

## Preparation and modification of nano-porous polyimide (PI) membranes by UV photo-grafting process: Ultrafiltration and nanofiltration performance

Ahmad Rahimpour<sup>†</sup>

Faculty of Chemical Engineering, Babol University of Technology, Babol, Iran  
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**Abstract**—Polyimide (PI) membranes were prepared via non-solvent induced phase separation. The prepared PI membranes were modified by ultraviolet light (UV) and graft polymerization of hydrophilic acrylic and amino monomers in the absence and presence of benzophenone (BP) onto the membrane surface to introduce more hydrophilic and lower fouling membranes. Acrylic acid (AA) and 2-hydroxyethylmethacrylate (HEMA) as acrylic monomers, 1,3-phenylenediamine (mPDA) as amino monomer and BP as photo-initiator were used. The unmodified and modified PI membranes were characterized by degree of grafting (DG) and contact angle measurements. They were also characterized by their ultrafiltration performance with pure water and non-skim milk and nanofiltration performance with 500 ppm NaCl and MgSO<sub>4</sub> single solutions. The DG was increased with increasing monomer concentration, especially at presence of BP. The contact angle measurements indicated that hydrophilicity of PI membrane was improved after UV photo-grafting of hydrophilic monomers onto the membrane surface in all cases. The ultrafiltration results showed that the pure water fluxes and milk water permeation of PI membrane declined after monomer photo-grafting while the protein rejection was extremely increased. The decrease in permeability was remarkable in the presence of BP. The mean pore size of base and modified PI membranes ranged from 8.3 to 0.55 nm when calculated from the solute transport data. Moreover, the irreversible flux loss and flux recovery of PI membrane were modified by UV photo-grafting of hydrophilic monomers. All modified membranes showed considerable NaCl and MgSO<sub>4</sub> rejections. In addition, the membrane modified with mPDA at presence of BP showed highest NaCl and MgSO<sub>4</sub> rejections.

**Key words:** Polyimide Membrane, Modification, UV Photo-grafting, Hydrophilic Monomers, Ultrafiltration Performance, Nanofiltration Performance

### INTRODUCTION

Most polymeric membranes with asymmetric structures are prepared by non-solvent induced phase separation (immersion precipitation) [1,2]. In this process, an initially single-phase homogeneous polymer solution is cast onto a suitable substrate to form a thin film and is then immersed in a coagulation bath, which results in diffusive exchanges of solvent and nonsolvent and the solidification of the polymer. Polyimides (PI) are generally known as polymers with excellent thermal stability because of their high glass transition temperature. They are also chemically resistant, which in the past was quite problematic for processing purposes. Despite their excellent chemical and thermal resistance, relatively few examples exist in literature concerning preparation and modification of nano-porous membranes from polyimides for liquid separation. A systematic study has been carried out by Kim and co-workers on the morphological change of PI membranes by the addition of PVP [3,4]. Sarbolouki [5] has described ultrafiltration membrane preparation based on polyimides. Dong and Zhu [6] prepared PI membranes by imidization of membranes prepared from pre-polymers. Nitto Electric Industrial Co. is one of the companies that produce polyimide ultrafiltration membranes [7].

One issue with PI is high hydrophobicity. Thus, the surface of

membranes prepared with this polymer has high hydrophobicity. This is the main disadvantage of the PI membrane. Accordingly, the membrane surface provides favorable conditions for serious fouling against solutions containing substances such as proteins. Protein is a severe foulant during milk concentration using PI ultrafiltration membrane. Consequently, the modification of PI membrane is a vital step for enhancing the hydrophilicity of the membrane surface.

Most PI membranes have been modified to improve the gas permeation behavior. Cross-linking modification of polyimides can be induced by several methods. UV light induces photo-chemically cross-linking reactions in benzophenone-containing polyimides [8-10]. The other method was to form semi-interpenetrating networks in the blends of polyimides and oligo-polyimides containing diacetylene groups by means of thermal treatment at elevated temperatures. According to Rezac and Schoberl's results, this approach might yield transport properties essentially equivalent to the virgin polyimide, but significantly improved its chemical resistance [11]. Hayes at Du Pont invented a new way of cross-linking modification of polyimides via immersing the polyimide membranes in an amino compound solution followed by thermal treatment at 80 °C to finish the reaction [12].

The UV modification of polyimide membranes was performed to improve the selectivity of membranes in gas separation by cross-linking the polymer chains using benzophenone as the photo initiator [13]. Similar studies were carried out by Matsui et al. [14,15] with low and high energy UV lamps for gas separation.

<sup>†</sup>To whom correspondence should be addressed.  
E-mail: ahmadrahimpour@yahoo.com, ahmadrahimpour@nit.ac.ir

Nanofiltration (NF), which is defined as a process between ultrafiltration (UF) and reverse osmosis (RO), is a relatively recent technology largely developed over the past decade. Typically, NF membranes show sodium chloride rejections between 20 and 80% and molecular weight cutoffs for dissolved organic solutes of 200-1,000 Da. The separation mechanisms of NF membranes frequently include both size and Donnan exclusion effects. NF membranes have found many applications in a variety of industries. In water treatment, for example, NF membranes are promising for the treatment of both organic and inorganic pollutants. Their low-pressure operation (5-10 bar) provides increased energy savings with significantly lower installation and operating costs [16,17].

The author and co-workers investigated the effect of UV photo-grafting of different hydrophilic monomers such as acrylic acid (AA), 2-hydroxyethylmethacrylate (HEMA), phenylenediamine (PDA) and ethylene diamine (EDA) onto the polyvinylidene fluoride (PVDF) and polyethersulfone (PES) membrane surfaces [18,19].

The main objective of the present study was the modification of PI membranes and consequently production of PI membranes with more hydrophilic surface and high performance. To achieve this objective, acrylic acid (AA), 2-hydroxyethyl methacrylate (HEMA) and 1,3-phenylenediamine (mPDA) were grafted onto the surface of PI membrane by UV irradiation grafting method. After grafting, the changes of membrane performance were evaluated by ultrafiltration and nanofiltration processes.

## EXPERIMENTAL

### 1. Materials

Polyimide (PI) from Alfa-Aesar and dimethylacetamide (DMAC) from BASF were used as membrane polymer and solvent, respectively. The solvent, DMAC, was used without further purification.

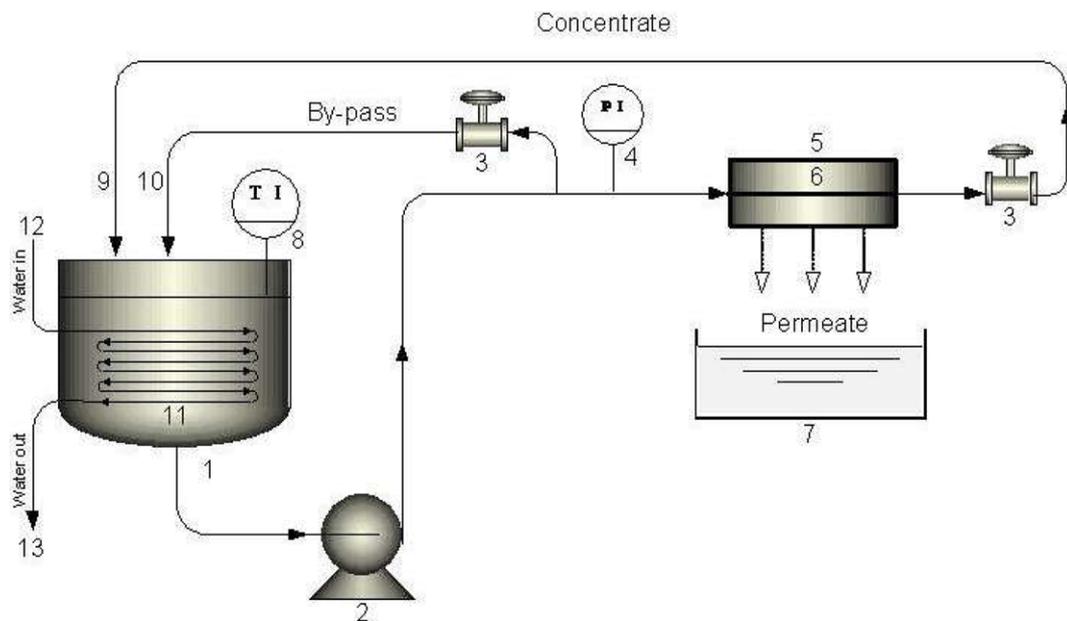
Polyvinylpyrrolidone (PVP) with 25,000 g/mol molecular weight ( $M_w$ ), acrylic acid (AA), 2-hydroxyethylmethacrylate (HEMA), 1,3-phenylenediamine (mPDA) and benzophenon (BP) were obtained from Merck. 2-propanol (IPA) was obtained from Minko Company. Distilled water was used throughout this study.

### 2. Preparation of PI Membrane

Original PI membranes were prepared using non-solvent induced phase separation technique. Polymer dope consisting of PI (16%, by weight of the solution), PVP (4%, by weight of the solution) and DMAC (80%, by weight of the solution) was dissolved at about 30 °C for 8 h with vigorous stirring. After the uniform polymer dope was formed, the casting solution was kept in closed and dry conditions for at least 2 h to remove air bubbles. Dope solution was cast using a homemade casting knife with 75  $\mu\text{m}$  thickness on polyethylene/polypropylene non-woven fabric. This was immediately moved to the non-solvent bath for immersion at room temperature without any evaporation. The non-solvent was a mixture of water (80 v.%) and 2-propanol (20 v.%). The prepared membranes were washed and stored in water for at least 1 day to completely leach out the residual solvents and additives. The membranes were kept in aqueous solution with 20 vol.% of 2-propanol as post treatment for 1 day. As the final stage, the membranes were dried by placing between two sheets of filter paper for 24 h at room temperature.

### 3. Surface Modification of Membrane by UV-photo Grafting

The modification of PI membrane was carried out by dip coating technique, which was followed by UV irradiating. Dip coating of membrane was carried out at two steps: in the first step, the membranes were only dipped in 1 and 6 wt% acrylic and amino monomer solutions for 30 min. The soaked PI membranes were placed in Plexiglas tube and illuminated by 160 W UV lamp (wavelength 259 nm, intensity 24.3 mW/cm<sup>2</sup>) for 5 min. Finally, the membranes were washed with distilled water and dried at room temperature. In



Scheme 1. Membrane evaluation system.

- |              |                    |                |                  |                  |
|--------------|--------------------|----------------|------------------|------------------|
| 1. Feed tank | 4. Pressure gauge  | 7. Permeate    | 10. By-pass      | 13. Water outlet |
| 2. Pump      | 5. Cross flow cell | 8. Thermometer | 11. Thermal coil |                  |
| 3. Valve     | 6. Membrane        | 9. Concentrate | 12. Water inlet  |                  |

the second step, the PI membranes were firstly dipped in benzophenone solution (5 wt% in methanol) for 5 min. After drying at 40 °C, the benzophenone-PI membranes were dipped in 1 wt% of AA, HEMA and mPDA for 30 min. The samples were UV irradiated with 160 W UV lamp for 5 min. The UV irradiated membranes were washed with distilled water and dried at room temperature. The degree of grafting (DG) was obtained by the following equation:

$$DG (\%) = (W_2 - W_1) / W_1 \quad (1)$$

where  $W_1$  and  $W_2$  are the weight of a membrane before and after grafting reaction, respectively.

#### 4. Characterization of Membranes

##### 4-1. Contact Angle Measurements

The water contact angle (CA) of PI membrane surface was determined on a contact angle system [G10, KRUSS, Germany] for evaluation of the membrane hydrophilicity. De-ionized water was used as the probe liquid in all measurements. To minimize the experimental error, the contact angle was measured at five random locations for each sample and the average value was reported.

##### 4-2. Ultra and Nanofiltration Experiments

The permeability experiments were performed on a homemade membrane evaluation system (Scheme 1) using the membrane specimen with filtration area in 24 cm<sup>2</sup>. The de-ionized water and non-skim milk with 3.2% protein and 1.5% fat were used for the evaluation of ultrafiltration performance of unmodified and modified PI membranes. The membranes were pre-compressed with pure water at 50 psi for 30 min. The pure water flux ( $J_0$ ) and milk water permeation ( $J_p$ ) were evaluated at 50 psi and at a flow rate of 5 l/min (or flow velocity of 2 m/s) for 30 min. The protein retention of membranes was obtained by measuring the amount of protein in the permeate using the standard Bradford method [20]. In addition, the nanofiltration performance of membranes was characterized using single solute solution containing 500 ppm NaCl and MgSO<sub>4</sub> at 30 °C and different pressures (0.5 and 1.0 MPas). The rejection of NaCl and MgSO<sub>4</sub> was measured by digital conductivity meter (Hana, Model: HI 8733).

##### 4-3. Fouling Analysis of Membranes

After 60 min ultrafiltration of non-skim milk, the membranes were washed with distilled water at 40 °C for 30 min and the water flux of washed membranes was measured ( $J_1$ ). To evaluate the fouling-resistant capability of membranes, flux recovery was calculated by using the following expression:

$$FR (\%) = \left( \frac{J_1}{J_0} \right) \times 100 \quad (2)$$

To analyze the fouling process in details, several equations were used to describe the fouling-resistant capability of the membrane:

$$\text{Total flux loss} = (J_0 - J_p) / J_0 \quad (3)$$

$$\text{Irreversible flux loss} = (J_0 - J_1) / J_0 \quad (4)$$

##### 4-4. Determination of Surface Mean Pore Size

The mean pore size of PI membrane surface was calculated from the separation data obtained by filtration of polyethylene glycol (PEG) with various molecular weights ranging from 200 to 5,000 Da [21]. The Stokes radius was applied to determine the size of the solute.

The Stokes radius of PEG is determined from its molecular weight using the equation:

$$a = 16.73 \times 10^{-10} M^{0.557} \quad (5)$$

where  $a$  is the Stokes radius (cm), and  $M$  the molecular weight of PEG (g/mol). After the measurement of the solute separation ( $R$ ) for different molecular weights of PEG, the solute separation and the Stokes diameter ( $d=2a$ ) were plotted on a log-normal probability graph paper and a regression line was drawn. The mean pore size ( $\mu_p$ ) was set equal to the diameter that corresponded to 50% of solute separation on the linear regression line. The standard deviation ( $\sigma_p$ ) was measured from the ratio of the diameters corresponding to 84.13 and 50% separations.

## RESULTS AND DISCUSSIONS

### 1. Degree of Photo Grafting and Membrane Hydrophilicities

The surface hydrophilicity of polymeric membranes is one of the most important factors to control the membrane fouling. The hydrophilicity of the membrane surface is estimated by contact angle measurement. The contact angle of the unmodified PI membrane is 81.4, i.e., the PI membrane possesses hydrophobic surface. However, a hydrophilic surface for membrane is favorable due to lower fouling tendency against various hydrophobic foulants such as proteins and fat. Accordingly, the modifications leading to an increase in hydrophilicity of the membrane surface are of interest. Therefore, the surface modification of PI membrane was carried out by UV grafting of hydrophilic monomers such as acrylic acid (AA), 2-hydroxyethylmethacrylate (HEMA) as acrylic monomers and 1,3-phenylenediamine (mPDA) as amino monomer onto the membrane surface at absence and presence of benzophenone (BP) as photo-initiator.

The degree of grafting (DG) of hydrophilic monomers with different concentration and at absence and presence of BP onto the PI membrane surface is shown in Fig. 1. The degree of grafting of PI membrane increased with increasing monomer concentration. When mPDA monomer is used as hydrophilic monomer, the highest value in the DG is observed. This suggests the competition between graft-induced polymerization due to UV irradiation. Moreover, the DG of modified membranes at presence of BP is higher than modified

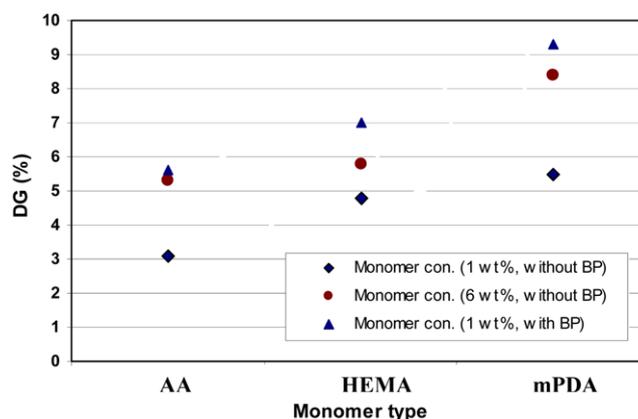


Fig. 1. Degree of grafting as a function of monomer type and monomer concentration.

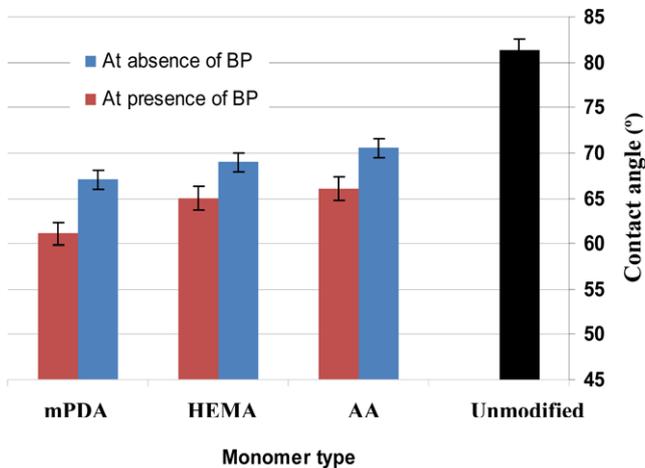


Fig. 2. Effect of monomer photo-grafting at absence and presence of BP on PI membrane contact angle.

membranes in absence of BP. The key step of this route is the hydrogen-abstraction from the support polymer by the photo excited BP. BP creates starting radical for photo-initiated surface grafting by hydrogen-abstraction from the polymer backbone [22]. Fig. 2 represents the contact angles of original and photo-grafted membranes in the presence and absence of BP. The contact angle was decreased with photo-grafting of hydrophilic monomers onto the PI membrane surface. The contact angle is a good criterion for evaluation of membrane hydrophilicity. The contact angle is reversely proportional to hydrophilicity. In two cases (in presence and absence of BP), the original PI membrane exhibits least hydrophilic surface, the AA and HEMA modified PI membranes show intermediate hydrophilicity and the mPDA modified PI membrane presents most hydrophilic surface. Moreover, the contact angle results emphasize that the hydrophilicity of PI membranes modified at presence of BP has the highest value. This may be due to higher degree of grafting. The improvement of hydrophilicity for modified membranes by UV photo-grafting confirmed that monomers were significantly polymerized onto the membrane surface.

**2. Ultrafiltration Performance and Antifouling Properties of Modified PI Membranes**

Pure water and non-skim milk were used to characterize the ultrafiltration performance of membranes. The effect of UV photo-graft-

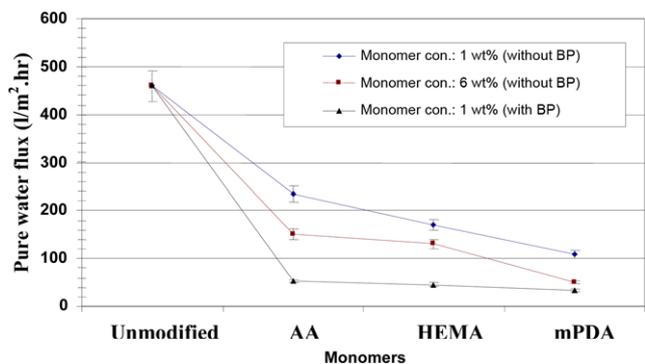


Fig. 3. Pure water flux of unmodified and modified PI membranes at presence and absence of BP.

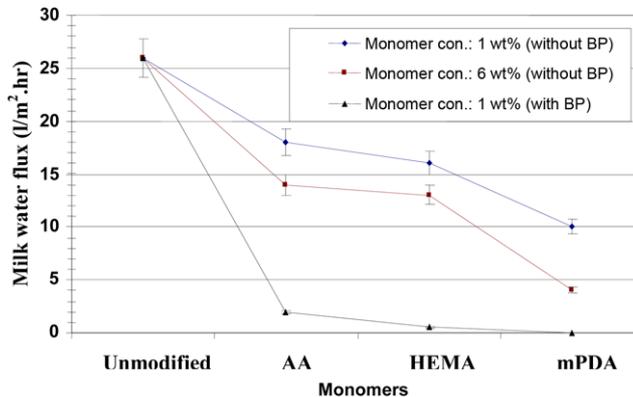


Fig. 4. Milk water permeation of unmodified and modified PI membranes at presence and absence of BP.

ing of hydrophilic monomers onto the PI membrane surface in absence and presence of BP on pure water flux and milk water permeation is shown in Figs. 3 and 4. From these figures, it can be found that the photo-induced grafting of hydrophilic monomers onto the base PI membrane surface resulted in a severe decline in the pure water and non-skim milk water permeability. This can be explained by formation of smaller pores due to grafting of hydrophilic monomer chains onto the PI membrane surface. A higher decline in permeability is observed for PI membranes when BP is used as photo-initiator in the grafting process. For example, the milk water permeation of mPDA-modified membrane in presence of BP was equal to zero. When BP is applied as photo-initiator the higher degree of grafting is obtained for PI membranes.

The milk protein rejection of unmodified and modified membranes as function of monomer type, monomer concentration and presence of photo-initiator is shown in Fig. 5. All monomer-modified PI membranes had higher rejections than the unmodified PI membrane, especially at higher concentration and in presence of BP. For mPDA-modified membrane, the protein rejection increased to 100%. The increment in protein rejection is an indication to decrease the surface pore size of membranes.

The surface mean pore sizes of unmodified and 1 wt% modified membranes with hydrophilic monomers in absence and pres-

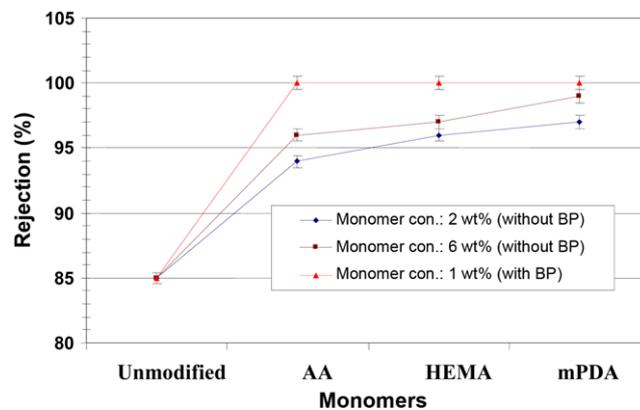


Fig. 5. Protein rejection of unmodified and modified PI membranes at presence and absence of BP.

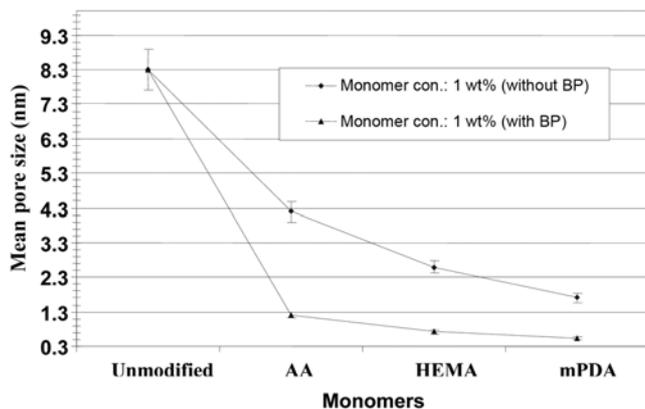


Fig. 6. Mean pore size of modified membranes at presence and absence of BP.

ence of BP were obtained from the transport data with PEG solute of various molecular weights. The rejection of PEG on ordinate was plotted versus its diameters on abscissa of a log-normal probability paper. The values of mean pore size ( $\mu_p$ ) and standard deviation ( $\sigma_p$ ) were determined as described in the experimental section, and the obtained results are shown in Fig. 6. It is evident from the results that the base PI membrane has a relatively larger mean pore size. The mean pore size of PI membrane decreased from 8.3 nm to 4.2, 2.6 and 1.7 nm in absence of BP and decreased from 8.3 nm to 2.2, 0.72 and 0.55 nm in presence of BP for 1 wt% monomer photo-grafted membranes. Grafting of mPDA at presence of BP, as measured by DM, was higher than the other monomers (see Fig. 1). This leads to formation of membrane with lower mean pore size. As mentioned, the decline in surface pore size of membranes may be due to pore constriction and plugging by UV photo-grafting.

It is well known that the hydrophilic surface has lower tendency to fouling. As we showed, the more hydrophilic surface was introduced for PI membrane by UV photo-grafting of hydrophilic monomers. To evaluate the influence of photochemical grafting of hydrophilic monomers on fouling parameters of membranes, the total flux loss, irreversible flux loss and flux recovery of unmodified and modified PI membranes were determined. The obtained results are summarized in Table 1. The total flux loss was increased while the

Table 1. Fouling analysis of unmodified and modified PI membranes with hydrophilic monomers at absence and presence of BP

Membrane	Total flux loss	Irreversible flux loss	FR (%)
Unmodified	0.94	0.69	31
Modified at absence BP:			
1 wt% AA	0.92	0.57	43
1 wt% HEMA	0.90	0.54	46
1 wt% mPDA	0.90	0.50	50
Modified at presence of BP:			
1 wt% AA	0.96	0.48	62
1 wt% HEMA	0.99	0.34	66
1 wt% mPDA	1.00	0.30	70

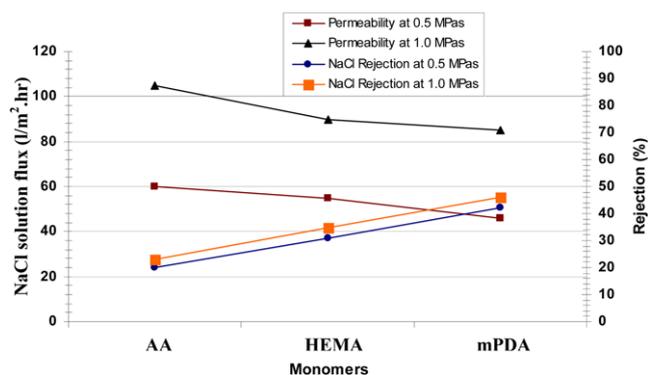


Fig. 7. Permeability and NaCl rejection of grafted membranes during filtration of NaCl solution at different pressures.

irreversible flux loss was decreased by UV photo-grafting. The increase in total flux may be due to decrease in pore size and pure water flux. The irreversible protein adsorption or deposition declined to a lower level by reduction in irreversible flux loss, and the milk flux could be mostly recovered after water washing. The value of flux recovery (FR) is a simple and direct parameter to evaluate the antifouling property of the membranes. The higher value of FR means the more excellent antifouling property for membranes. The FR for the PI membranes was increased considerably by photochemical modification, especially at the presence of BP. The higher flux recovery indicates that the most protein fouling was reversible due to the introduction of improved surface.

### 3. Nanofiltration Performance of Modified PI Membranes

To evaluate the nanofiltration performance of modified PI membranes, three AA, HEMA and mPDA modified membranes in presence of BP were selected and their permeability and rejections during filtration of single solute solution containing NaCl and  $MgSO_4$  were measured at two different pressures (0.5 and 1.0 MPas). Figs. 7 and 8 demonstrate the permeability and retention of grafted membranes during filtration of NaCl and  $MgSO_4$  single solute solutions, respectively. As shown in these two figures, the permeability of modified membranes changed with the following increasing order: AA-modified membrane > HEMA-modified membrane > mPDA-modified membrane. This behavior can be explained based on the membrane's surface pore size. The results of the solute rejection dem-

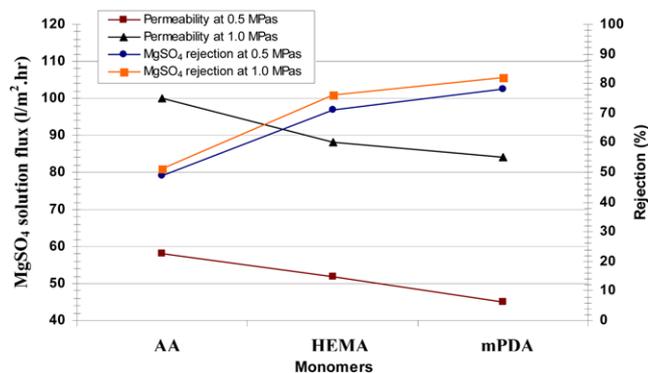


Fig. 8. Permeability and  $MgSO_4$  rejection of grafted membranes during filtration of  $MgSO_4$  solution at different pressures.

onstrated that the membrane modified with mPDA at presence of BP had highest NaCl and MgSO<sub>4</sub> rejections. Moreover, all modified membranes showed considerable monovalent and divalent solute rejections. Considering the solute rejection behavior and the size of the surface pores of selected membranes (1.2 nm for AA-modified membrane, 0.72 nm for AA-modified membrane and 0.55 nm for mPDA-modified membrane) compared to the hydrodynamic radius of the ion (0.33 nm for Na<sup>+</sup>, 0.36 for Cl<sup>-</sup> and 0.38 for SO<sub>4</sub><sup>2-</sup>), these results exhibit that the solute retention is mainly determined by charge effects.

The permeability of modified membranes increased with an increase in pressure (TMP) from 0.5 to 1.0 MPas. Spiegel-Kedem model [23] describes this behavior:

$$J_v = L_p(\Delta P - \sigma \Delta \pi) \quad (5)$$

where  $J_v$  is the water flux,  $L_p$  is the pure water permeability,  $\Delta P$  is the transmembrane pressure (TMP),  $\sigma$  is the reflection factor of the membrane, and  $\Delta \pi$  is the osmosis pressure. Moreover, the solute rejections increased with an increase in applied pressure. The dependence between rejection and pressure can provide understanding into the nature of the separation mechanisms of the membrane. Typically, the rejection of RO membranes increases with an increment in pressure. The non-porous solution-diffusion model can explain this, where the solute retention increases with applied pressure. For micro and nano-porous membranes, the effect of increasing applied pressure is often a decline in the solute rejection due to convective solute transport and concentration polarization effects. Figs. 7 and 8 indicate that the modified PI membranes acted similar to non-porous RO membrane, i.e., rejection increased with increasing pressure, although pores definitely existed within the membrane surface. This can be attributed to the Donnan-steric-pore model. This model is described by the extended Nernst-Planck equation with equilibrium partitioning due to a combination of Donnan and steric mechanisms [24].

## CONCLUSION

Novel nanofiltration and hydrophilic ultrafiltration PI membranes were prepared by UV photo-grafting of hydrophilic monomers such as AA, HEMA and mPDA onto the PI membrane surface. The DG was increased with increasing monomer concentration, especially in presence of photo-initiator. Contact angles of the modified PI membranes tended to considerably decrease with UV photo-grafting in presence of BP. The permeability and surface mean pore size of all modified PI membranes were significantly decreased, as shown by ultrafiltration experiments. Moreover, the protein rejection and antifouling properties of modified PI membranes were improved.

The evaluation of performance of modified membranes in presence of BP during filtration of single solute solutions (NaCl and MgSO<sub>4</sub>) indicated that the PI nanofiltration membranes were created at these conditions.

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