High temperature pervaporation performance of ceramic-supported polyimide membranes

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ECN

Energy research Centre of the Netherlands

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Industrial application of membranes

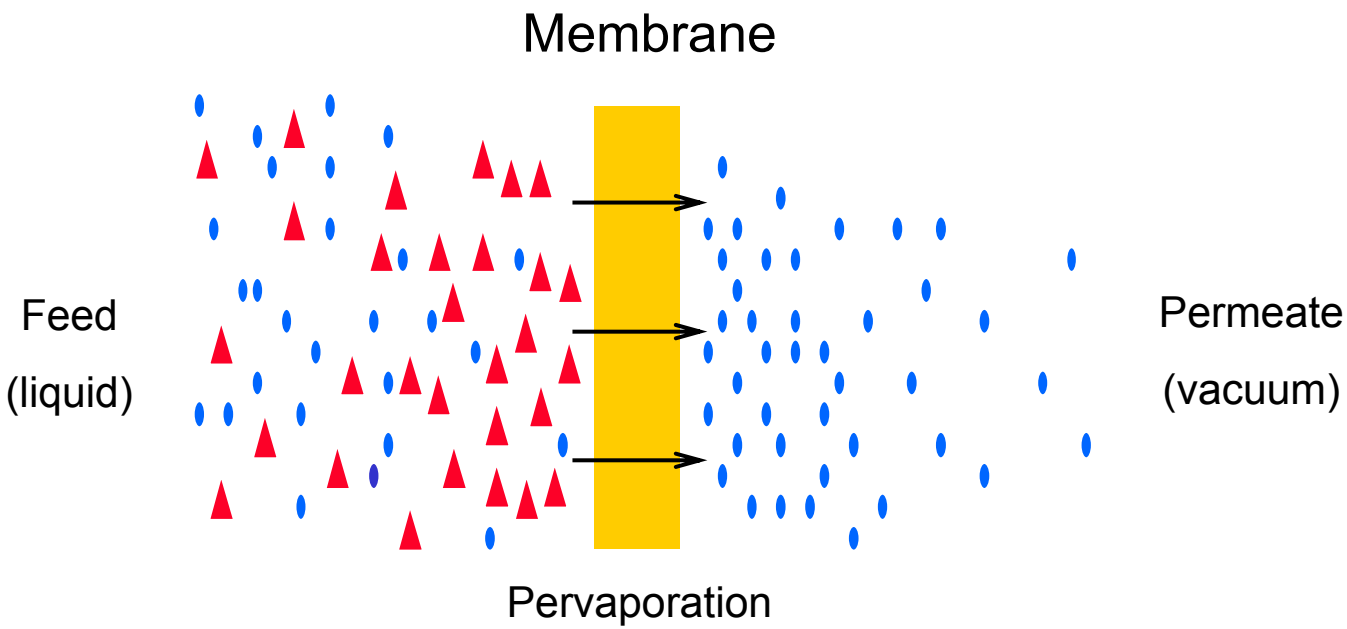
• Dewatering of organics *savings potential for NL:*	10 PJ/y
• NH_3 separation	4 PJ/y
• Hydrogen separation	25 PJ/y
• Oxygen separation	6 PJ/y
• Hydrocarbon separation	25 PJ/y

1 PJ = 10^{15} J = 32 Mm^3 natural gas

Total industrial energy use (NL): 200 PJ

Pervaporation (PV)

- Much more energy efficient than distillation
- Saves 2-5% of industrial energy use worldwide
- Combination of *per*meation and e*vaporation*

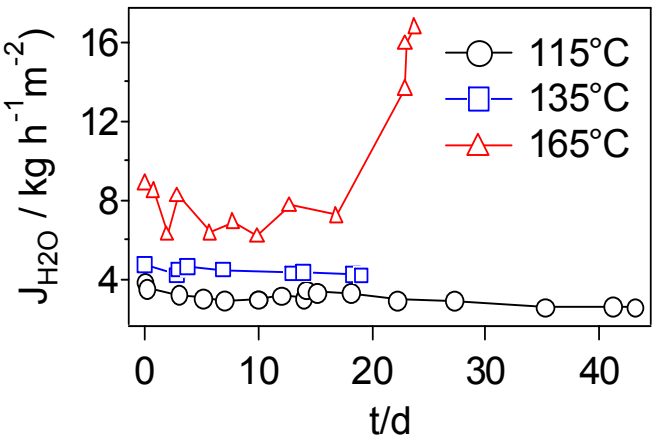


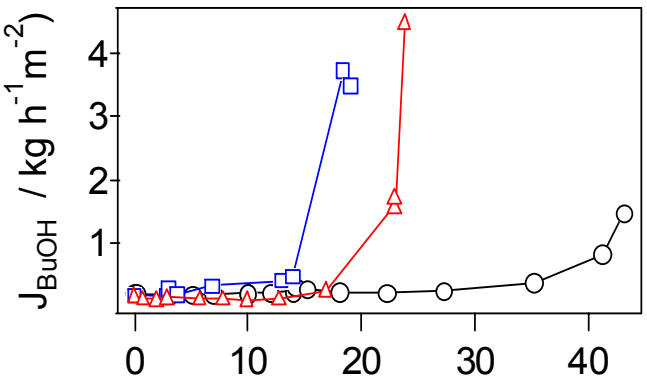
Industrial performance demands

Standard ECN test: 5 wt% water in *n*-butanol

- Fluxes 3-5 kg/m^{2}h
- Selectivity > 360 (>95% H_2O in permeate)
- Life-time 2 - 3 years
- Conditions pH of 2-10, T of 100-150°C

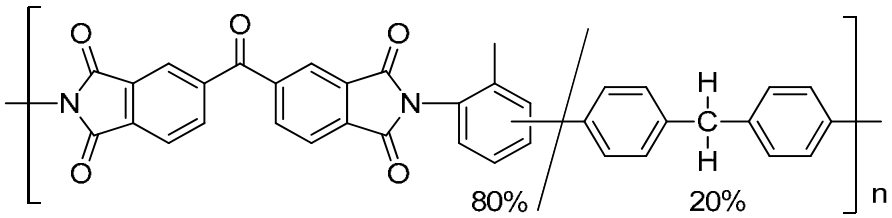
SiO_2 or Me-SiO_2 membranes are not stable



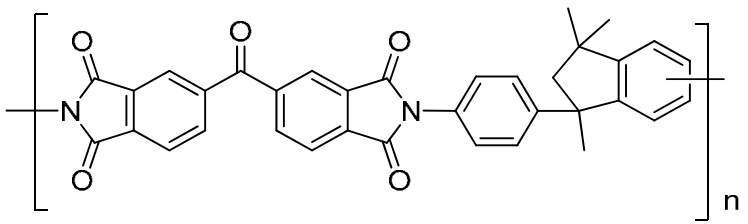


Campaniello et al. *Chem. Commun.* (2004), 834

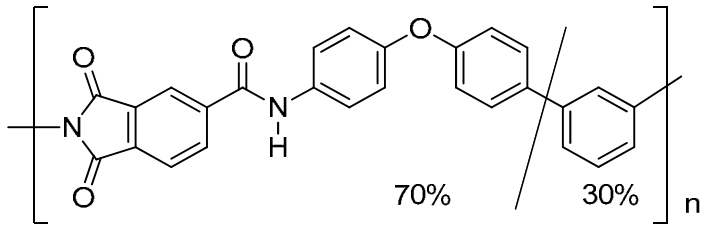
Polymer types



P84



Matrimid



Torlon

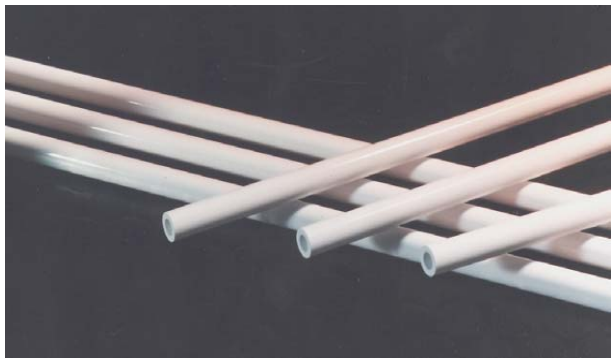
Temperatures of 60-100 °C

F. Zhou, and W. J. Koros *Ind. Eng. Chem. Res.*, 45 (2006), 1787

R. Liu, X. Qiao, and T. S. Chung *Chem. Eng. Sci.*, 60 (2005), 6674

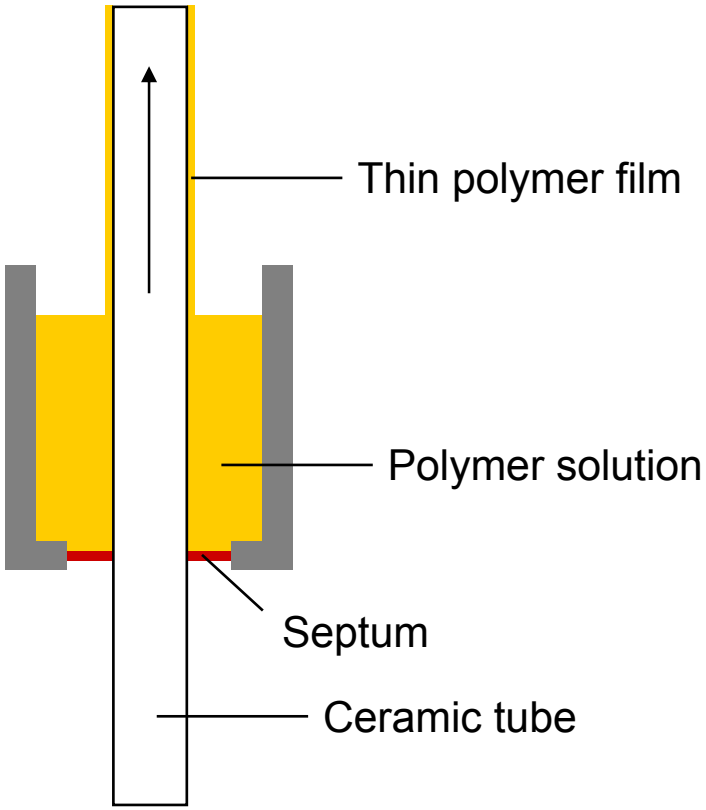
X. Qiao, T. S. Chung, and K. P. Pramoda *J. Membr. Sci.*, 264 (2005), 176

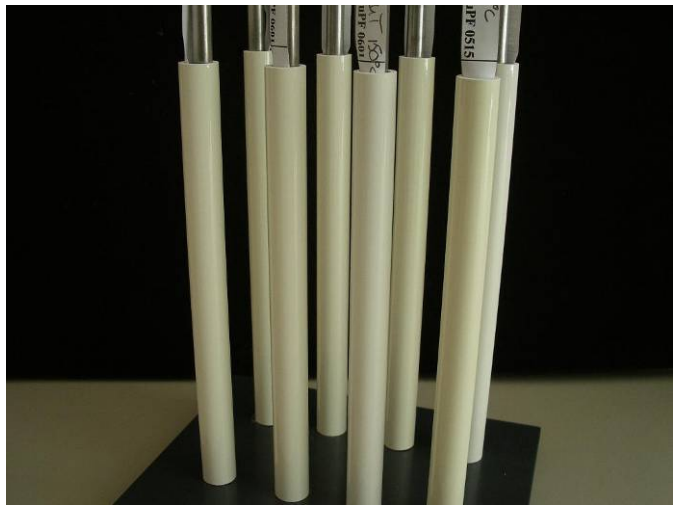
Ceramic-supported polymers (CSP)



- Mechanically robust
- Highly permeable material
- No flow limitations
- Available technology
- Compatible with existing module and sealing designs

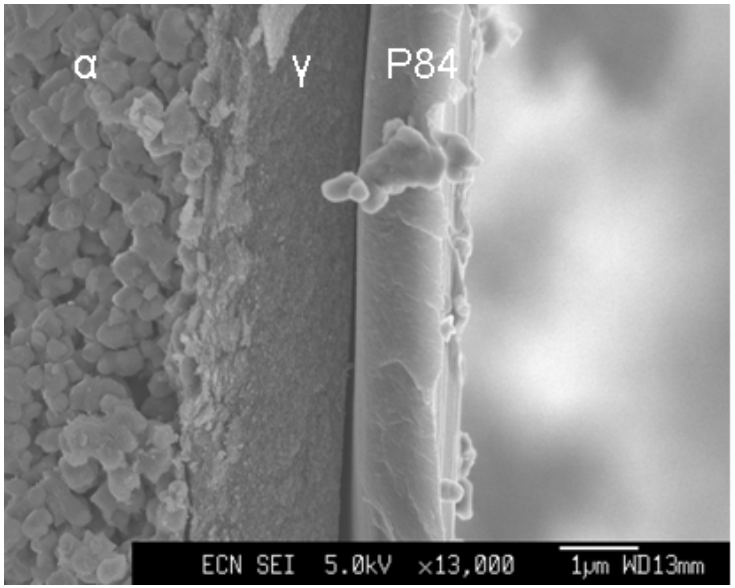
Film coating of polymer layers

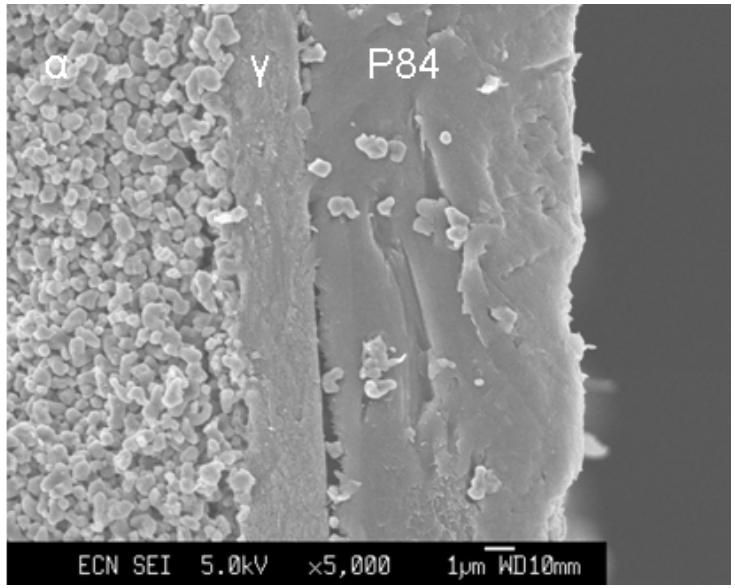




- Around 60 membranes prepared
- 120-400 cm^2 per tube
- Scale-up is possible

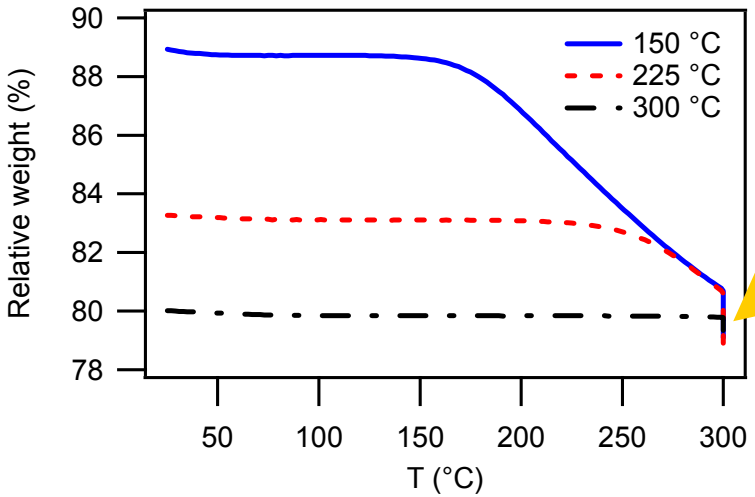
Thickness of polymer layer





- Concentrations: 1-12 wt% polymer in NMP
- Layer thickness: 1-10 μm

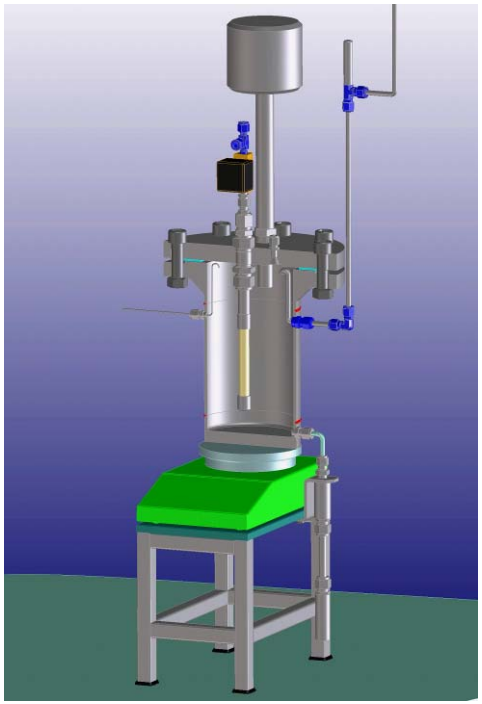
Thermo stability, solvent content (P84)



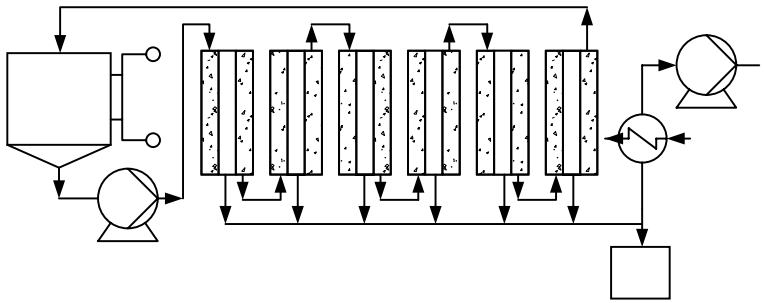
Dwell at 300 °C

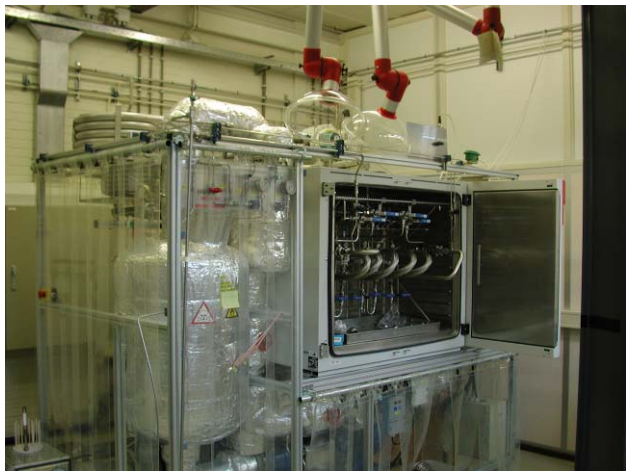
- P84 stable up to ~400 °C in air
- After curing at 300 °C no NMP left

Pervaporation: test equipment



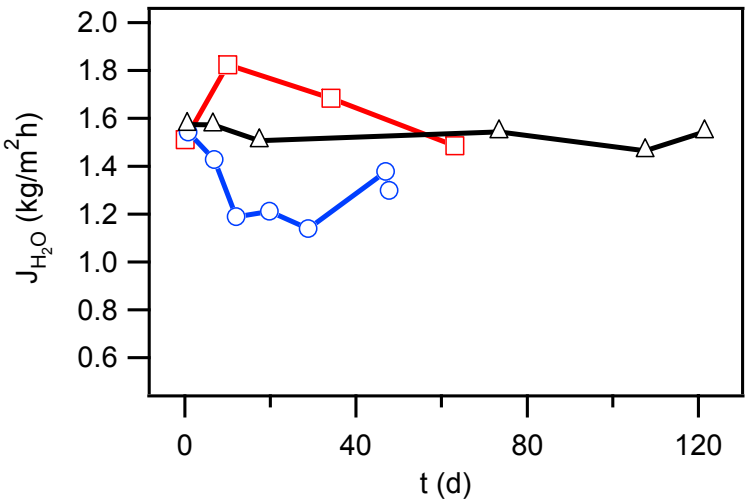
Single tube

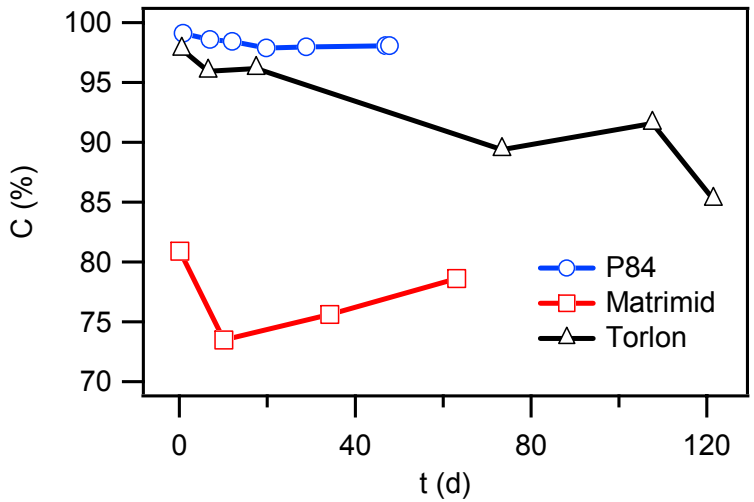




Multiple tube

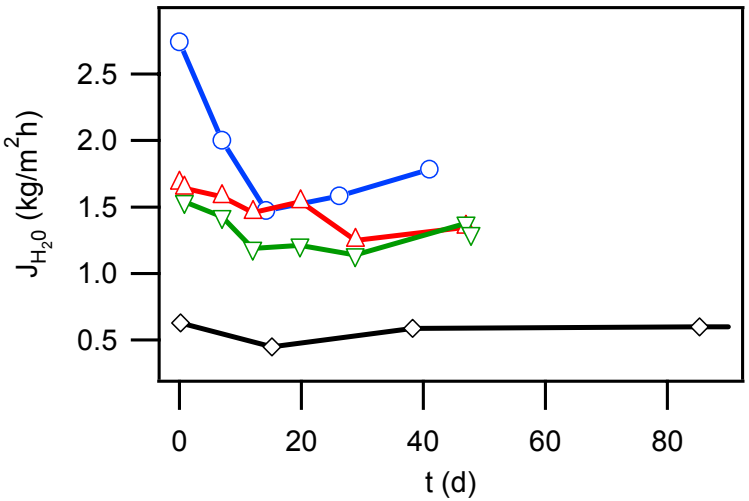
Polymer type - *n*-BuOH/water (95/5 wt%)

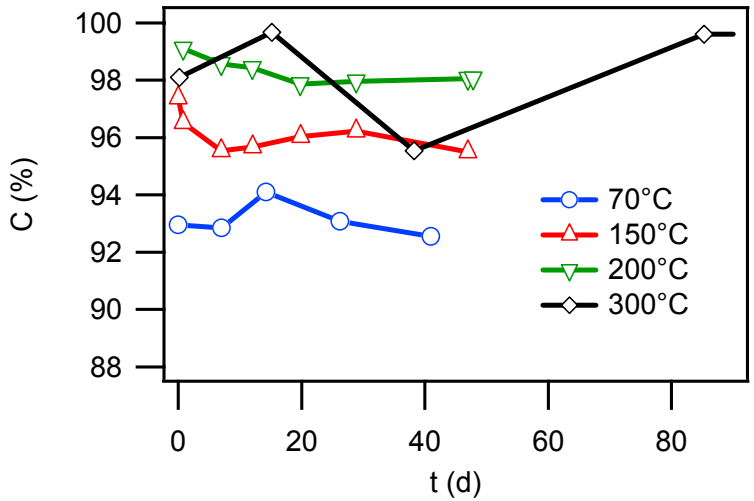




- Fluxes in the same range
- P84 most selective *Selected for further use*

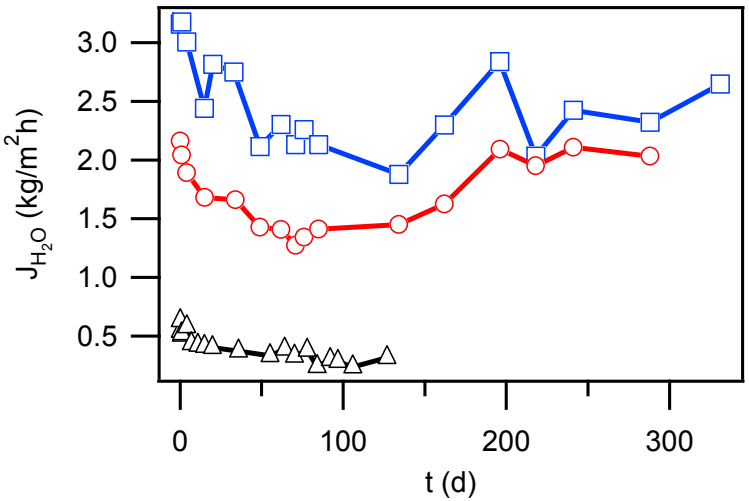
Effect of curing temperature

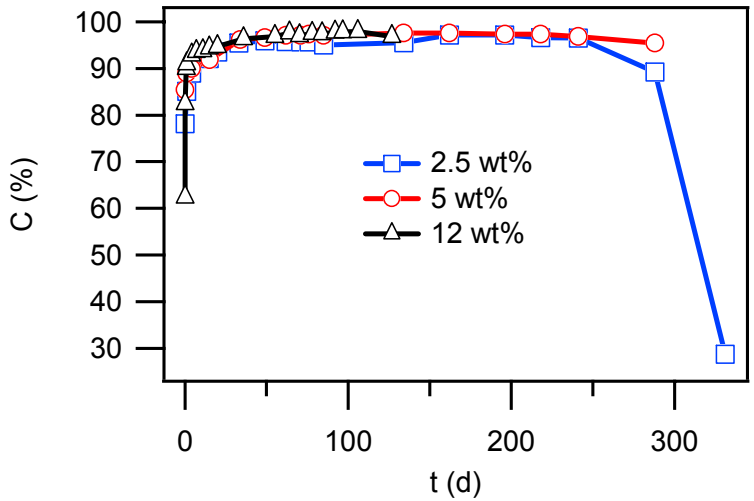




- Flux decreases at higher curing T
- Selectivity increases

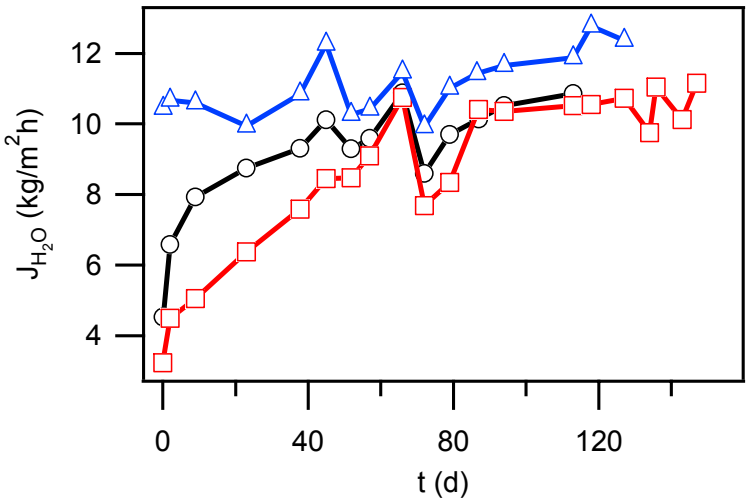
Long term PV at 95 °C

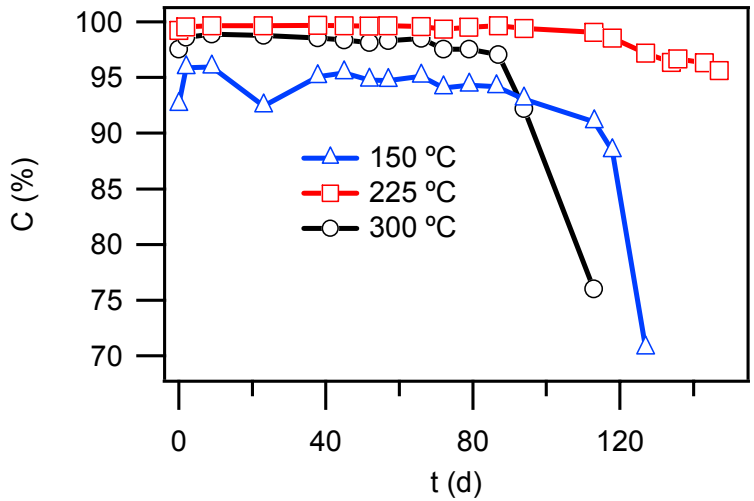




- P84 performs well for at least 300 days
- Thinnest membrane breaks down first

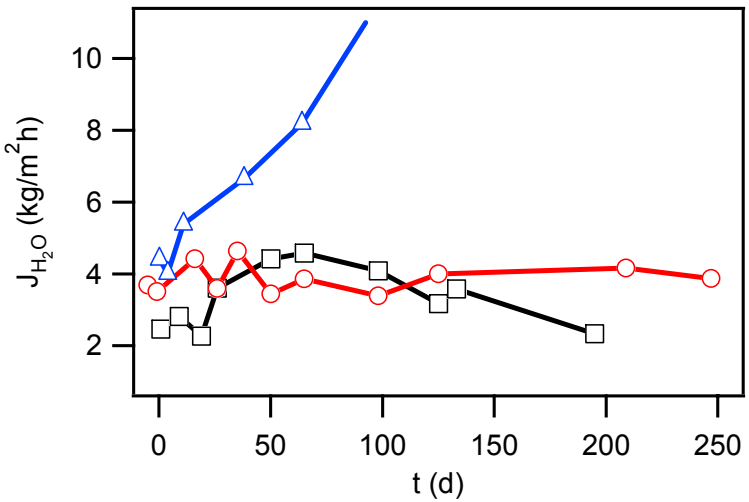
High temperature PV (150 °C)

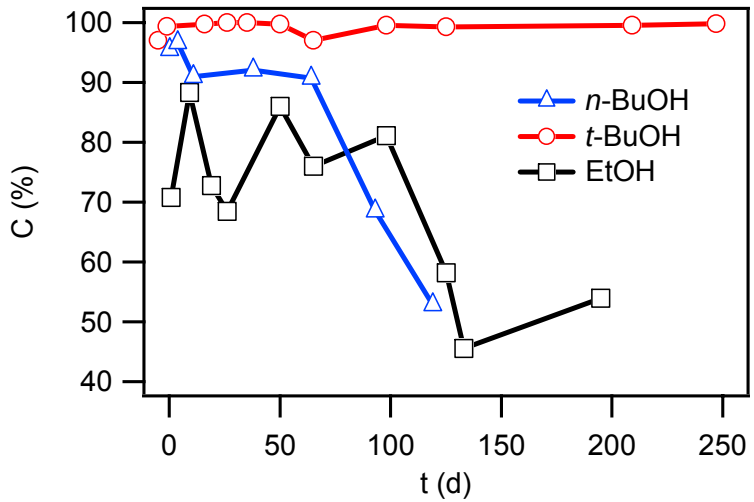




- Life times 80-140 days
- No clear relation with curing T

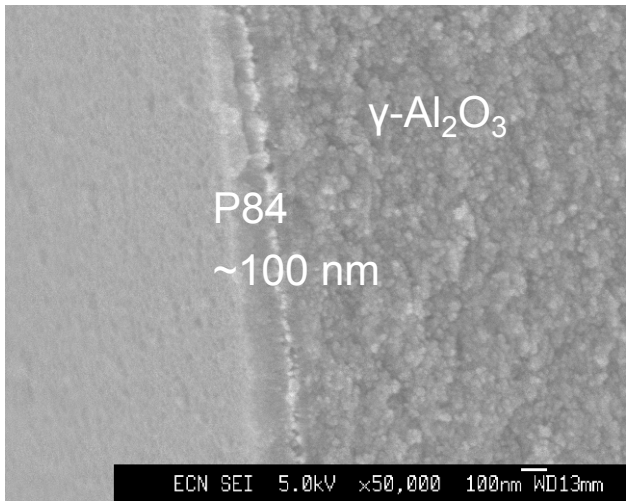
Other alcohols (*t*-BuOH, EtOH, 150 °C)

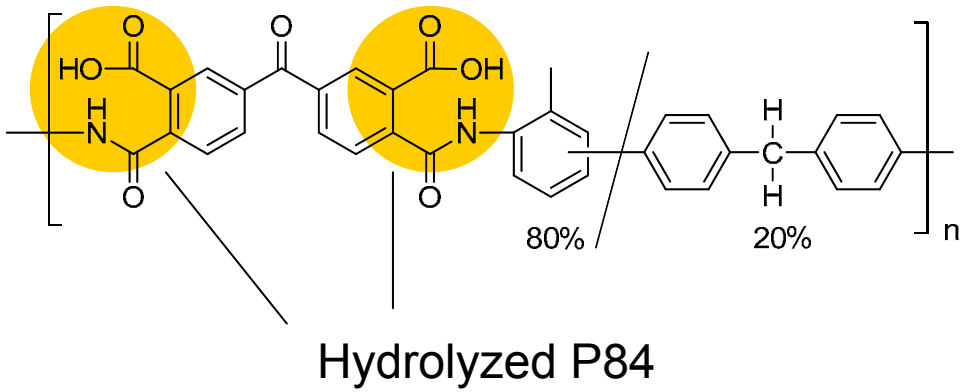




- *t*-BuOH/water (95/5 wt%): stable for >250 days
- EtOH/water reasonable selectivity

Membrane break down: hydrolysis





Hydrolyzed P84

- After long-term PV polyimide layer is reduced to ~10%
- IR on polyimide films confirms hydrolysis
- Imide-hydrolysis causes membrane break-down

Conclusions

- CSP membranes can be used for HT-pervaporation
- Fluxes are among the highest for polymer membranes

- Stability of P84 in *n*-BuOH/water is limited
- Performance in *t*-BuOH/water is very promising

- Hydrolysis to be addressed: *new polyimides?*

Acknowledgements

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