Gas-Separation Membranes Hot Paper

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Hypercrosslinked Additives for Ageless Gas-Separation Membranes

Cher Hon Lau, Xavier Mulet, Kristina Konstas, Cara M. Doherty, Marc-Antoine Sani, Frances Separovic, Matthew R. Hill,* and Colin D. Wood**

Abstract: *The loss of internal pores, a process known as physical aging, inhibits the long-term use of the most promising gas-separation polymers. Previously we reported that a porous aromatic framework (PAF-1) could form a remarkable nanocomposite with gas-separation polymers to stop aging. However, PAF-1 synthesis is very onerous both from a reagent and reaction-condition perspective, making it difficult to scale-up. We now reveal a highly dispersible and scalable additive based on α,α′-dichloro-p-xylene (p-DCX), that inhibits aging more effectively, and crucially almost doubles gas-transport selectivity. These synergistic effects are related to the intimately mixed nanocomposite that is formed though the high dispersibility of p-DCX in the gas-separation polymer. This reduces particle-size effects and the internal free volume is almost unchanged over time. This study shows this inexpensive and scalable polymer additive delivers exceptional gas-transport performance and selectivity.*

Super glassy polymer membranes are leading candidates for low-energy gas separations because they display high permeabilities and selectivities.[1] Currently, their widespread implementation is hindered by a rapid performance loss due to physical aging.[2] Physical aging is a phenomenon where polymer chains relax and converge[3] which reduces the performance of polymeric gas-separation membranes. This has been the hurdle in the ultimate deployment of leading super glassy polymers, such as poly(1-trimethylsilyl-1-propyne) (PTMSP). Attempts to prevent this aging typically reduce gas permeabilities[4] or require prohibitively expensive additives.[5] There is a clear need for alternative additives to inhibit aging in super glassy polymers that combines high performance with low cost. Herein we describe the development of inexpensive mixed-matrix PTMSP membranes with class-leading permeability and selectivity performance.

We recently incorporated a porous aromatic framework additive, PAF-1,[5b,6] into a super glassy polymer membrane which prevented physical aging in the membranes whilst enhancing gas permeabilities. The similar chemical composition of PAF-1 and PTMSP was crucial for stopping physical aging in the membrane.[5b] PAF-1 pores are decorated with aryl-H groups that interact with the methyl groups of PTMSP. Whilst PAF-1 was an effective additive for reducing physical aging in mixed-matrix membranes, its complex synthesis route renders it too expensive for commercial uptake.

Hypercrosslinked polymers (HCPs) are a class of nanoporous organic network that can be synthesized using Friedel–Crafts chemistry to generate extensive cross-linking within existing polymers, lightly cross-linked networks, or small molecules.[7] The resulting polymers consist of aromatic rings joined together through multiple methylene bridges (Figure 1 a). They have been studied for physisorptive gas storage and can adsorb significant quantities of H_2,[8] CH_4,[9] and CO_2.[10] The high gas uptakes are ascribed to high Brunauer–Emmett–Teller surface areas (1200 to 2000 $m^2 g^{-1}$).[11] Structurally, HCPs are similar to PAF-1 so they could be used as alternatives to PAFs. The aim of this study was to develop and test low-cost, non-aging, tunable, mixed-matrix membranes with high permeability (Figure 1 b,c).

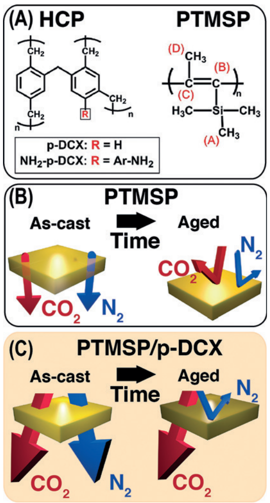

Figure 1. A) Chemical structures of HCPs used in this work, and PTMSP. B) PTMSP membranes age over time and gas permeabilities are reduced. C) By adding *p*-DCX into PTMSP gives a selective-aging membrane in which H_2 and CO_2 transport is preferred over CH_4 and N_2.

In this work, HCPs were synthesized using Friedel–Crafts polymerization of α,α′-dichloro-*p*-xylene to generate *p*-DCX. The resulting polymer was also post-synthetically modified using aniline to yield an aminated NH_2-*p*-DCX. Unlike previous HCP syntheses, the polymers in this study were synthesized at room temperature in an open-vessel on a relatively large (30 g) scale. This simple synthetic approach

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[*] Dr. C. H. Lau, Dr. X. Mulet, Dr. K. Konstas, Dr. C. M. Doherty, Dr. M. R. Hill, Dr. C. D. Wood
CSIRO
Bag 10, Clayton South 3169, VIC (Australia)
E-mail: Cherhon.Lau@csiro.au
Matthew.Hill@csiro.au
Colin.Wood@csiro.au

Dr. M.-A. Sani, Prof. F. Separovic
School of Chemistry, Bio21 Institute, The University of Melbourne
VIC 3010 (Australia)

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is flexible and scalable as it is based on Friedel–Crafts chemistry so it can be used to generate a broad number of HCPs using a diverse range of different aromatic building blocks[7] for applications, such as molecule storage and separation, and as additives. The surface area of the resulting polymer was 1400 $m^2 g^{-1}$ (Figure S1 in the Supporting Information) which is in line with previous reports that employed elevated temperatures and rigorous synthesis conditions. It was recently reported that HCP polymers swell in thermodynamically weak solvents, such as CO_2,[10] which is an extension to the known plasticization ability of CO_2 for polymers, such as polystyrene.[12] We also found that the *p*-DCX also swells in CH_4 to a lesser extent than in CO_2 (Figure S2). The unique swelling capability of HCPs is due to the physical strain resulting from the extensive hypercrosslinking.[13]

Based on the structural similarities to PAFs and the high surface area of the *p*-DCX, mixed-matrix membranes were fabricated by incorporating 10 wt% of *p*-DCX into PTMSP. Visual and SEM observations of the resulting membranes showed that the *p*-DCX did not agglomerate. Pure H_2, N_2, and CO_2 permeabilities of PTMSP were enhanced by 20–46% with the inclusion of *p*-DCX, while CH_4 permeability was reduced by 46% (Figure 2a). Figure 2a shows that the largest increase in permeability for the *p*-DCX containing membrane was seen with CO_2, and could be ascribed to the strong interaction of *p*-DCX with CO_2. The reduction in CH_4 permeability was attributed to smaller *p*-DCX pores and lower affinity towards CH_4.

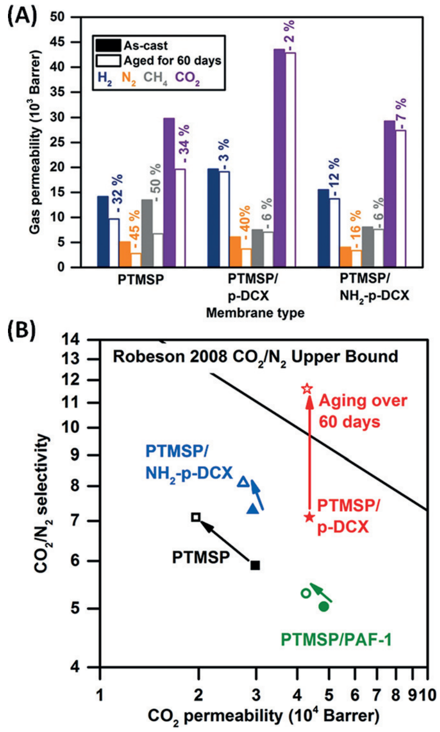

Figure 2. A) Pure-gas permeabilities of PTMSP and mixed-matrix membranes loaded with *p*-DCX and NH_2-*p*-DCX. B) Comparison of PTMSP, PTMSP/PAF-1, PTMSP/*p*-DCX, and PTMSP/NH_2-*p*-DCX membranes on Robeson's 2008 CO_2/N_2 Upper Bound.[14] Deviations in gas permeabilities are ±10%. Filled symbols = as-cast membranes, open symbols = membranes aged for 60 days

Similar to PTMSP mixed-matrix membranes containing functionalized PAF-1,[6a] the *p*-DCX version displayed selective-aging properties. Changes in H_2, CH_4, and CO_2 permeabilities of PTMSP/*p*-DCX were negligible, while the N_2 permeability was significantly lower (40%) than the native PTMSP. Over time, the CO_2/N_2 separation performance of the PTMSP/*p*-DCX membrane increased from 7 to 12, whilst CO_2 permeability was maintained at 44000 Barrer (Figure 2b). The increase in CO_2/N_2 selectivity is attributed to a 40% decrease in N_2 permeability. This remarkable selective-aging effect of the *p*-DCX is comparable to an optimized functionalized PAF-1,[6a] and enables the application of PTMSP/*p*-DCX membranes in industrial gas separation.[15]

The relationship between physical-aging rates and free fractional volume (FFV) content in PTMSP and PTMSP/additive membranes is illustrated in Figure 3. Larger losses in FFV content lead to faster physical aging rates.

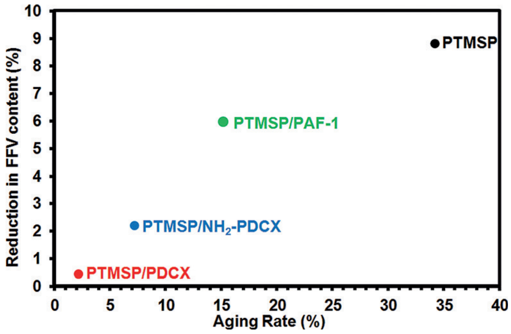

Figure 3. Relationship between loss in FFV content and physical aging rates for CO_2 permeability.

The interactions between *p*-DCX and PTMSP chains were investigated using ^{13}C solid-state NMR spectroscopy to resolve the mechanism behind the retention of FFV content. The relative differences between the T_1 relaxation times of carbon atoms obtained from ^{13}C solid-state NMR analyses have been correlated to the mobility in these carbon atoms.[16] A decrease in T_1 relaxation times corresponded to enhanced atom mobility, while an increase signified the opposite. During physical aging of pure PTMSP, the bulky trimethylsilyl group, which is key to driving the PTMSP main chains closer,[16a] became more mobile as the T_1 of carbon atom (a; see Figure 4) was reduced by 13% (Figure 4). The PTMSP main-chain carbon atoms (b and c) and side-chain atoms (d) became less mobile, which could be attributed to a lack of space, that is, collapsed FFV content to hinder movement of these atoms compared to as-cast PTMSP. There was no change in the mobility of the carbon atom (a) of aged PTMSP/*p*-DCX membranes; indicating immobilization of the bulky trimethylsilyl group. In aged PTMSP/*p*-DCX, the change in T_1 relaxation time of main chain carbon atom (b) was less than 5%. This infers that the bulky part of the PTMSP chains was immobilized by the *p*-DCX. The reduced T_1 relaxation time of carbon atom (c) relative to that of as-cast PTMSP indicates that this atom became more mobile in aged PTMSP/*p*-DCX. The immobilization of one part of the main chain, whilst allowing the other end to be mobile was

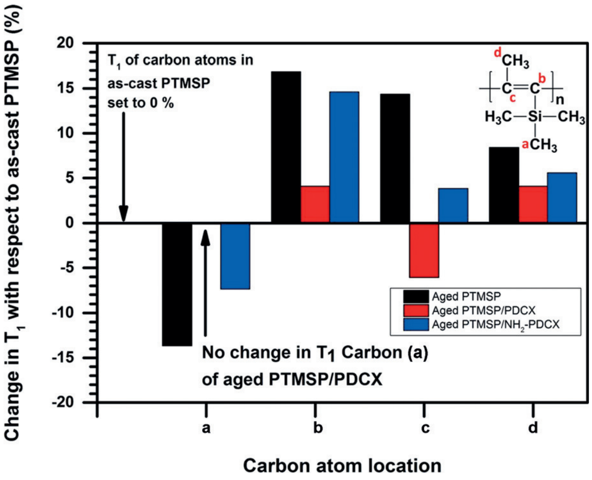

Figure 4. T_1 relaxation times of PTMSP carbon atoms.

also detected in our previous work, and is crucial for selective-aging membranes. This selective-aging mechanism of membranes described herein was further supported through SAXS/WAXS and PALS investigations (Supporting Information).

The creation of *anti*/selective-aging mixed-matrix membranes requires a strong and intimate interaction between the additive and the membrane polymer. This interaction can be assessed through intrinsic viscosity measurements. Non-Newtonian behavior was observed for the *p*-DCX/PTMSP systems (Figure 5). Non-Newtonian behavior of polymer/nanoparticle mixtures is typically attributed to one or more of the following factors: polymer chain adsorption on particle surfaces which reduces chain entanglement in solution,[17] additional free volume from unfilled pores of porous particles,[18] void creation between polymer chains and particle surface,[19] or the threading of polymer chains through particle pores.[20] The non-Newtonian behavior of PTMSP/*p*-DCX and PTMSP/NH_2-*p*-DCX were more obvious in lower concentrations of additives. These solutions became increasingly Newtonian with increasing additive concentration.

The effect of mixing duration and additive concentration on the intrinsic viscosity of PTMSP and PTMSP/nanoparticles is of particular importance for membrane fabrication. The difference between intrinsic viscosities of PTMSP/*p*-DCX solutions pre-mixed for 24 h and 0.5 h was negligible, while PAF-1, and fumed silica nanoparticles required 24 h of pre-mixing with PTMSP solutions to achieve the desired non-Newtonian behavior. This is a significant reduction in the solution-processing time for the fabrication of selective-aging membranes. Membrane fabrication is a key component for the implementation of these high-performance membranes.

Further processability advantages of *p*-DCX over PAF-1 are linked to the size of the porous particles. Dynamic light scattering (DLS) experiments showed that PAF-1 nanoparticles were eight-times larger than *p*-DCX in PTMSP solutions at the same concentration (10 wt %). SEM images reveal that PAF-1 nanoparticles are about 100 nm in diameter, whilst *p*-DCX particles were not observed in the PTMSP/*p*-DCX film (Supporting Information). This fine dispersion indicates the superior processability of *p*-DCX for membrane fabrication and is crucial to the development of selective-aging membranes.

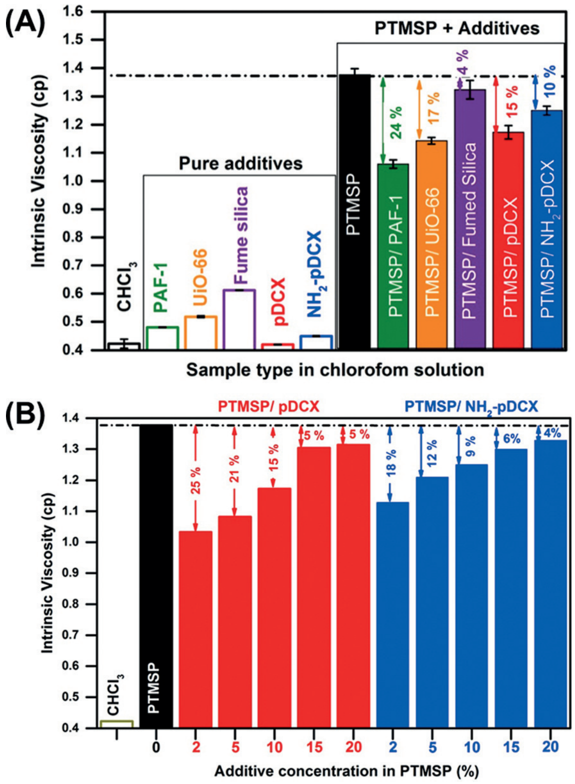

Figure 5. Intrinsic viscosity measurements of A) PTMSP solutions containing various additives. B) PTMSP/HCP solutions as a function of additive (*p*-DCX or NH_2-*p*-DCX) concentration.

In conclusion, this study highlights three key breakthroughs. First, a cost effective, alternative additive has been identified and produced on a comparatively large scale that is capable of reducing physical aging in super glassy membranes. Second, the smaller particle size and open pores of *p*-DCX promote intimate interactions between *p*-DCX and PTMSP polymer chains to provide a significant processability advantage over PAFs (98 % faster). Third, the key to interactions that yielded selective-aging membranes is the chemistry between additives and polymers, and the pore sizes of the additive. The use of *p*-DCX as additives that tailor physical aging in super glassy membranes will open up the way to commercialize high-performance, selective-aging membranes for carbon capture from flue gases and natural-gas streams.

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