



# Development of a positively charged nanofiltration membrane for use in organic solvents



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## ABSTRACT

In this work, a positively charged nanofiltration membrane was developed by chemical modification of a P84 copolyimide ultrafiltration membrane using branched polyethylenimine. The effect of reaction temperature on membrane morphology, surface charge, and separation performance was investigated. A reaction temperature of 70 °C was optimal as the membrane showed best performance in terms of salt rejections and water fluxes when Na<sub>2</sub>SO<sub>4</sub>, NaCl and CaCl<sub>2</sub> aqueous solutions were used as feeds. Such membrane had a molecular weight cut off (MWCO) of 226 Da indicating its effectiveness for separation of organics. Rejections to three dyes in methanol solutions were in the order of methyl orange (negative, MW: 327 Da) < disperse red (neutral, MW: 314 Da) < safranin O (positive, MW: 351 Da). The results suggest that the positive charge on membrane surface induce higher rejection to positive organic molecules due to the charge repulsion effect. Additionally, the membrane had very high stability in organic solvents; no significant changes in membrane performance and membrane structure were observed after being immersed in dimethyl formamide (DMF) for 1 month.

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## 1. Introduction

Due to their thermal stability, chemical stability and mechanical strength [1,2], polyimides (PI) have been widely used for membranes in the field of solvent resistant nanofiltration (SRNF) [3,4]. There are series of commercial PI membranes from DuPont, W.R. Grace-Davison (recently acquired by UOP), Solsep (Netherlands), and Evonik (UK) [5]. These commercial PI membranes have been widely used in catalytic applications [6], petrochemistry and aromatics enrichments [7,8], pharmaceutical and food processing [9], microfluidic purification and membrane bioreactors [10,11].

However, PI membranes are not stable in many organic solvents such as polar aprotic solvents and chlorinated solvents. To solve the problem, a common approach is to form a crosslinking structure induced by thermal treatment [12], UV irradiation [13] and chemical reactions. For example, diols and diamines have been used as chemical crosslinking agents for PI membranes. Diols such as ethylene glycol [14], 1,4-butylene glycol [14], 1,3-propanediol [15], 1,10-decanediol [16], 1,4-cyclohexanedimethanol [14] have been used for crosslinking of PI membranes containing

carboxylic acid groups. Diamines, including aliphatic [17], aromatic [18] and polymeric diamines [19,20] can react on both ends with polyimide chains, resulting in breakage of imide bonds and formation of intermolecular amide bonds.

PI membranes crosslinked by diamines have shown enhanced solvent resistance with molecular weight cut off (MWCO) ranging between 200 and 400 g/mol [21,22]. High rejection (> 95%) of low molecular weight dyes by aromatic crosslinked PI membranes was also reported [23,24]. However, to the authors' knowledge, diamine crosslinked membranes have surfaces of neutral or slightly charged. It has been known that membrane surface charge has strong influence on separation of charged ions and organics due to the Donnan effect [25]. A positively charged nanofiltration membrane may be very effective for separation of charged organic molecules in non-aqueous system. For example, reactive dyes contain functional groups with positive, negative, or neutral charge [26]. Heavy metal catalysts and antibiotics can also be charged in organic solvents [27,28]. For these applications, the development of positively charged NF membranes by a simple method seems very important.

In a previous study [29], positively charged NF membranes were prepared by chemical modification of P84, a co-polyimide of 3, 3', 4, 4'-benzophenone tetracarboxylic dianhydride with 80% toluenediisocyanate and 20% ethylphenylene-diisocyanate (BTDA-TDI/MDI), asymmetric membranes using branched

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polyethylenimine (PEI). The remaining amine groups on the membrane surface made the membranes positively charged. The prepared membrane showed efficient removal of multivalent heavy metal ions (> 95%) in aqueous system. However, the use of this NF membrane in organic systems has not been reported. The positive surface charge may interact with the organic molecules via charge interactions. Such membranes may have potential applications in separation of charged molecules such as dyes in organic systems.

In the present study, the effect of reaction temperature on membrane performance by chemical modification between P84 and PEI was studied. These membranes were characterized by surface charge, MWCO and stability measurements. Additionally, the NF membranes were used for separation of dye molecules in methanol.

## 2. Experimental

### 2.1. Chemicals

P84 powder was obtained from HP Polymer Inc. and used as received. PEI (Mw: 25,000, Mn: 10,000) was purchased from Sigma Aldrich. All the salts including NaCl, CaCl<sub>2</sub>, Na<sub>2</sub>SO<sub>4</sub> were obtained from Fisher Scientific. For selected dyes, methyl orange and safranin O were obtained from Alfa Aesar while disperse red was from MP Biomedicals, LLC. A series of alkanes including C<sub>10</sub>H<sub>22</sub>, C<sub>14</sub>H<sub>30</sub>, C<sub>18</sub>H<sub>38</sub> and C<sub>22</sub>H<sub>46</sub> were all from Sigma Aldrich. All the chemicals were used as received unless specially indicated.

### 2.2. Preparation of the crosslinked NF membranes

Asymmetric porous P84 membranes were prepared by phase inversion technique [30]. A solution of 23% of P84 in DMF was cast onto a polyester non-woven fabric support followed by immediate immersion into a room temperature tap water bath. After precipitation, the membrane was kept in a water bath overnight in order to completely remove DMF from the membrane and then rinsed with deionized (DI) water for further modifications.

The crosslinked NF membranes were prepared using a modified procedure as described previously [29]. P84 membranes were immersed in a 1% PEI solution (wt/vol) in a mixture of isopropanol and water (1:1 in volume) at temperatures of 25 °C, 50 °C, 70 °C and 90 °C for 60 mins. The resultant membranes were rinsed with and stored in DI water.

### 2.3. Nanofiltration tests

The desalination performance of the membranes was carried out using a dead-end filtration cell (Sterlitech™ HP4750) under a pressure of 13.8 bar (200 psig) at room temperature. A standard magnetic stirrer (Corning Stirrer/Hot Plate, Model PC-420) was used to minimize the influence of concentration polarization. Typically, 300 ml of 2 g/L NaCl solution was used as feed. Permeate

samples were collected until a stable permeation flux was achieved. The concentration of the permeate solution was determined using a Corning pH/ion analyzer 455. The salt rejection *R* of the membrane was determined by the equation of

$$R = (1 - C_p/C_f) \times 100\% \quad (1)$$

while *C<sub>p</sub>* and *C<sub>f</sub>* representing the permeate concentration and feed concentration respectively.

Similarly, membrane performance was also characterized using 2 g/L of CaCl<sub>2</sub> and 2 g/L of Na<sub>2</sub>SO<sub>4</sub> aqueous solutions as feeds. By comparing the rejections to these three solutes, the surface charge of the membranes can be determined qualitatively.

### 2.4. MWCO (Molecular weight cut off) measurement

The procedure used for MWCO determination was based on the method described by See Toh et al. [31]. A series of *n*-alkane test solutions including decane, tetradecane, octadecane and docosane were prepared by dissolving these solutes in methanol with a concentration of 100 mg/L. These solutions were used as feeds of the membranes in the dead-end filtration cell. The concentrations of the permeates were determined using an Agilent 7890 A Gas Chromatograph (GC) equipped with a standard 5975 C mass selective detector and a commercial Wiley and NIST libraries (2008 edition) for mass spectra interpretation. By plotting a graph of rejection of solutes against solute molecular weight, MWCO can be determined by finding the molecular weight corresponding to the 90% rejection.

### 2.5. Separation of dyes in methanol solution

Several organic dyes in methanol solution was used as probes to determine separation performance of the NF membranes in organic system since organic dyes are easy to be measured using spectrophotometric techniques [32,33]. Three dyes including disperse red, methyl orange and safranin O were selected due to their similar molecular weight (MW) but different charges. The feed concentration was 100 mg/L, while the concentration of the permeate was determined using a Varian Cary 5 G Ultraviolet (UV) spectrophotometer. The molecular weight, charge, detection UV wavelength and molecular structure of these dyes were listed in Table 1.

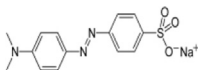
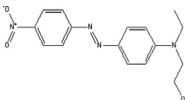
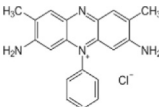
### 2.6. Determination of membrane stability in organic solvents

The membrane stability in organic solvent was determined by measuring weight change after immersing in DMF for two weeks using the following equation [23]:

$$\text{Gel content} = W_a/W_b \times 100\% \quad (2)$$

while *W<sub>b</sub>* and *W<sub>a</sub>* are the dry weight of the membrane before and after soaking in DMF, respectively. DMF was completely removed by soaking in water for several days and the membrane samples were dried in oven.

**Table 1**  
Principle characteristic of the selected dyes.

Dyes	Methyl orange	Disperse red	Safranin O
MW (g/mol)	327.3	314	350.85
Charge	Negative	Neutral	Positive
Max. wavelength (nm)	422	570	528
Molecular structure			

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