



**Note**

“We can understand things better. We can never understand things fully”  
Physicist David Deutsch, University of Oxford

## ARTIFICIAL WATER CHANNELS IN SUPRAMOLECULAR POLYMERIC MEMBRANES, EXHIBITING HIGH WATER PERMEABILITY

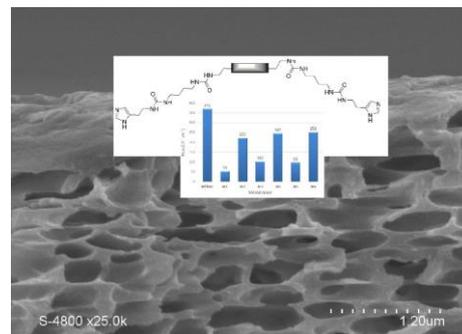
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The modular design of supramolecular polymeric membrane materials has attracted a great deal of interest for the optimization of the filtration performances requiring a detailed knowledge of chemical microstructure and nanoscale morphology. In this context, the supramolecular synthesis provides a powerful tool for the controlled generation of self-organized functional membrane materials. We therefore decided to use this strategy employing a novel supramolecular synthetic route in order to control the formation of Artificial Water Channels -AWC within thin layer polymeric films. Such controlled generation of self-organized channels for water transport has yet to be realized and represent a straightforward approach for the design of a novel class membranes for water purification. Herein we report self-assembled membranes including I-quartet (resulted from self-assembly of four imidazoles with water molecules) and T-channels (resulted from self-assembly of amino-triazoles with water molecules) water channels that are homogeneous, flexible and show both high thermal and chemical stabilities. They were surveyed for their ability to form nanochannels, reaching high water permeation. These results provide new insights into the basic features that control the convergence of supramolecular self-organization with the water conduction function and suggest tools for developing the next generation of water purification membranes.



Numerous biomimetic channel systems able to perform efficient water transport across membranes have been developed in the last decades.<sup>1</sup> Most of synthetic methods utilized to construct such water selective membranes result in random or statistical disposition of functional hydrophilic (*i.e.* imidazole, sulfonic, phosphonic, carboxylic, etc.) or hydrophobic (phenyl, poly-phenyl, alkyl, fluoro-alkyl, etc.) groups along the self-organized transporting pathways.

Artificial Water channels-AWCs offer a unique opportunity to set up highly performant membranes

with both high-water permeability and complete selective rejection of ions.<sup>2-7</sup> Recent results have made possible the design of AWCs, that feature efficient permeability of water, but their selectivity issues remain in the most of the cases still unsolved. Having an artificial nature, the AWCs present the important advantages: a) their structural design is simple; b) they are easily tuneable to be optimized for higher recognition of water clusters; c) they can be synthesized on a large amount, at lower cost than biological counterparts; d) their engineering scale-up becomes simpler and more reproducible without bio

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related processing steps with e) they should be easily included in membranes without the use of specific additives and f) they are robust and stable when incorporated into membranes. We know that the active cross-section area of the AWCs is less important than that of natural Aquaporins-AQPs, which increase their permeability per membrane surface area when compared with AQPs membranes.

Nanophase segregation methodologies were extensively used through precision synthesis of random and block copolymers to generate specific conduction pores.<sup>8-12</sup> One of the key issues is to maximize the water permeability of the membrane by increasing the water pathways transport content. A possible further step is to take advantage of the self-assembly of these hydrophilic groups in

directional oriented pathways and to control the nanomaterial build-up by self-organization. Within this context, hydrophilic/hydrophobic nanomaterials produced by self-assembly are the subject of various investigations.<sup>5-7</sup>

Many groups including our own have found new strategies for the elaboration of such self-organized materials based on AWC precursors, in which the functional hydrophobic and hydrophilic self-assembled networks are covalently connected. Recently, we proved the possibility to create self-organized directional hydrophilic superstructures<sup>6,7</sup> and urea supramolecular ribbons are used to transcribe the oriented self-organization in a polymeric matrix by a self-assembly.<sup>8,9</sup>

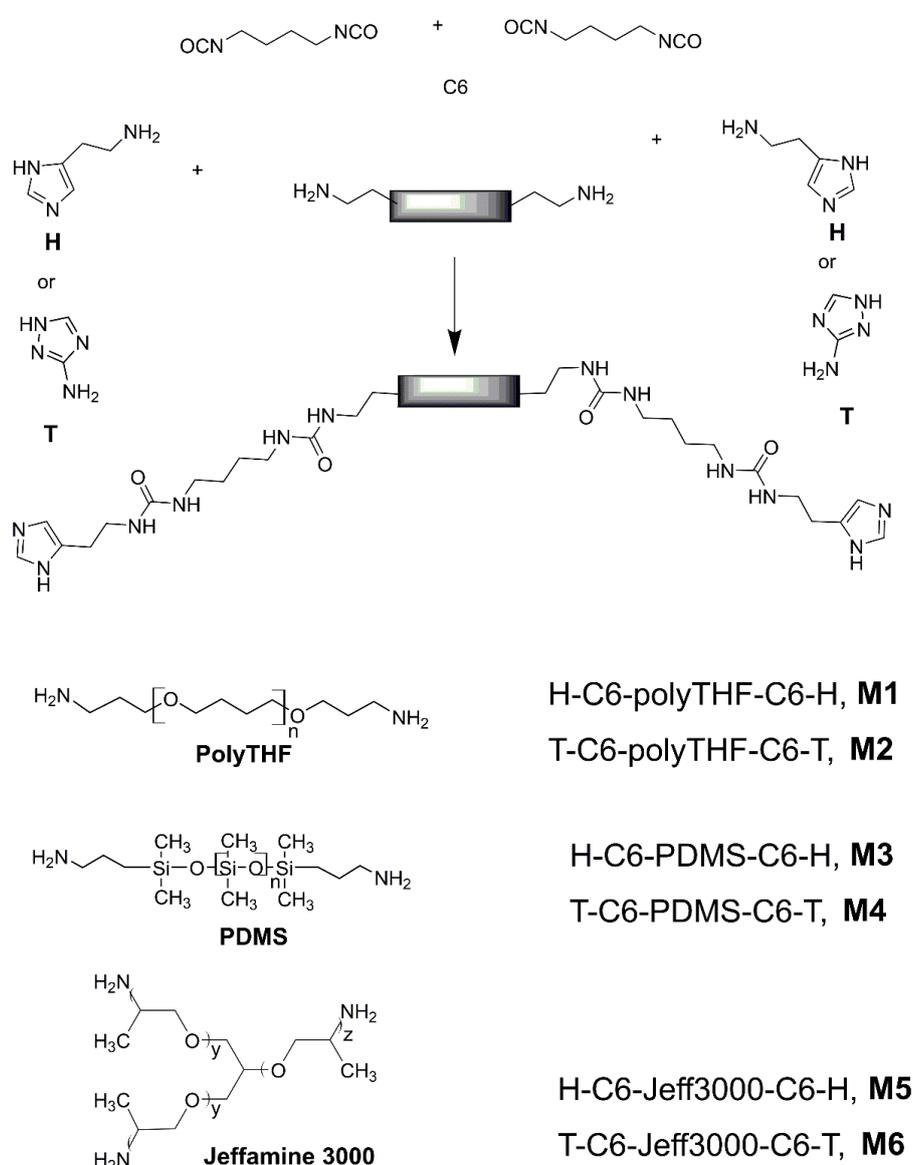


Fig. 1 – Chemical structures of functional molecular and macromolecular precursors used to construct self-organized membranes **M1-M6**: Histamine, **H** and Amino-Triazole, **T** generate self-organized water channels; **PolyTHF**, **PDMS** and **Jeffamine3000** are used as hydrophobic components, while hexyl-diisocyanate, **C6** is used as cross-linking agent.

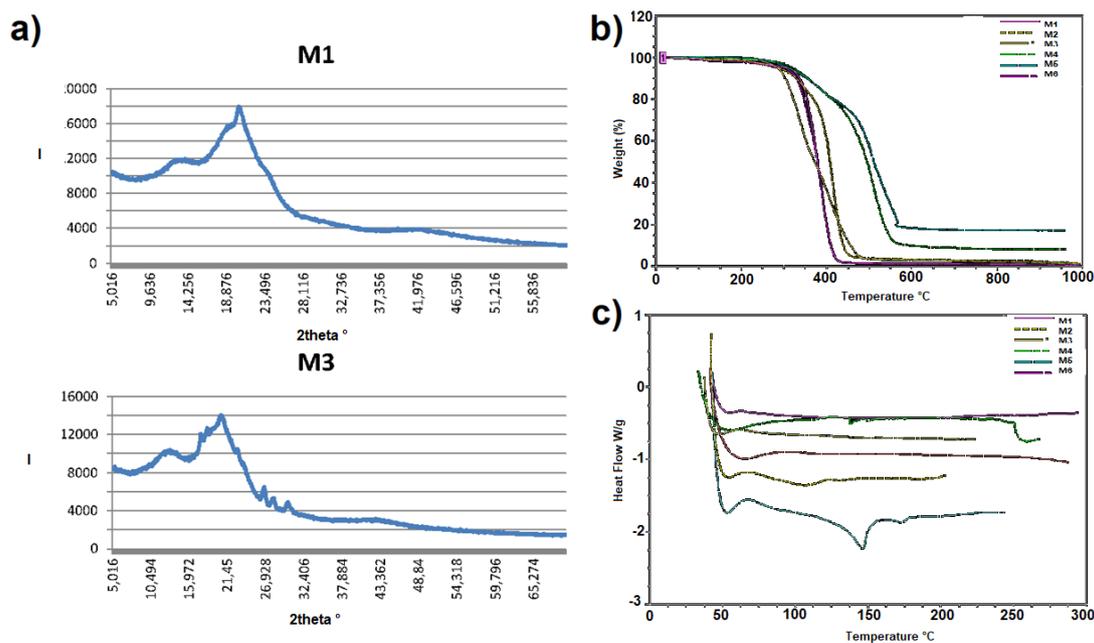


Fig. 2 – Characterization of hybrid membrane materials. a) X-ray powder diffraction patterns **M1** and **M3**. b) Thermal Gravimetric analysis-TGA and Differential scanning calorimetry DSC analysis of materials **M1-M6**.

Toward this objective, our aim has been to develop membranes for selective water transport, using a combined supramolecular strategy involving self-assembled AWCs included in hydrophobic host matrixes. Several compounds have been used as commercial synthetic precursors for the fabrication of self-organized membranes described here: the hexyl-diisocyanate **C6** was treated with the corresponding hydrophobic macromonomers: 1,1'-(poly-tetrahydrofuranyl)bis(3-(2-(aminopropyl)), **polyTHF** ( $M_n=1100$  g/mol), Poly(dimethyl siloxane)bis(3-aminopropyl) terminated, **PDMS** ( $M_n=2500$  g/mol), and Polypropylene-bis(3-aminopropyl)terminated, Jeffamine T-3000, **Jeff3000** ( $M_n=3000$  g/mol) and the hydrophilic histamine, **H** and amino-triazole, **T** heterocyclic compounds, previously used by our group as water-binding head groups for the construction of active artificial water channels.<sup>6,7</sup> The resulting supramolecular polymers combines three encoded structural features 1) a water binding functional groups allowing the water binding *via* H-bonding in a hydrophobic polymeric matrix, which is heavily relied with both permeability and water uptake behaviours of the resulted membrane materials; 2) several H-bonding groups trough head-to-tail H-bond association of the urea groups, used to align the hydrophilic water conducting with 3) the hydrophobic macromolecular segments. They are non-covalently bonded to bis-ureidohexyl residues, allowing by H-bonding process to self-organize superstructures from solution and in a solid film material (Figure 1).

The macromolecular plasticizers, **polyTHF**, **PDMS**, **Jeff3000** have been reacted with 1,6 hexyl isocyanate and with the active terminating water binding heads **H** and **T** in order to produce mechanically and thermally stable dense membrane films, **M1-M6** (Figure 1). As a result of their hydrophilic nature the water H-bonding precursors **H** and **T**, might optimally self-segregate in a lipophilic environment, thus maximizing the water transport between self-organized hydrophobic pathways, reminiscent to proton conduction within hybrid siloxane membrane<sup>8</sup> or of hybrid heteropolysiloxane macrocyclic self-organized membrane films<sup>9</sup> previously reported by our group.

FTIR spectroscopic analyses of solids **M1-M6** demonstrate the formation of strong urea H-bonding. The H-bond vibration shifts of urea moiety were detected at  $\nu_{C=O}=1690$  to  $1650$   $\text{cm}^{-1}$  indicating the urea ribbon formation. The  $^1\text{H}$  NMR spectra are in accord with proposed formula and will be reported elsewhere.

Of particular interest is the potential ability of hydrophobic-hydrophilic dense membranes to present percolating domains by self-assembling at the supramolecular level. Hence, particular attention was given to the nano structuration of resulted materials, which is in direct relation with the nature of used macro-precursors. It may be perceived as a formidable potentiality for increasing the intrinsic permeability of a membrane. In order to minimize the cross-linking of the network and to maximize the self-organization of functional channel forming

moieties, we have conducted the synthesis experiments in chloroform at reflux by using increasing amounts of head molecules **H** and **T** 0.5 to 1 and 2 molar ratio compared to macromolecular precursors. This allows to generate semi crystalline to amorphous materials with the highest ratio of 2 for hydrophylic heads as proved by X-ray diffraction XPRD studies (Figure 2a). The XPRDs of the hybrids **M1-M6** preserve certain order when embedded within ureido-connected plasticizers, which remains after the co-condensation step with the precursor **H**, albeit less pronounced than in the precursor **T** (not shown).

A high thermal and chemical stability of membranes is a key property that is necessary for the durability under water treatment operation. In the present case, the thermal stability was investigated by Thermal Gravimetric analysis-

TGA (Figure 2b) and the decomposition occurred in two distinctive steps, identified for all membranes **M1-M6**. The temperature at which the membranes retained 90 wt% of their initial weight increased gradually from 200°C to 350°C and is attributed to the loss of strongly H-bonded water. Then the decomposition occurred above 400-450°C and highlighting a very good thermal stability of the resulted hybrid materials gradation temperature. From the results obtained in Differential scanning calorimetry DSC (Figure 2c), we can find that the materials **M1-M6** are stable in the temperature range 40-250°C studied. However, the DSC results show an endothermic reaction at 100°C, corresponding to a phenomenon of dehydration followed by crystallization, in agreement with the results observed in XPRD.

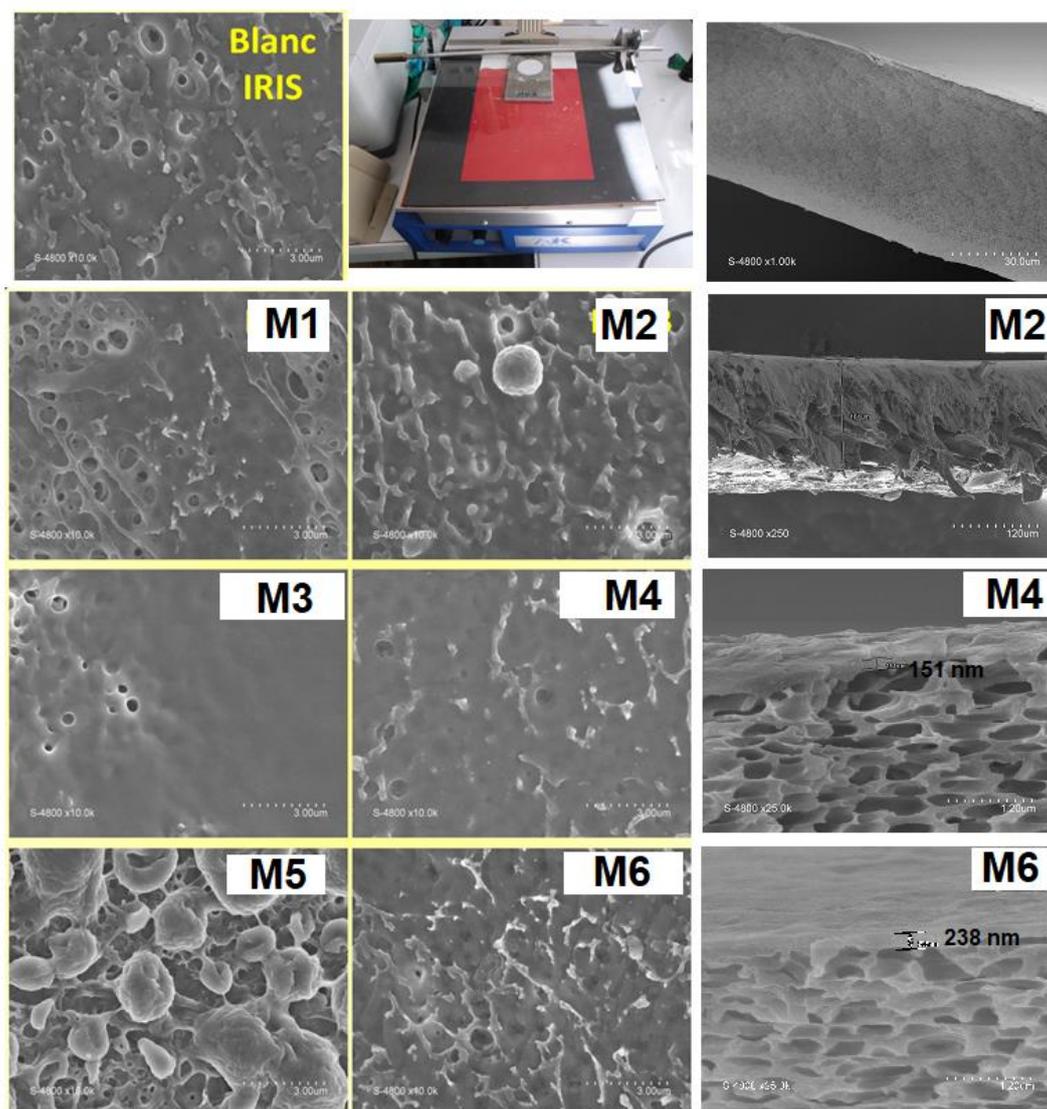


Fig. 3 – Image of mechanically stable homogeneous supported hybrid membranes prepared by tape casting and SEM image of the surfaces of membranes **M1-M6** and of cross-section of membranes **M2, M4** and **M6**.

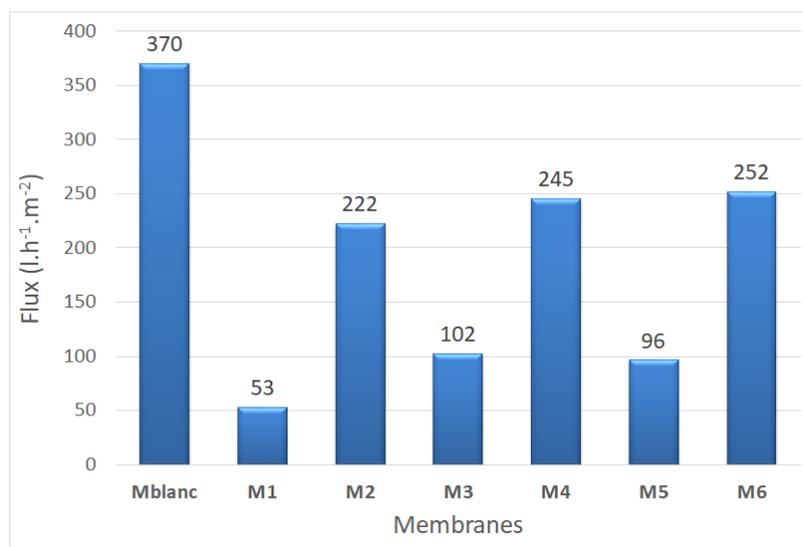


Fig. 4 – Experimental water flux of control support membranes and **M1-M6** membranes incorporating AWCs.

Six supported membranes **M1-M6** (Figure 3) of good quality were obtained by tape-casting coating of the solutions of the polymers by adding the adjustable amounts of a functional polymers onto planar Polysulfone membrane supports and then dried for by using a specific thermal treatment. Scanning electron microscopy (SEM) reveals that the supported films (thickness between 115 and 250 nm depending on the nature of used monomers) were dense, without pinholes. Figure 3 depicts a typical large scan area SEM image of the films and shows well-resolved details continuous films (see the cross-section images of **M2**, **M4** and **M6** membranes) with the formation of self-organized nanoparticles over the long domains at the surface of the membrane. The analysis of the surfaces of the membranes showed distinct less roughened structures reminiscent with the formation of crystalline at the surface domains following the solvent evaporation.

The novelty of these findings with respect to our previous work on the hybrid dense heteropolysiloxane materials<sup>8,9</sup> that can accurately self-organize over the dozens or hundreds of nanometers, the present materials obtained exclusively via H-bonding self-assembly of urea ribbons and H-bonding AWCs, show semicrystalline behaviours reminiscent with an overall self-organization of channel superstructures confined within the hydrophobic scaffolding environment.

The molecular arrangement in membrane **M1-M6** defines a particularly attractive functional transport device that encodes the required information for directional-diffusion transport of

water in the membrane material (Figure 4). It defined translocation pathways in a similar manner that the hydrophilic pore-type proteins assist the ion diffusion along the hydrophobic cell membrane.

The water permeability of the membranes **M1-M6** is of particular importance. The **polyTHF**, **PDMS** and **Jeff3000** materials used a hydrophobic matrix to generate water channel superstructures within the membrane films are typically a poor water permeable unless water channels are present. It is noted during the handling that all studied membranes kept their mechanical strength after they were immersed in water. The reference support membrane **Mblanc** exhibited, as expected, a high-water flux of 370 LMH. The water fluxes values of membranes **M1-M6** were found to be lower: 50-100 LMH for histamine, **H** based membranes **M1**, **M3**, and **M5** and 220-250 LMH for triazole, **T** based membranes **M2**, **M4**, and **M6**, indicating that the dimension of the channels formed by **H** (I quartet= 2.6 Å)<sup>6</sup> and **T** (T-channel =5 Å)<sup>7</sup> is highly important for the diffusion of water clusters within membranes. On the other hand, the nature of the matrix is highly important as lower water permeabilities were obtained for highly hydrophobic and compact **polyTHF**-based membranes **M1** and **M2**, while the permeabilities are practically doubled for the soft **PDMS**-based **M3** and **M4** and crosslinked and probably slightly porous **Jeff3000**-based, **M5** and **M6** membranes. The mechanism of water permeability is different to the related previous studies on most porous membranes used for desalination and is mostly related to the wettability. These data are indicative

of the formation of water-filled channels hierarchically self-organized along of hydrophobic domains in order to generate efficient percolated water conducting domains, which in turn results in correspondingly water permeability.<sup>10</sup>

In conclusion, we describe in this paper different membrane systems in which the self-organized precursors H and T generates nanometric water channel superstructures a scaffolding hydrophobic hybrid material. The controlled generation of connected self-organized channels for directional water diffusion via phase segregation,<sup>11,12</sup> represents a straightforward approach for the design of a novel hybrid membranes with high permeabilities for water purification.<sup>13-16</sup> This led to the discovery of new functional supramolecular architectures offering new insights into the basic features that control the design of polymers, nanocomposites or supramolecular assemblies for water filtration membranes with desirable properties compared or superior to commercial ones.

All these results demonstrate that the synergetic incorporation of hydrophobic/hydrophobic components is crucial for the induced phase segregation within the structures used for the membrane preparation.<sup>11,12</sup> Straightforward synthetic access to asymmetric membranes give rise to novel strategies to constitutionally built up under supramolecular control very productive transport membranes for high added value applications as water purification. They might provide new insights into the basic features that control the design of functional materials mimicking the natural water channels with applications in water purification technology, chemical separations, sensors or as storage-delivery devices.

**General methods.** Reagents were obtained from commercial suppliers and used as received. <sup>1</sup>H-NMR spectra were recorded on an ARX 300 MHz Bruker. ATR-FTIR spectra were recorded on a NEXUS spectrometer. The ATR accessory contained a monolithic diamond crystal at a nominal angle of incidence of 45°, yielding about 1 internal reflection at the sample surface. All spectra were recorded at 25°C in the region 625–4000 cm<sup>-1</sup>. SEM images were obtained with a Hitachi S-4500 apparatus, under a tension of 0.5–30 kV. X-ray powder diffraction measurements were performed with Cu-K $\alpha$  radiation at 20°C using a Philips X'Pert Diffractometer equipped with a Xcelerator detector. Thermogravimetric analysis (Hi-Res TGA 2950, TA Instruments, Nitrogen, 50–

600°C at 10°C/min) and Differential Scanning Calorimetry (DSC 2920 Modulated, TA Instruments) were used to evaluate thermal stability of the dimeric materials. Water transport property was tested by Sterlitech HP4750 stirred cell, with active membrane area of 14.6 cm<sup>2</sup>, maximum processing volume of 300 mL and cell height of 22.4 cm.

**General procedure for synthesis of membrane materials M1-M6:** 1 equivalent of macromonomers have been solubilized in 40 mL of methanol (**Jeff3000**) or 40 mL of chloroform (**polyTHF, PDMS**) and 1, 1.5 or 2 equivalents of **H** or **T** were added in 10 mL of methanol. After a brief mixing, 2 equivalents of hexyl isocyanate were added and the mixture was refluxed at 80°C for 24 hours. For example, one equivalent; 1g of poly THF (Mn= 1100 g/mol) and 0.111g of H (M = 111 g/mol) were reacted with 162  $\mu$ l hexyl isocyanate (MM 168 g/mol). After the 24 hours of reaction, the solvents are evaporated and the final products are isolated as viscous gels or as powders. The elaboration of the membranes starts from these products, which are solubilized in methanol to obtain a viscous solution. Which is then dropped on the surface of the polysulfone GR60PP membrane supports from Alfa Laval by tape-casting under a speed of 3.3 cm/s at room temperature. The membrane is then dried (8h at 40°C, 4h at 60°C, 4h at 80°C) to give the thin layer membranes **M1-M6**. It noted during the handling that all membranes were transparent, homogeneous and kept their mechanical strength. The membranes were then preserved in MiliQ water.

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