 in the casting solution increased the number and size of macrovoids, especially from PEG 6 wt-%–8 wt-% in Fig. 3(c). The results revealed that addition of PEG to the casting solution influences the shape and size of macrovoids in the membranes.

In this study, it was observed that as the concentration of PEG600 increased in the casting solution the size of microvoids increased and the presence of the spongy top layer was observed, which contributed to high flux resistance and thus explained the low flux exhibited but excellent solute separation performance. Addition of PEG600 as additive helped to improve the mechanical strength and increased the solute separation although the flux rate decreased. However, the opposite effect of PEG200 as compared to PEG600 occurred because of their different viscosities. It has been reported that when the concentration of PEG200 increases, its viscosity decreases sharply in the PEI/NMP solution [21].

3.2 Pore size distribution

Figure 4 shows the effects of additive content on pore size and distribution of PEI membranes. From Fig. 4, it can be observed that the virgin PEI-UF membranes had pore radius ranging from 12.6–12.8 nm. It can be also noticed that the average pore radius of the PEI membranes became larger and larger with the increasing additive content, and pore distribution became wider. Furthermore, from Fig. 4, it can be seen that the pore radius changed remarkably compared with virgin PEI membranes even if a little

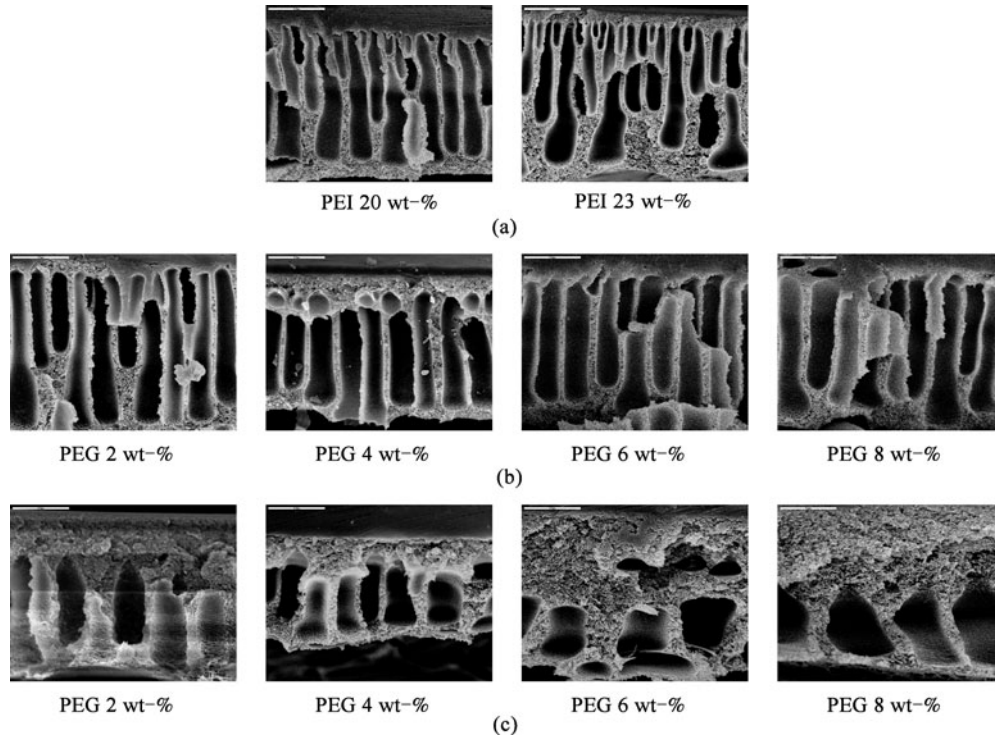


Fig. 3 Influence of PEI and PEG concentration on cross-section structure of the membranes
 (a) SEM cross-section images of PEI membranes without PEG in dope formulation; (b) SEM cross-section images of PEI (20 wt-%) membranes with PEG additive; (c) SEM cross-section images of PEI (23 wt-%) membranes with PEG additive

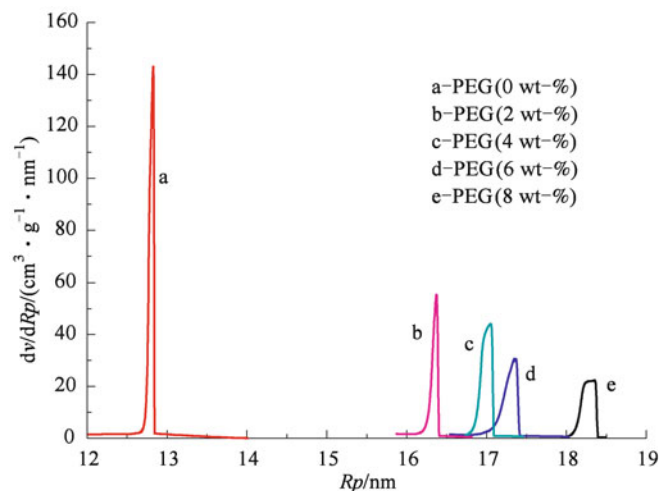


Fig. 4 DSC result of PEI membranes without and with PEG additive (PEI 20 wt-%)

content of additive and the pore radius changed obscurely, as the additive content ranged from 4 wt-% to 8 wt-%.

It should be pointed out that pore sizes determined by the DSC technique seem to be larger than the real values [22,23]. However, these results from DSC measurement are a valuable tool in understanding plasma graft actions and controlling the membrane structure. An investigation on accurate measurement of membrane pore sizes is in progress.

3.3 Influence of PEG and PEI concentration on viscosity of the casting solution

The influence of PEG concentration on viscosity of the casting solution is shown in Fig. 5. It was observed that PEG600 additive had significant influence on the viscosity of the casting solution. Apparently, viscosity of the casting solution increased as the concentration of PEG increased from 0 wt-% to 8 wt-%. Furthermore, as PEI reached

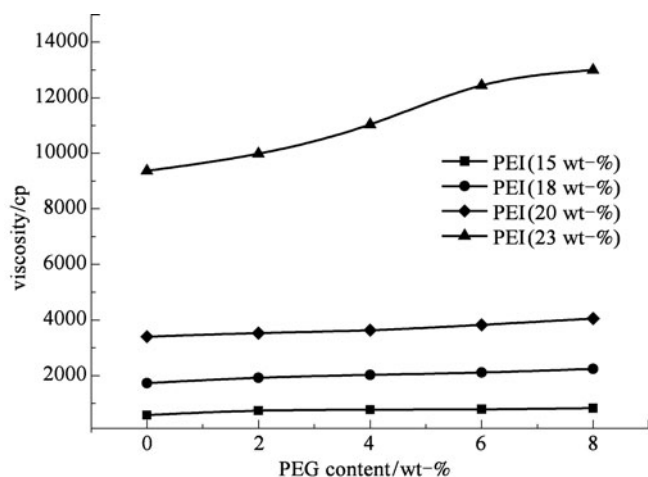


Fig. 5 Influence of PEG concentration on viscosity of the casting solution

23 wt-%, the viscosity of the casting solution increased obviously with the increasing PEG additive. These results could be explained by the membrane forming system's thermodynamic and kinetic properties, which can be assessed by coagulation value and viscosity.

Moreover, Fig. 5 indicates the influence of PEI concentration on viscosity of the casting solution. The most important parameter for tailoring membrane properties that has been identified is polymer concentration. In addition, the solvent ratio also plays an important role along with polymer concentration during membrane formation. The simultaneous adjustment of these two key parameters allows for an increase in the viscosity of the dope solution without significant loss in productivity and selectivity. In order to induce chain entanglement and therefore reduce the formation of the macrovoid in the skin layer, a higher polymer concentration is required. Therefore, the separation capability (rejection) of the membrane will be increased but the permeability (flux) will be reduced. The addition of more polymers to the dope solution increases its viscosity and tends to promote selective but less productive membranes.

In view of this, special attention was given to the control of the morphology and performance of the formed membrane by changing the ratio of PEG600 to NMP in the casting solution, and it was interpreted by using coagulation value, viscosity. The flux of aqueous solvent mixtures was also observed through PEI membranes with various pore sizes.

3.4 Influence of PEG concentration on pure water flux

The effect of additive concentration on flux is presented in Fig. 6, and the concentration of PEG was from 0 wt-% to 8 wt-%. Figure 6 clearly shows that pure water flux was significantly affected by PEG added to the casting solution and shows that the pure water flux of PEI membranes

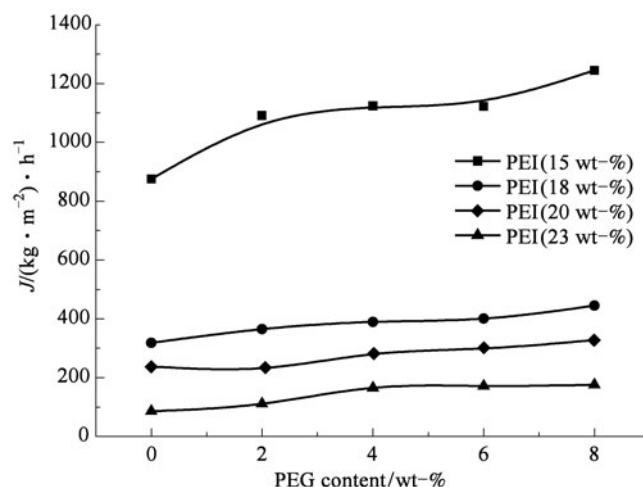


Fig. 6 Influence of PEG concentration on pure water flux

increased with increasing PEG concentration. Apparently, the results indicate that addition of PEG additive with different concentrations influences the formation of membrane pore size. Ultrafiltration membrane permeability is conceptually related to its pores [24]. According to Darcy's law, the flux of porous membranes mainly depends on the solution viscosity. However, with a decreasing membrane pore size, the matrix of the membrane is affected by the solvent (swelling).

Moreover, due to the small pore size, other physical properties like molar volume and surface tension can alter the membrane flux. Many researchers have investigated the effect of solvent on the flux of asymmetric or composite membranes [25,26]. Furthermore, as the PEI content came to 15 wt-%, pure water flux changed remarkably with the increase in PEG additive. This result agreed well with the SEM photographs of cross-sectional images of the PEI ultrafiltration membrane.

3.5 Influence of PEG and PEI concentration on rejection

The γ -globin separation for PEI ultrafiltration membranes with PEG additive is depicted in Fig. 7. By definition, molecular weight cut off (MWCO) is molecular weight that is 90% rejected by the membrane [27]. It was observed that the γ -globin separation increased with increase in molecular weight of solutes. MWCO is a pore characteristic of the membranes and it is related to rejection for a given molecular weight of solutes. The molecular weight cut off has a linear relationship with pore size of the membranes [27].

It was observed that all PEI ultrafiltration membranes show a diffuse profile. As can be seen in Fig. 7, it is clearly demonstrated that PEI ultrafiltration membranes with PEG600 as additive exhibit higher MWCO compared to PEI ultrafiltration membranes without additive.

The γ -globin separation for PEI ultrafiltration mem-

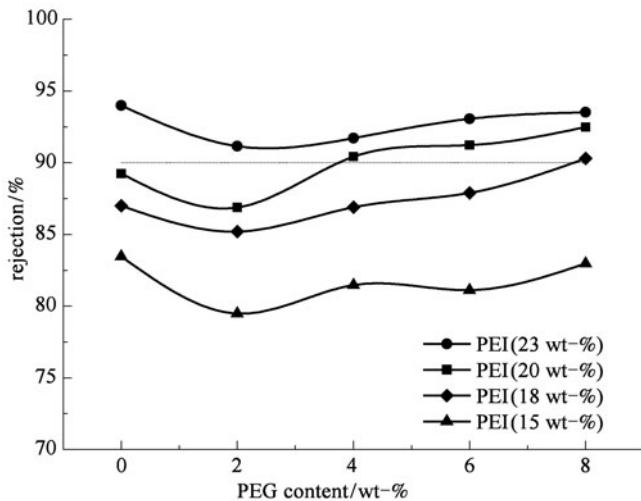


Fig. 7 Influence of PEG concentration on rejection

branes with PEG additive is presented in Fig. 8. It was observed that the γ -globin separation increased with increase in molecular weight of solutes. Ultrafiltration membrane permeability is conceptually related to its pores. Furthermore, as the PEI content reached 15 wt-%, pure water flux changed remarkably with increasing PEG additive. This result agreed well with the SEM photographs of cross-sectional images of the PEI ultrafiltration membrane.

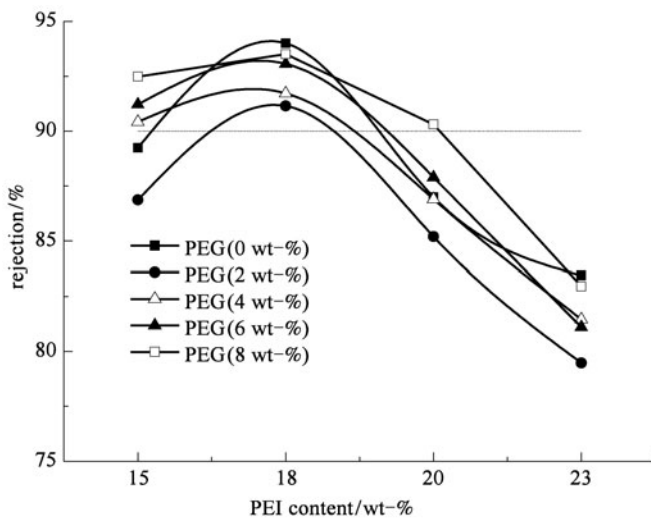


Fig. 8 Influence of PEG concentration and PEI concentration on rejection

4 Conclusions

Porous asymmetric membranes were prepared by the phase inversion technique, using PEI as the polymeric material

and PEG as the additive. The addition of additive into polymer solutions significantly alters membrane morphological structure, thus directly affecting membrane separation performance. SEM photographs indicated surface and membrane morphology changes with addition of different molecular weight additives in the casting solution. It can be concluded from DSC that the average pore radius of the PEI membranes became larger and larger with the increase in additive content and pore distribution becomes wider. As additive concentration is increased, the membranes possess a thinner top layer and larger membrane pore sizes. PEI ultrafiltration membranes with PEG 600 as additive exhibit higher MWCO compared to PES ultrafiltration membranes without additive. In addition, the number of membrane pores increase while the macrovoids disappear. The additive concentration has been proven to be one of the most influential parameters in membrane fabrication and needs careful attention if a better performing membrane is to be fabricated.

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