



# UV-cured polysulfone-based membranes: Effect of co-solvent addition and evaporation process on membrane morphology and SRNF performance



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## ABSTRACT

Membranes consisting of a semi-interpenetrating network of polysulfone (PSU) and cross-linked polyacrylate were synthesized via non-solvent induced phase inversion followed by UV-treatment. Tetrahydrofuran (THF) or 1,4-dioxane (DIO) was added as co-solvent to the *N,N*-dimethylformamide (DMF)-based polymer solutions and cast films were subjected to evaporation prior to coagulation. Effects of synthesis variables on the membrane morphology and solvent resistant nanofiltration (SRNF) performance were investigated by using a Rose Bengal solution in isopropanol. By increasing the evaporation time from 0 to 100 s for the membranes prepared with THF and DIO as co-solvent respectively, rejections increased from 65.3% to 94.2% and 60.1–89.1%, while permeances decreased from 0.29 to 0.01 l/m<sup>2</sup> h bar and 0.41–0.08 l/m<sup>2</sup> h bar. A similar effect was observed when the co-solvent/solvent ratio was increased from 0/100 to 100/0: rejections increased from 63.1% to 94.9% and 59.2–90.6%, while permeances decreased from 0.43 to 0.01 l/m<sup>2</sup> h bar for THF-based membranes and to 0.07 l/m<sup>2</sup> h bar for DIO-based membranes respectively. A post-treatment was performed to increase the flux by immersing UV-cured PSU-based films in DMF for 48 h. The resultant membranes showed higher permeances and lower rejections, making them especially useful as potential candidates for stable supports to apply selective layers upon, such as e.g. in thin film composite (TFC) membranes. As observed in scanning electron microscopy, higher evaporation times and lower initial co-solvent concentrations resulted in less or even no macrovoids.

## 1. Introduction

Polymeric membranes are extensively employed in gas and liquid separations due to their good processability and low cost [1–3]. These membranes mostly demonstrate an asymmetric structure and are fabricated via the phase inversion process where a polymer solution is cast on a support, followed by immersion in a non-solvent bath where polymer precipitation and membrane formation appears [4–11]. Solvent resistant nanofiltration (SRNF) is a contemporary process that allows the separation of organic mixtures down to a molecular level by applying a pressure gradient over a membrane [12,13]. It is entering as an innovative technology in petrochemical, food & beverage, pharmaceutical industries where organic solvent streams need to be treated. Besides permeability and selectivity, the chemical stability of the membranes is of great importance for such applications. In SRNF, both polymeric and inorganic membranes are used with molecular weight cut-offs in the range of 200–1000 Da [9,14–19].

Polysulfone (PSU) has strong thermal and mechanical properties which makes it an ideal candidate for broad membrane applications [20–25]. However, performance of these membranes and many others,

such as polyimide (PI) and polyether ketone, are still inadequate in the SRNF process because of their low resistance in aprotic solvents, such as *N*-methylpyrrolidone (NMP) and *N,N*-dimethylformamide (DMF) [26,27]. This problem can be solved by introducing cross-linking. The most common method to realize this is via chemical cross-linking [26,28–31]. However, it is less suitable for PSU due to its limited chemical reactivity. Additionally, chemical cross-linking generally requires a series of reaction steps which induce toxic contaminants such as diamines [26]. Therefore, radiation treatment via UV or electron beam (EB) can be a preferred alternative procedure for PSU [32–35]. The high cost and relative complexity of EB-curing units render UV-curing generally preferred [36]. Usually, surface modification of PSU-membranes is targeted via UV radiation to realize grafting [37,38]. Very recently, a simple and effective method was developed to depth-cure PSU-membranes via UV-curing [39]. In this approach, UV-irradiation was applied to PSU membrane films containing cross-linker and photo-initiator, prepared via non-solvent induced phase separation (NIPS) process. Combinations of various photo-initiators and cross-linkers were investigated to find a practically useful system [40,41]. As well-known, the final SRNF performance and membrane morphology

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can be modified easily through even slight changes in synthesis protocol or composition of the casting solution. In-depth analysis of the phase inversion parameters is thus still necessary to achieve the best performance with UV-cured PSU-membranes via this method.

Among the most effective parameters to tune phase inversion parameters [9,42–46], evaporation time prior to immersion, choice of co-solvent and solvent/co-solvent ratio are easily accessible and well understood [41,46–52]. In present study, the influence of evaporation time and the role of co-solvent (tetrahydrofuran (THF) or 1,4-dioxane (DIO)) on the formation, performance and morphology of UV deph-cured PSU-based is thus investigated to further optimize this type of interesting membranes with respect to use in SRNF.

## 2. Experimental

### 2.1. Materials

Polysulfone (PSU) (Udel P-1700 LCD,  $M_n=21\,000\text{ g mol}^{-1}$ ) was kindly provided by Solvay (Belgium) and dried for 24 h at 100 °C prior to use. The polyethylene terephthalate non-woven fabric (PET Novatexx 2413) was kindly supplied by Freudenberg (Germany). Dipentaerythritol penta-acrylate (SR399LV, Sartomer) was used as cross-linker. 2,4,6-Trimethylbenzoyl-diphenyl-phosphine oxide was purchased from Sigma-Aldrich and used as photo-initiator. Table 1 shows details of photo-initiator and cross-linker used. Rose Bengal (RB) was obtained from Sigma-Aldrich. *N,N*-dimethylformamide (99.5%, DMF), tetrahydrofuran (99.5%, THF) and 1,4-dioxane (99%, DIO) were purchased from Acros and used as received.

### 2.2. Membrane synthesis

Two different series of membranes were prepared to determine the influence of evaporation time and the role of co-solvent as phase inversion parameters on the performance and morphology of the UV-cured PSU-membranes. In the first series, the influence of evaporation time was analyzed by using a DMF-based solution, with two different co-solvent (THF and DIO) with a ratio of DMF to co-solvent equal to 85/15. As evaporation times 0, 10, 20, 30, 60 or 100 s were used. It has to be mentioned that all membranes were evaporated for roughly about

5 s extra, which is the required time to move the cast film from the casting equipment to the coagulation bath. In the second series, the influence of co-solvent was analyzed by using a DMF (boiling point, 153 °C) based solution with the same THF (boiling point, 66 °C) and DIO (boiling point, 101 °C) as co-solvent keeping evaporation time constant (30 s), but with various ratios of DMF to these co-solvents: 100/0, 75/25, 50/50, 25/75 and 0/100. All samples were prepared at room temperature under the atmospheric pressure. In both series, the polymer concentration was kept constant at 21 wt%. Cross-linker and photo-initiator were used at 5 wt% and 3 wt%, respectively. After obtaining a homogenous polymer solution, membranes with a wet thickness of 200  $\mu\text{m}$  were cast at a speed of 1.81 m/min onto a glass plate or a polypropylene/polyethylene non-woven fabric (Novatexx 2413) impregnated with DMF. Before immersion into the coagulation bath, the membrane was kept in ambient air for a certain time. The membranes were stored in distilled water prior to the UV treatment.

### 2.3. UV-curing of asymmetric PSU-based membranes

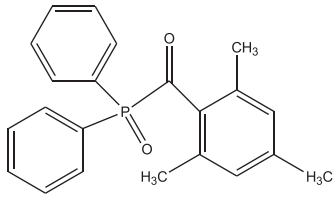
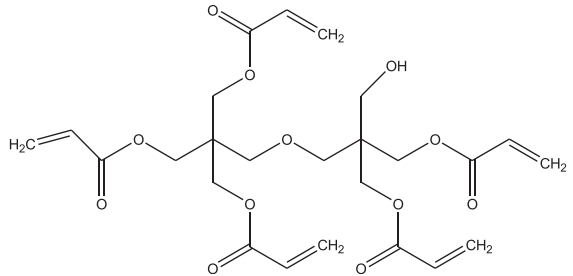
The PSU-based membranes were passed through a UV-curing set up (UVAPrintS200, HonleUV France) on a conveyor belt at a line speed of 10 m/min. UVA (320–390 nm) was used as the main irradiation light. According to our previous study [39], the dose of energy to cure the membranes was chosen as 5 J/cm<sup>2</sup>.

To increase the flexibility and prevent pore collapse for better filtration, some of the cross-linked PSU-membranes were impregnated after the UV-curing. The membranes were stored in a solution including 40% (v/v) of glycerol and 60% (v/v) of propan-2-ol for 48 h at room temperature, and subsequently air-dried. ATR-FTIR and SEM were performed to non-impregnated UV-cured PSU-membranes.

### 2.4. Viscosity measurements

Viscosity measurements were carried out with an Anton Paar MCR501 rheometer with a cone-plane geometry with solvent trap at 20 °C. The polymer solution was loaded onto the plate, and the cone was lowered onto the sample. It was then covered by a lid to avoid solvent evaporation. The sample temperature was controlled by a Peltier element with high accuracy. Viscosity at different shear rates

**Table 1**  
Photo-initiator and cross-linker used in this study.

Name	MW (g mol <sup>-1</sup> )	Structure
2,4,6-Trimethylbenzoyl-diphenyl-phosphine oxide (Darocur™ TPO)	348	
Dipenta-erythritol penta-acrylate (Sartomer™ SR399LV)	524	

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