



Solvent and thermal resistant ultrafiltration membranes from alkyne-functionalized high-performance polymers

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ABSTRACT

Polymeric porous membranes with excellent thermal (T_d higher than 500 °C) and solvent resistance were prepared. The membranes were based on three high-performance polymers (polyoxindolebiphenylene, polytriazole and polybenzimidazole), functionalized with alkyne side groups. The functionalization enabled the polymer crosslinking by a fast and simple wet-state thermal process in hot glycerol. The effect of crosslinking time and temperature was evaluated. The obtained membranes were characterized by spectroscopy and thermal analysis. The membrane morphology was investigated by electron microscopy. The liquid separation performance of the crosslinked membranes was evaluated in several organic solvents. The stability in filtration experiments was demonstrated in dimethylformamide at temperatures up to 140 °C. The solvent resistance in various solvents was confirmed in long-term tests (up to 21 days) at room temperature.

1. Introduction

Membrane-based separations can have a major contribution for improving the efficiency of purification processes in the chemical industry [1,2]. During the last decade, the membrane technology has been moving into more challenging applications, extending the widespread use in water-based separations to analogous processes such as ultrafiltration, nanofiltration [3,4], reverse osmosis [5] and forward osmosis [6] conducted in organic solvent medium.

Besides the resistance to organic solvents, thermal robustness is desirable to target processes that currently are being addressed only with ceramic membranes. Although ceramic membranes are known for their good solvent and thermal resistance [7], polymer membranes surpass them regarding manufacture, processability and capital cost.

The development of thermal resistant dense polymer membranes has been successful for a variety of applications. Examples are fuel cell [8] technology, gas separation, such as CO₂/H₂ [9], syngas [10], and others. Much less has been reported regarding porous membranes. Among their applications are hot gas filtration [11], steam sterilization [12], and heat resistant battery separations [13].

Aromatic high-performance polymers, such as polyimide, polysulfone, polyphenylenesulfide (PPS), polyarylsulfone and, polyethersulfone, are those mostly used for organic solvent nanofiltration. They require crosslinking to achieve the desired solvent resistance. Frequently, the crosslinking step incorporates chemical groups that

hamper the thermal resistance of the material. To overcome this issue, a thermal resistant crosslinking segment would be required. In this work, we explored a functionalization strategy that enables a further step of thermally induced crosslinking and leads to materials with inherent thermal resistance. Different thermal approaches have been proposed to obtain membranes with low plasticization for gases or vapor separation. Lee's group [14,15] pioneered in the polymer thermal rearrangement for this purpose, without crosslinking. Thermal crosslinking has been explored by Chung's group for polyimide membranes [16–19] applied for hydrocarbon separation. Koros et al. [20] reported crosslinked hollow fibers obtained by thermal decarboxylation.

An interesting approach for polymer crosslinking involves different reactions of carbon triple-bonds, which can be part of the polymer backbone or be present as pendant or terminal groups. This has been previously applied for gas separation [21], fuel cell [22], optical [23–26] and photosensitive materials [27], sensors [28–31], polymer nanoparticles [32], crosslinked micelles [33], shape memory polyurethane [34], high temperature performing materials [35–37], and mechanically stable polyamides [38]. Some of the reactions involving triple bonds are click cycloaddition [39], photo-activated thiol-yne chemistry [40] and Glaser-Hay coupling [41]. For membrane crosslinking, carbon triple bond functionalizations have been explored aiming at gas separation [42–47], desalination [48] and fuel cell [49–52] [53]. Carbon double-bond thermal crosslinking have been previously applied to membranes [54–56].

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In this work, we explore for the first time for organic solvent resistant porous membranes a crosslinking approach based on a thermal carbon-carbon triple bond reaction. We functionalized polymers known for high thermal stability with propargyl groups and thereby enabled their thermal crosslinking. The three chosen high-performance polymers were polyoxindolebiphenylene (POX-NH), hydroxyl-polytriazole (PTA-OH), and polybenzimidazole (PBI-NH), which have all thermal degradation temperature, T_d , above 500 °C. These polymers have been previously used to manufacture membranes for organic solvent resistant applications [57–61], crosslinked by using other routes. The solvent resistance was achieved, but the crosslinking segments contributed to reduce the thermal stability. The main advantage of the new crosslinking strategy is that the high thermal stability of the pristine polymers is retained after the reaction. Furthermore, the modification with propargyl is an easy one-step room-temperature method that could be applied to different polymer systems. The thermal crosslinking was achieved by simply immersing the membranes in hot glycerol for a short time, without the need of additional chemicals or catalysts.

2. Experimental

2.1. Materials

Biphenyl (99.5%), isatin (97%), potassium carbonate (K_2CO_3 , 99%), trifluoromethanesulfonic acid (TFSA, 98%), *N,N*-dimethylformamide (DMF, 99%), *N*-methyl-2-pyrrolidone (NMP, 99%), dimethyl acetamide (DMAc), dimethyl sulfoxide (DMSO), glycerol, propargyl bromide (80% toluene solution), acetonitrile (MeCN), and polyethylene glycol (PEG) were purchased from Aldrich. Trifluoroacetic acid (TFA, 99.5%) was provided by Alfa-Aesar. Polyester (PET) and phenylene sulfide (PPS) non-wovens were used for membrane casting.

2.2. Synthesis of membrane polymeric materials

Three different polymers were used as base for the membrane preparation: polybenzimidazole (PBI-NH), polytriazole (PTA-OH) and polyoxindolebiphenylene (POX-NH). The termination NH and OH are used in the text to indicate the groups available for reaction and later incorporation of the triple bonds. For the PBI-NH membranes, a commercial 26 wt% PBI solution in DMAc was purchased from PBI Performance Products.

2.3. Synthesis of hydroxyl functionalized polytriazole (PTA-OH)

Hydroxyl-functionalized polytriazole (98% monomer functionalization) (PTA-OH) was synthesized according to a procedure previously reported in ref [60], using polyoxadiazole as precursor [61]. In a typical reaction, polyoxadiazole (50 g, 0.135 mol) was dissolved in a 2 L three neck flask and dissolved in 333 mL of NMP. To the homogeneous solution, 2 g of PPA and 37 g of 4-aminophenol was added and then the reaction was brought to 195 °C. The reaction was kept under nitrogen for 15 h. The resulting polymer solution was precipitated in a mixture of water-methanol at 60 °C. The obtained polymer was purified by re-precipitation in methanol from a 15 wt% polymer solution in NMP.

2.4. Synthesis of amino-functionalized polyoxindole (POX-NH)

Amine-functionalized polyoxindole was synthesized by superacid condensation of isatin and biphenyl following the procedure reported in ref [62], as is described below. Biphenyl (1.542 g, 10 mmol), trifluoroacetic acid (TFA, 4.65 mL) and trifluoromethanesulfonic acid (TFSA, 8.00 mL) were added into a 25 mL single-neck round-bottom flask. The mixture was magnetically stirred and cooled down to 0 °C. The isatin (1.4715 g, 10 mmol) was promptly added to the mixture. The reaction was kept under inert atmosphere. The cooling bath was removed 15 min after the reaction started. The reaction continued at

room temperature during 3 h. The resulting polymer solution was precipitated in methanol at room temperature. The obtained polymer was purified by re-precipitation in methanol from a 15 wt% polymer solution in NMP.

2.5. Alkyne functionalization

The introduction of the alkyne groups was conducted to later promote the thermal crosslinking. In the case of PBI-NH, the modification was performed after the membranes preparation, while for the PTA-OH and POX-NH the modification was done in solution, before casting the membranes.

2.6. Modification of PTA-OH and POX-NH

The polymer (1 g) was dissolved in *N*-methyl-2-pyrrolidone (NMP) (19 mL) in a 50 mL single-necked round-bottom flask and magnetically stirred until a transparent homogeneous solution was obtained. Potassium carbonate (K_2CO_3) (2 g, 14.4 mmol) was added. Propargyl bromide (80% toluene solution) (2 mL, 18.5 mmol) was dropwise poured to the reaction mixture. The reaction was kept at inert atmosphere and room temperature for 24 h for POX-NH and 48 h for PTA-OH. The polymer reaction mixture was precipitated in water. The obtained threads were copiously washed with water and methanol and then dried in vacuum-oven overnight. The modified polymers were further purified by re-precipitation in water from NMP 15 wt% solutions. The modification procedures are shown in Schemes 1 and 2.

2.7. Membrane preparation

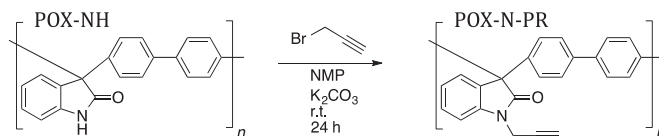
Porous membranes were prepared by non-solvent induced phase separation (NIPS). Polymer (plain PBI and alkyne-functionalized PTA-OH and POX-NH) solutions in DMAc were poured onto a glass plate, PET or PPS non-wovens and the solution was homogeneously spread with a casting knife adjusted with a 150 μ m gap. Immediately after (no evaporation time), the incipient membrane was immersed in MiliQ water (25 °C). The membranes were kept in water for 4 h before use. The plain PBI membrane was then post-modified with propargyl bromide as described below.

2.8. PBI-NH modification

The pre-cast PBI membranes were immersed in a 10 wt% propargyl bromide solution in acetonitrile (MeCN). 5 wt% potassium carbonate was added, the system was kept at room temperature under stirring for 48 h. After the modification was completed, the membranes were washed with MeCN and transferred to methanol. The modification's route is shown in Scheme 3.

2.9. Membrane crosslinking

The membrane crosslinking was promoted by thermal reaction between alkyne groups, as illustrated in Scheme 4. The membranes with alkyne-containing polymer membranes were immersed in glycerol, followed by a temperature increase to 200 °C. The membranes were kept at this temperature for 1 h. After this time, the membranes were transferred to a glycerol bath at room temperature and then to a methanol bath, where they were kept during 12 h before use. Before



Scheme 1. Modification of polyoxindolebiphenylene (POX-NH).

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