



# Hydrophilic nanofiltration membranes with reduced humic acid fouling fabricated from copolymers designed by introducing carboxyl groups in the pendant benzene ring



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## ABSTRACT

In this study, strategy of designing new polymers by copolymerization of carefully chosen monomers was explored to synthesize high performance nanofiltration membranes. A series of copolymers with different content of carboxyl groups were successfully synthesized by polymerization of 2-(bis(4-hydroxyphenyl)methyl)benzoic acid (BHPBA), 4,4'-dichlorodiphenyl sulfone (DCDPS). These copolymers have a high glass transition temperature and decomposition temperature, although a large amount of carboxyl groups was introduced in the chains of copolymers. Membranes fabricated from these polymers kept a reasonable tensile strength, even when 100% carboxyl groups were introduced in the polymer. Furthermore, Prepared membranes had a hydrophilic surface, and a high rejection of dyes and salts with relatively large flux. The antifouling measurements demonstrated that the fouling of both humic acid and BSA were greatly reduced with an increasing amount of carboxyl groups in the copolymer. These copolymer membranes exhibited superhigh antifouling of humic acid with a flux recovery ratio (FRR) of 100%, making them promising to be applied in the treatment of water with high content of humic acid.

## 1. Introduction

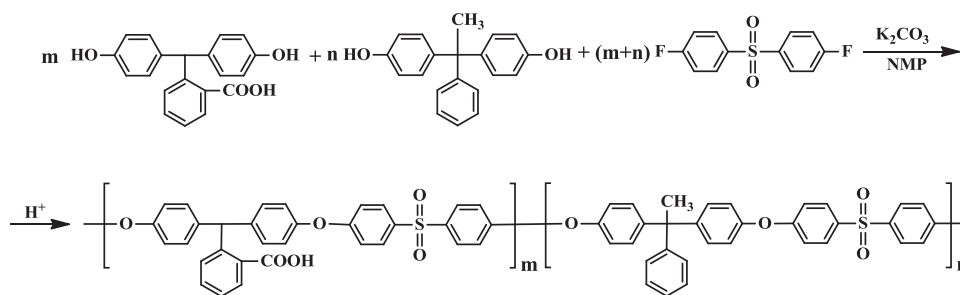
Nanofiltration (NF) has drawn great attention for advanced separations, due to its high permeate flux at relatively low operation pressure, good selectivity for different salts and low cost [1–3]. The main rejection mechanisms of NF are size exclusion and charge effects, resulting in a varying removal capacity of different solutes up to a size of 2 nm, with a molecular weight cut-off of 200–1000 g mol<sup>-1</sup> [4–6]. NF-based integrated processes are increasingly used for sustainable purification of seawater and industrial water to remove low molecular weight organic compounds (dyes, pesticides, etc.), heavy metals and multivalent salts from aqueous solution [7–9]. In order to enhance the separation efficiency and lower the energy consumption, a promising high-performance NF membrane should have a high permeate flux, high selectivity, and excellent antifouling properties [10].

A great number of commercial polymers such as poly sulfone (PSU),

poly (ether sulfones) (PES), polyaniline (PANI), poly (ether ether ketone) (PEEK), polyimide (PI) and polyamide (PA) have been developed into nanofiltration membranes through phase inversion [11,12]. Because these commercial polymers have homogeneous chemical and physical properties, asymmetric membranes fabricated from these polymers usually have a very stable filtration performance in applications. However, with the increasing differentiation of requirements from the industry, the need for high performance and functional membranes cannot be met by these commercial polymers [13,14]. Accordingly, many methods like grafting, plasma treating, nanoparticles incorporation and dopamine co-deposition have been explored to modify the membrane surface, or to create an additional functional layer on the support membrane to improve the membrane separation performance by tuning the surface charge and pore size [15–18]. In this strategy, nanoparticles and charged organics are often incorporated in the membrane separation layer. Nevertheless, the incorporated

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**Scheme 1.** The synthesis routes of copolymers (20-COOH, 40-COOH, 60-COOH, 80-COOH and 100-COOH).

nanoparticles and charged organics are not always stable and can be detached from the membrane surface, shortening the lifetime of a membrane and deteriorating the product water quality [19]. Furthermore, the weak interaction between the separation layer and the support membrane could diminish the mechanical strength of this functional layer, resulting in an unstable filtration performance. Therefore, it is of great importance to discover new modification methods to fabricate high performance, functional membranes with stable properties.

Chemical modification of the bulk commercial polymer, which enables the polymer with uniform chemical and physical properties, has been proven to be a feasible approach to endow membranes with a stable hydrophilicity, and antifouling properties [20,21]. Chung et al. fabricated high performance hydrophilic membranes by using sulfonated polyphenylenesulfone (sPPSU) with two sulfonic acid groups introduced in the benzene ring in the backbone of the repeating unit [22]. Economy et al. found that a nanofiltration membrane fabricated by coating a layer of sulfonated poly(ether ether ketone) on a positively charged membrane surface has an excellent antifouling performance [23,24]. Zhang et al. carboxylated poly(arylene ether ketone) by introducing a carboxyl group in the benzene ring, and synthesized ultrafiltration membranes with this polymer. These membranes were found to have an excellent antifouling performance and a reduced adsorption of dyes [25]. The studies mentioned above show that additional stable properties like antifouling and hydrophilicity can be obtained by incorporating functional groups in the chains of commercial polymers. However, not all commercial polymers can be chemically modified, restricting the application of this method. Furthermore, the introduction of functional groups like carboxyl and sulfonic acid in the polymer chains normally results in a great loss of thermal resistance, thermal stability and mechanical strength, lowering the lifetime of the membrane. Designing new polymers by copolymerization of carefully chosen monomers with functional groups is expected to result in membranes with stable hydrophilicity and antifouling properties, without substantially sacrificing the thermal properties and mechanical strength.

In this study, copolymers with different content of carboxyl groups were successfully synthesized by copolymerization of 2-(bis(4-hydroxyphenyl)methyl)benzoic acid (BHPBA), 1,1-bis(4-hydroxyphenyl)-1-phenylethane (BHPPE), and 4,4'-dichlorodiphenyl sulfone (DCDPS). The incorporation of carboxyl groups is expected to improve the hydrophilicity and to reduce fouling of nanofiltration membranes fabricated from such copolymers. In order to alleviate the negative impact of carboxyl groups on thermal resistance, thermal stability and mechanical strength of copolymer membranes, the monomers used for the polymerization reaction were carefully chosen. Generally, polymers synthesized from monomers with a high content of benzene rings would have a high thermal resistance, thermal stability and mechanical strength. Therefore, DCDPS (2 benzene rings) and BHPPE (3 benzene rings) were selected as monomers in the polymerization. In addition, the carboxyl groups are attempt to introduced in the pendent benzene ring rather than in the benzene ring in the main backbone because the backbone of the polymer chains has great effect on thermal resistance,

thermal stability and mechanical strength of a polymer. Accordingly, BHPBA with 3 benzene rings and a carboxyl group in the side benzene ring was included in the copolymerization. New copolymers designed by applying these three monomers in polymerization are expected to have a reasonable glass transition temperature, decomposition temperature, good mechanical strength and exhibit hydrophilic properties. A series of nanofiltration membranes was fabricated from these copolymers by nonsolvent induced phase inversion. The water permeability, dye and salt rejection and antifouling performance of BSA and humic acid are investigated.

## 2. Experimental

### 2.1. Materials

Toluene (AR), potassium carbonate (AR), 4,4'-dichlorodiphenyl sulfone (DCDPS) (AR) were obtained from Sichuan ChengDu KeLong Chemical Reagent Company. N-methyl-2-pyrrolidone (NMP, 99%) were purchased from Sigma-Aldrich and used as solvent in the membrane preparation.  $\text{Na}_2\text{SO}_4$ ,  $\text{MgCl}_2$ , NaCl, and  $\text{MgSO}_4$ , reactive blue 2 ( $M_w = 840$  Da), reactive orange 16 ( $M_w = 618$  Da), humic acid and Bovine serum albumin (BSA) were obtained from Sigma-Aldrich. Deionized water was used throughout in this work. 1,1-bis(4-hydroxyphenyl)-1-phenylethane (BHPPE), 2-(bis(4-hydroxyphenyl)methyl)benzoic acid (BHPBA) was prepared as reported earlier [26].

### 2.2. Copolymers synthesis

As show in Scheme 1, the polymerization reaction was carried out with a nucleophilic substitution method. The  $\text{K}_2\text{CO}_3$  was used as alkali to neutralize the hydrogen of the hydroxyl (-OH) and carboxyl (-COOH) units. BHPBA (12.8 g), BHPPE (17.4 g),  $\text{K}_2\text{CO}_3$  (24.8 g), DCDPS (28.7 g), toluene (25 ml) and NMP (180 ml) were added into a three-necked round bottom flask; then the reaction mixture was heated to 150–160 °C and maintained for about 1.5 h to form the organic salt of bisphenol and to remove the by-product water, which was beneficial for the reaction of nucleophilic substitution and to obtain higher molecular weight copolymers. The by-product water and solvent mixture was collected by reflux condensation. When the collected liquid was about 30 ml, the end of the dehydration process was assumed. Afterwards, a reaction temperature of 195–200 °C was applied for 8 h to further increase the molecular weight of the polymer. During this procedure the viscosity of the mixture gradually increased. After the mixture was poured into water, the white fibrous solids were obtained with mixing. The fibrous solids further acidified with dilute hydrochloric acid. After that they were filtered, and the collected solids were washed with hot water to remove some of the solvent which wrapped in the fibrous solid. After pulverizing the fibrous solids into powder, it was washed by deionized water and ethanol. Repeating the washing procedure 3 times, the copolymers were finally obtained; they were dried in a vacuum oven for 10 h at 100 °C, named 40-COOH (Yield: 94.2%). Using the same procedure, 20-COOH, 40-COOH, 60-COOH, 80-COOH and 100-COOH were prepared with adjusting the content of BHPBA and BHPPE. Table S1

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