



# Incorporating hyperbranched polyester into cross-linked polyamide layer to enhance both permeability and selectivity of nanofiltration membrane



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## ABSTRACT

To prepare thin film composite (TFC) nanofiltration (NF) membranes with improved flux and rejection performance at low pressure, hyperbranched polyester (HPE) was selected as the nano-sized macromonomer and successfully incorporated into the skin layers on PVC hollow fiber substrates via interfacial polymerization between trimesoyl chloride and the mixtures of hydroxyl-terminated HPE/piperazine (PIP). The resultant NF membranes were characterized using ATR-FTIR, FESEM, AFM and surface zeta potential, while their performance was evaluated in terms of permeate flux and rejection rates of different inorganic salts and neutral solutes. When the HPE content was lower than 60 wt% in HPE/PIP mixtures, the increased membrane surface roughness and the HPE embedded in skin layer effectively enhanced the permeate flux without sacrificing salt rejection for the prepared TFC NF membranes. Further increasing HPE content in HPE/PIP mixtures yielded looser polyamide skin layer, which led to the decline of solute rejection. Due to the larger size and good interfacial compatibility with cross-linked polyamide matrix, the incorporated HPE could exist stably in the skin layer. And thus, the prepared TFC NF membranes showed good flux and rejection stability in a long-term filtration process.

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## 1. Introduction

With the continuing decline of available freshwater supplies and the increasing demand of clean water due to population booming and industrial development, desalination based separation membrane technologies have gained great attention in recent years [1]. Among them, thin film composite (TFC) membranes are considered as the most efficient way for desalination. The TFC membrane normally consists of an ultra-thin selective layer responsible for separation and a porous substrate providing mechanical support. To date, most commercially available reverse osmosis (RO) and nanofiltration (NF) membranes are a kind of polyamide TFC membrane prepared through interfacial polymerization technique, which first put forward in 1965 by Morgan [2–4]. Although TFC RO/NF membrane process has been widely recognized as one of the best candidates to resolve water scarcity, there still exist some problems that need urgently to solve in the

operation of large scale desalination plant. One of the major obstacles is high energy consumption, which accounts for above 40% of the whole desalination costs due to requiring high operating pressure during the membrane desalination process [5]. Thus, more and more efforts have been focused on preparing low-pressure-driven RO/NF membranes with higher flux and rejection performance.

Most of ever researches for enhancing performance of polyamide TFC membranes were conducted by optimizing the interfacial polymerization process or exploiting new monomers and additives [6]. Additives in the aqueous phase or/and in the organic phase are able to influence the formation of polyamide skin layer structures during the interfacial polymerization, and then, the structures and properties of the resultant TFC membranes can be tailored [7]. For example, the addition of polar aprotic solvents (e.g., dimethyl sulfoxide, hexamethyl phosphoramide) in the aqueous phase could increase the size and number of network pores in the polyamide skin layer, which result in the enhancement of water permeability of TFC membranes. But the larger size of aggregate pores led to larger defect pores that deteriorate the salt rejection performance [8–10]. Polyvinyl alcohol (PVA)

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dissolved in the aqueous phase solution via interfacial polymerization could generate high flux and antifouling NF membranes without a considerable loss of salt rejection [11]. The usage of various hydrophilic additives in aqueous phase could also increase the flux of typical RO membranes. These additives provided an additional pathway for the transport of water molecules while the electrostatic repulsion for reducing salt passage [12,13]. In addition, inorganic salt calcium chloride ( $\text{CaCl}_2$ ) was used as the additive in aqueous phase to generate a loose polyamide skin layer, resulting in a remarkable increase in the water flux and a slight decrease in solute rejections [14]. However, the aforementioned experimental results indicated that using additives during the interfacial polymerization could enhance water flux of these TFC membranes but at the expense of salt rejection due to the existence of trade-off relations between permeability and selectivity. At present, it is still a challenge to enhance both permeability and selectivity performance of polyamide TFC membranes [15,16].

As a kind of TFC membranes, thin film nanocomposite (TFN) membranes were also investigated to solve the trade-off between permeability and selectivity. For the typical TFN membranes, inorganic nanomaterials including zeolites [17,18], silicas [19], metal oxides [20], carbon nanotubes [21], and graphenes oxides [22], etc., were used as fillers incorporated into polyamide matrix via interfacial polymerization technique. In the well prepared TFN membranes, the inorganic nanofillers could increase the free volume between polymer chains or/and provide the internal water channels in the polyamide skin layer, which led to an increase in permeability without deteriorating selectivity [23]. Despite the significant achievements, there are still some intrinsic drawbacks encountered during the TFN membrane preparation. These include the possible formation of non-selective voids due to the aggregation and exfoliation of inorganic nanofillers in the polyamide matrix, and poor interfacial compatibility between nanofillers and polymer as well as the internal pore blockage of porous fillers, which will not only decrease the performance reliability, but also restrict the large scale preparation and application of TFN membranes [24–26]. Accordingly, it is still essential to search for a new alternative material that can be applied for fabricating defect free polyamide skin layers.

Hyperbranched polymers (HBPs) are a kind of randomly branched macromolecules with an individual size generally ranging from several nanometers to dozens of nanometers. Although HBPs do not have perfectly branched architecture, they are considered to have similar properties to dendrimers. Moreover, unlike the complex synthesis and purification of dendrimers, HBPs can be produced on a large scale by simple one-pot synthesis. Therefore, they are considered possible alternatives of dendrimers in many practical applications [27–29]. Compared with most of inorganic nanomaterials used as the additives for the membrane preparation, HBPs had good dispersion in the solution because of their excellent interfacial compatibilities in many mixture systems. The nanometer-sized voids inside HBPs provided additional water channels to enhance water permeability performance. Moreover, the rate of interfacial reaction could be controlled by the incorporation of HBPs with abundant terminal functional groups. Despite many advantages of HBPs, using HBPs as the only reactive monomer in the aqueous phase for the preparation of TFC membranes reported in the literature showed poor salt rejection due to their large free volume [30–32]. Accordingly, it is necessary to explore a new approach for developing high performance TFC membranes using commercially available HBPs.

Here, for the first time, hydroxyl-terminated hyperbranched polyester (HPE) was chosen as a macromonomer of interfacial polymerization to modify the traditional piperazine (PIP)-trimesoyl chloride (TMC) polyamide based TFC NF membranes, which

normally have 50–200 nm thick functional skin layer. The nano-sized pores (e.g. 0.5–2.0 nm) in this skin layer are considered as permeation channel of water and solutes. Considering the unique characteristics of HPE, it should be a reasonable and interesting new strategy to tailor the structures and properties of TFC NF membranes by incorporation of HPE into the polyamide skin layers for enhancing both permeability and selectivity.

## 2. Experimental

### 2.1. Materials and reagents

A hydroxyl-terminated HPE of the fourth pseudo-generation (BOLTORN H40), which is commercial synthesized using 2,2-bis(methylol)propionic acid (bis-MPA) as the tri-functional  $\text{AB}_2$  monomer and ethoxylated pentaerythritol as the tetra-functional B4 core molecule, was purchased from the Perstorp Specialty Chemicals AB (Sweden). The molecular structure of HPE BOLTORN H40 is presented in Fig. 1. And the characteristics of HPE BOLTORN H40 are shown in Table 1 [28,33]. The monomers of PIP and TMC were purchased respectively from Aladdin Reagent and Shanghai Kaisai Chemical Co., China. Polyvinyl chloride (PVC) hollow fiber ultrafiltration (UF) membranes were provided by Hainan Litree Purifying Technology Co., Haikou, China. The properties of the PVC-UF substrate membrane are presented in Supplementary material. Magnesium sulfate ( $\text{MgSO}_4$ ), sodium sulfate ( $\text{Na}_2\text{SO}_4$ ), magnesium chloride ( $\text{MgCl}_2$ ), sodium chloride ( $\text{NaCl}$ ), anhydrous sodium phosphate ( $\text{Na}_3\text{PO}_4$ ) and n-hexane were purchased from Sinopharm Chemical Reagent Co., China. Polyethylene glycol (PEG) with molecular weights of 200, 400, 600, 800 and 1000 Da was purchased from Aladdin Reagent Co., China. Deionized (DI) water ( $\text{pH} \approx 6.0$ ), which was treated with RO membranes, was used in all experiments. All chemicals were analytic reagents and used as received.

### 2.2. Preparation of TFC NF membranes

HPE were incorporated into the polyamide skin layer via a typical interfacial polymerization route. Throughout the study, the concentration of TMC in n-hexane was fixed at 0.5 wt%, while the compositions of aqueous phase solution containing HPE/PIP with varying ratios and acid absorbent  $\text{Na}_3\text{PO}_4$  are listed in Table 2. To begin with, the aqueous phase solution was extruded into the lumen side of hollow fiber membranes for 10 min, then excess aqueous solution was drained off and the soaked surface was air-dried using an air compressor. Subsequently, the organic phase solution was introduced in the same way, and the interfacial polymerization proceeded between TMC and absorbed HPE/PIP for 50 s, which resulted in the formation of a polyamide skin layer on the inner surface of PVC-UF membrane. After removing excess organic phase solution, the hollow fiber membranes were heated for 10 min in an oven at 60 °C for further polymerization. Finally, the membranes were stored in DI water before carrying out NF experiments. The resultant membranes prepared from different weight ratios of HPE/PIP were coded as NF $\chi$  ( $\chi=0, 1, 2, 3, 4, 5, 6, 7, 8$ ) respectively.

In addition, PVC-UF flat sheet membranes were prepared via immersion precipitation phase inversion method used as the substrates for TFC NF membranes to perform some membrane characterizations. The composition of casting solution of the flat sheet membranes was as same as the PVC-UF hollow fiber membranes used in the experiments, and thus their surface properties are similar. A series of TFC NF flat sheet membranes were prepared according to the abovementioned interfacial polymerization conditions.

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