



Synthesis, cross-linking modifications of 6FDA-NDA/DABA polyimide membranes for ethanol dehydration via pervaporation

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ABSTRACT

A novel polyimide, copoly(1,5-naphthalene/3,5-benzoic acid-2,2'-bis(3,4-dicarboxyphenyl) hexafluoropropanedimide (6FDA-NDA/DABA), has been synthesized and modified via various cross-linking modifications for ethanol dehydration as a pervaporation membrane. Three different cross-linking approaches – thermal, diamino and diol cross-linking modifications – are employed; their effects on membrane morphology and separation performance are investigated with the help of various characterization techniques. Thermal treatment at high temperature (425 °C) facilitates the decarboxylation-induced cross-linking, therefore restricting the membrane swelling, creating a higher *d*-space among polymer chains, and contributing to high permeation fluxes and comparable separation factors of the resultant membranes for ethanol dehydration. Diamino cross-linking modification changes imide groups in the polyimide into amide groups but post heat-treatment converts them back. However, the interactions among polymer chains are irreversibly changed by the formation of chemical cross-linking and charge transfer complexes, as well as the enhanced hydrophilicity, which bring out the improvement in membrane performance. Diol cross-linking also constrains the membrane swelling and results in a higher *d*-space by the cross-linking spacer, and therefore leading to a higher flux but a lower separation factor than membranes modified by the above two other methods. This work may provide useful insights for polyimide synthesis and cross-linking modifications for biofuel separation.

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1. Introduction

For bioalcohol dehydration, membrane pervaporation is a potential process because of its energy efficiency and environmental benignity [1,2]. Based on the solution-diffusion transport mechanism for pervaporation process, high selectivity and permeability can be achieved if one component in the feed has a higher affinity to the membrane material and a smaller molecule size to diffuse faster across the membrane than others. For pervaporation dehydration, researches in the early stage have been focused on highly hydrophilic polymeric membrane materials, such as polyacrylic acid (PAA), poly(vinyl alcohol) (PVA), chitosan, etc., which have a higher affinity with water molecules than with organic molecules [3–7]. However, these membranes

generally have weak mechanical strength and low stability due to the severe membrane swelling in aqueous solutions, leading to a significant decrease in selectivity. Except polymeric membranes, inorganic membranes based on silica, alumina or zeolites have gained more and more attention in recent years for biofuel separation [8,9]. Since they are not subjected to any solvent-induced swelling and have a superior thermal, chemical and mechanical stability, they typically exhibit a greater selectivity and flux than most polymeric membranes, especially for some specific separations in harsh environments [10]. However, the high cost and low processibility of inorganic materials still limit their applications in membrane separations [8].

Emerged as one potential candidate of polymeric membrane materials for pervaporation dehydration, polyimide possesses attractive mechanical properties, excellent thermal stability as well as good chemical resistance to most organic solvents [11–18]. They have also been reported to show good selectivity towards water, ascribed to the hydrogen bonding interaction of imide groups with water molecules. In addition, the most important advantage of polyimide is that by careful selection of suitable monomers (dianhydrides and diamines) for its syntheses, its chemical structure and therefore its final separation performance as a membrane material could be manipulated and optimized according to the separation target.

Abbreviations: 6FDA, 2,2'-Bis(3,4'-dicarboxyphenyl) hexafluoropropane dianhydride; AFM, atomic force microscopy; BDM, 1,4-benzenedimethanol; CTC, charge transfer complex; DABA, 3,5-diaminobenzoic acid; EDA, ethylenediamine; EG, ethylene glycol; FTIR, Fourier transform infrared spectroscopy; NDA, naphthalene diamine; NMP, N-methyl-pyrrolidone; SEM-EDX, scanning electron microscope- energy-dispersive X-ray spectroscopy; TGA, thermogravimetric analysis; THF, tetrahydrofuran; XDA, *p*-xylenediamine; XPS, X-ray photoelectron spectroscopy; XRD, X-ray diffraction

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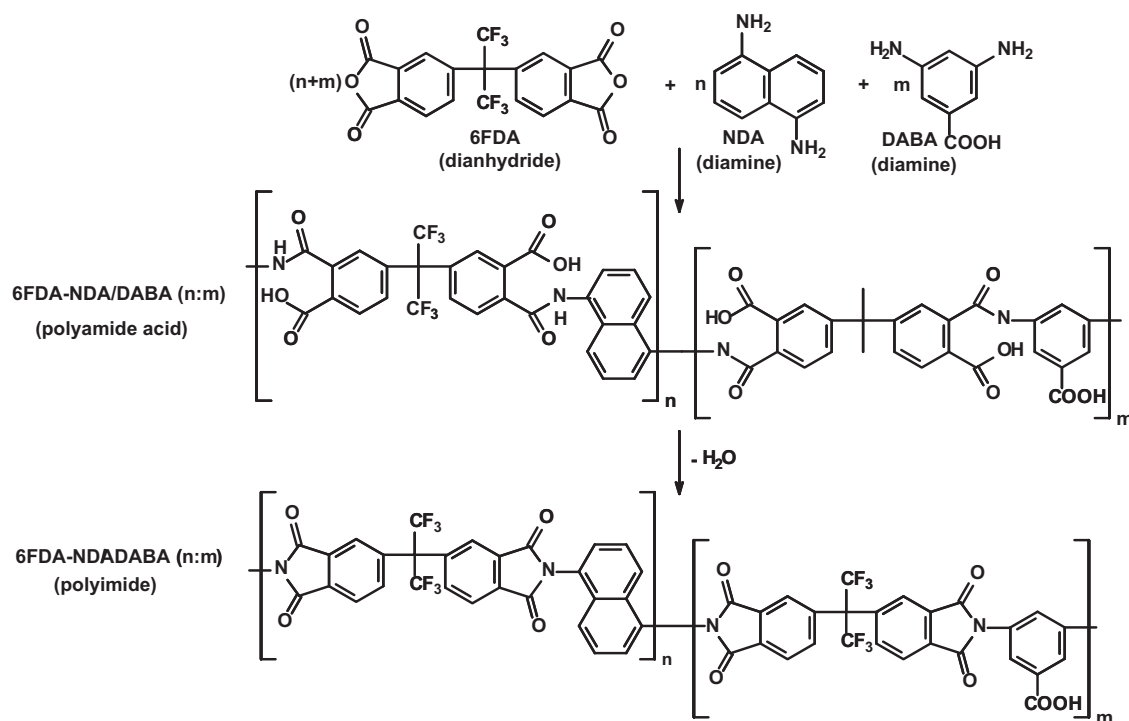


Fig. 1. Synthesis route of 6FDA-NDA/DABA polyimide.

However, in spite of the low degree of swelling for polyimide membranes in aqueous solutions compared to most conventional materials, the swelling might still spoil the pervaporation performance significantly. Various modification techniques of polyimide materials have been explored by researchers in order to achieve a stable membrane performance. Among them, cross-linking is a simple and efficient way to improve the membrane performance. It can be carried out by thermal treatment or using a chemical agent as bridges among polymer chains. Thus, the polymer chain mobility is constricted; the size and the number of free volume in the material are redistributed. The effects of cross-linking modification on membrane permeability and selectivity are strongly dependent on polymer molecular structure, cross-linking agent and cross-linking method. For polyimides, diamino cross-linking method was the most common method. It was first conducted by Hayes [19], and extensively explored by Chung's group [20–23] for gas and pervaporation membranes with improved performance by using various diamines. For carboxylic-group containing polyimides, thermal cross-linking [24–26] and diol cross-linking [27–31] have also been investigated. Thermal cross-linking is one kind of decarboxylation-induced cross-linking reactions at a sufficiently high temperature; while diol cross-linking involves the esterification reaction between diol agents and pendant carboxylic groups. All the cross-linking modifications are proved to be efficient to enhance membrane performance through tightening the membrane structure and restricting the membrane swelling. However, although many researches on chemical cross-linking of polyimides have been developed during the last 2 decades, there are no studies to head-to-head compare the effectiveness of various cross-linking approaches on polyimide membranes for pervaporation dehydration.

Therefore, in this study, a novel 6FDA-NDA/DABA polyimide is synthesized and modified via three different cross-linking methods – thermal, diamino and diol cross-linking – for pervaporation dehydration of ethanol/water mixtures. 6FDA-NDA/DABA is synthesized from 2,2'-bis (3,4-dicarboxyphenyl) hexafluoropropane

dianhydride (6FDA) and two types of diamine, 1,5-naphthalene diamine (NDA) and 3,5-diaminobenzoic acid (DABA). The chemical structures of the monomers and the synthesized polyimide 6FDA-NDA/DABA are shown in Fig. 1. The fluorine groups $-CF_3$ in 6FDA and the bulky spatial structure of NDA are expected to prevent compact chain packing and result in a larger free volume of the synthesized polyimide and higher diffusion coefficients of the permeants. The DABA monomer could increase water solubility because of the interaction between the carboxyl groups of DABA moieties and water molecules via hydrogen bonds. In addition, the introduction of carboxyl groups opens up a great number of ways for post-treatments or modifications of the polyimide in order to improve its separation performance for dehydration application. For the diamino modification, two cross-linking agents – ethylenediamine (EDA) and *p*-xylenediamine (XDA) – are chosen, which represent the smallest cross-linker and a large, rigid cross-linker. For the diol cross-linking, ethylene glycol (EG) and 1,4-benzenedimethanol (BDM) are selected as cross-linking agents correspondingly based on the similar principle, in order to compare the efficiency of diamino and diol cross-linking modifications on pervaporation performance of the 6FDA-NDA/DABA membrane. The structures of the used diamines and diols used are shown in Fig. 2.

The main purposes of this study are to: (1) synthesize 6FDA-NDA/DABA polyimide material for pervaporation dehydration of ethanol solutions through a suitable selection of monomers; (2) study the effects of various cross-linking modifications on morphology and physicochemical properties of the resultant polyimide membranes; (3) investigate the membrane performance for ethanol dehydration via pervaporation as a function of the cross-linking modification. We believe this work can provide useful database for the synthesis and cross-linking modifications of polyimide materials as membranes in the application of solvent dehydration via pervaporation, and valuable insights for future work on next-generation pervaporation membranes.

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