

Thin-film composite membranes for organophilic nanofiltration based on photo-cross-linkable polyimide



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ABSTRACT

This work demonstrates that it is possible to prepare new, competitive thin-film composite (TFC) membranes with a polyolefin ultrafiltration membrane as support and with a non-porous photo-cross-linked polyimide as separation layer for organic solvent nanofiltration. The commercial polyimide Lenzing P84[®] was modified by a polymer-analogous reaction to introduce side groups with carbon–carbon double bonds to increase its photo-reactivity with respect to cross-linking. Polymer characterization revealed that this was successfully achieved at acceptable level of main chain scission. The higher reactivity of the photo-cross-linkable polyimide had been confirmed by comparison with the original polymer; i.e., shorter gelation times upon UV irradiation, higher suppression of swelling by solvents and complete stability in strong solvents for not cross-linked polyimide such as dimethylformamide (DMF) had been obtained. For films from unmodified and modified polyimide, the degree of swelling in various solvents could be adjusted by UV irradiation time. Photo-cross-linking of the original polyimide did not lead to stability in DMF. TFC membranes had been prepared by polymer solution casting on a polyethylene ultrafiltration membrane, UV irradiation of the liquid film and subsequent solvent evaporation. Polyimide barrier film thicknesses between 10 and 1 μm were obtained by variation of cast film thickness. Performance in organic solvent nanofiltration was analyzed by using hexane, toluene, isopropanol and DMF as well as two dyes with molar masses of ~ 300 and ~ 1000 g/mol. Permeances of TFC membranes from unmodified polyimide were low (< 0.1 L/hm² bar) while rejections of up to 100% for the dye with ~ 1000 g/mol could be achieved. TFC membranes from modified and photo-cross-linked polyimide had adjustable separation performance in DMF with a trade-off between permeance and selectivity, in the same range (e.g.: 0.3 L/hm² bar and 97% rejection for the dye with ~ 1000 g/mol) as a commercial conventional polyimide membrane tested in parallel. The established membrane preparation method is promising because by tuning the degree of cross-linking of the polymeric barrier layer, the membrane separation performance could be tailored within the same manufacturing process.

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1. Introduction

Organophilic nanofiltration (oNF) is a special field within the membrane technologies which is growing continually because of the high potential to save energy. Using oNF membranes for exchange of organic solvents or concentrating solutions of organic substances avoids a phase change during separation and, consequently, the energy requirement is much less than for conventional thermal separations such as distillation [1]. Especially in the context of discussions about climate change or limited resources, this argument became very important. For example, oNF separations can be used in the production of biodiesel [2,3], in various steps

in the pharmaceutical industry [4] or to recover or recycle homogeneous organic catalysts [5,6].

Currently, not many commercial membranes are available for such applications. Most of these membranes (e.g., StarMem[®], or DuraMem[®] [7]) have an integral-anisotropic structure with a thin top layer on a porous support, both from the same polymer. The main method to prepare such membrane type is the controlled phase separation (PS) of polymer solutions [8]. Typically that is induced by a non-solvent (i.e., the NIPS process) [1,9]. Another possible way to prepare an oNF membrane is to use a reactive coating of the active layer polymer (e.g., cross-linked polyurethane) onto a suited support membrane from another polymer (e.g., polyacrylonitrile, PAN [10]). There are more examples for composite membranes prepared by various methods to coat thin polymeric separation layers (polypyrrole [11], block copolymers [12], polyelectrolyte multilayers [13], or polymers with inherent

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microporosity [14]) on suited porous supports. Furthermore, based on technologies established since long time for manufacturing water desalination membranes [8,9], some recent works have presented thin-film composite (TFC) membranes for oNF, produced by interfacial polymerization leading to barrier layers from cross-linked polyamides [15–19]. Organic polymers are the main membrane materials; examples include polyolefin, PAN, polysulfone, poly(ethersulfone) or polyimide, either as support or as barrier layer. The barrier layer is non-porous, and depending on the combination of solvent and membrane polymer, the permeability and selectivity are affected by the swelling and solvent resistance of the membrane polymer [1,20]. Consequently, in many cases there is a need for additional polymer cross-linking [10,21–31].

A very interesting class of polymers for oNF is polyimide [32]. These polymers are excellently suited for preparation of membranes because of their outstanding heat resistance and good mechanical strength, as well as their chemical resistance including stability in many solvents. Most membranes consisting of polyimide are produced by the NIPS process and have an integral-anisotropic structure [1]. However, in order to obtain a completely solvent-resistant membrane, in particular to achieve also resistance against polar solvents such as dimethylformamide (DMF), a second step, i.e. cross-linking, is necessary during membrane manufacturing [21]. Chemical cross-linking with diamines is very popular; this cross-linker attacks imide groups in adjacent polyimide chains and can lead to complete solvent resistance [25,27,30,31,33]. However, chemical waste in the cross-linking bath can make the manufacturing process less sustainable. Organic additives to the polymer casting solution or the precipitation bath which are required to obtain the desired cross-section and barrier layer structures during the first step, the NIPS process, further increase the amount of waste during membrane production [34,35].

The motivation for this work was to eliminate the need for chemicals (e.g., diamines) in the second step of the membrane preparation by using UV irradiation for direct cross-linking [36]. Furthermore, the selective barrier layer should be created without additives like it is the case in the NIPS process. These two aims were to be achieved by developing a method for preparation of a

thin-film composite membrane using a UV cross-linkable modified polyimide (Fig. 1). Similar to manufacturing of TFC reverse osmosis membranes, an ultrafiltration (UF) membrane was used as porous support membrane [16,37]. A solution of the reactive polymer should be cast on the UF membrane, cross-linked by UV irradiation and after removing the solvent by evaporation a thin solvent-resistant selective layer would be obtained. The challenge was to synthesize a highly UV reactive polymer and to tune the process parameters like casting thickness, UV irradiation conditions as well as post-treatment conditions. Such process would be most promising because by tuning the degree of cross-linking of the barrier layer, the membrane separation performance could be tailored within the same manufacturing process. A somewhat related approach based on photo-cross-linking had been reported recently [38]. However, different from this work, a mixture of a photo-initiator and a cross-linker monomer had been added to a casting solution of a membrane polymer (for instance polysulfone or polyimide), a membrane had been formed by non-solvent induced phase separation and thereafter the UV irradiation had been performed to yield a stabilized membrane via formation of a semi-interpenetrating polymer network.

In this work the polyimide Lenzing P84[®] was used [39,40]. As known from the literature, Lenzing P84[®] contains a substituted benzophenone group in its repeating unit. Therefore it is photo-reactive; it is possible to cross-link such a polyimide by UV irradiation [41]. The basic mechanism is the abstraction of hydrogen from a, preferably, aliphatic hydrocarbon group by the UV-excited benzophenone, creating two radicals followed by the recombination of the two radicals to a new covalent bond (Scheme 1) [42]. In order to further increase the intrinsic UV reactivity and to be able to obtain a completely solvent-resistant polymer film, new reactive side groups had been introduced into the polyimide by polymer-analogous reactions. The here used aminoethylmethacrylate (AEMA) can react with the polymer chain via opening of the imide bond (the same reaction which is also used to cross-link PI with help of diamines; cf. above) and introduce double bonds as side groups to the polyimide chain (Scheme 2). It had been speculated that this will lead to more efficient cross-linking via main

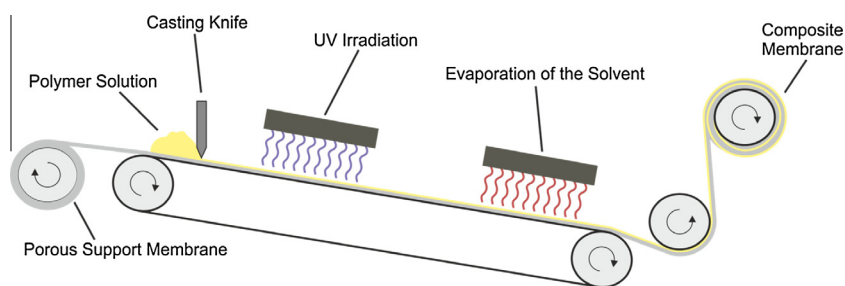
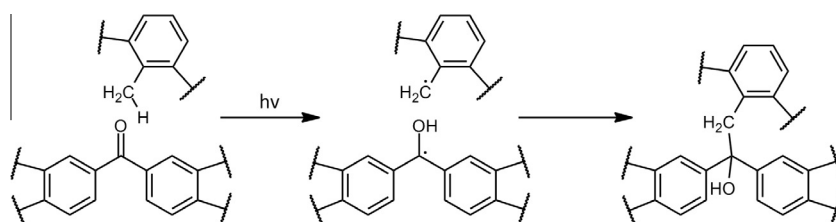


Fig. 1. Scheme of the membrane preparation process, starting with casting a polymer solution onto a porous support membrane, followed by an UV irradiation initiated cross-linking of the polymer, and solvent evaporation leading to a thin-film composite membrane.



Scheme 1. Basic mechanism of the UV-induced cross-linking of a polyimide containing benzophenone groups in the main chain and aliphatic hydrocarbon groups enabling hydrogen abstraction.

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