



Energy research Centre of the Netherlands

# **High temperature pervaporation performance of ceramic-supported polyimide membranes**

**R. Kreiter**

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# High temperature pervaporation performance of ceramic-supported polyimide membranes

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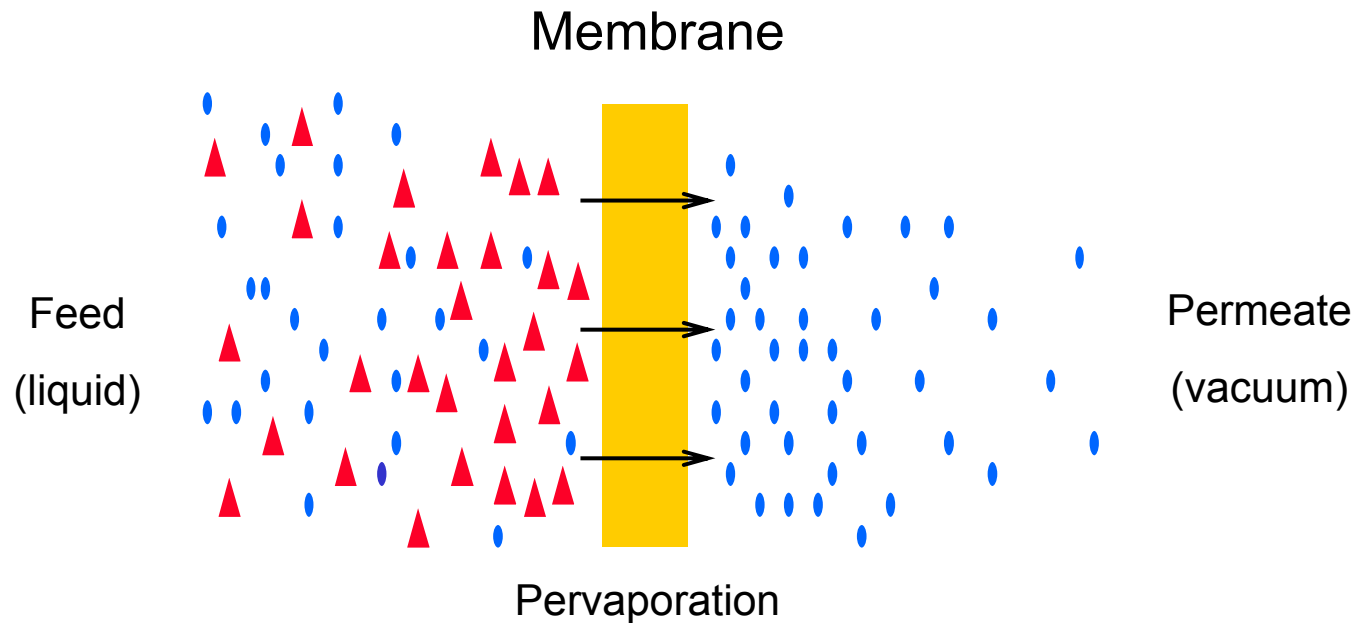
# Industrial application of membranes

- Dewatering of organics  
*savings potential for NL:* 10 PJ/y
- NH<sub>3</sub> 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<sup>3</sup> 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 *permeation* and *evaporation*

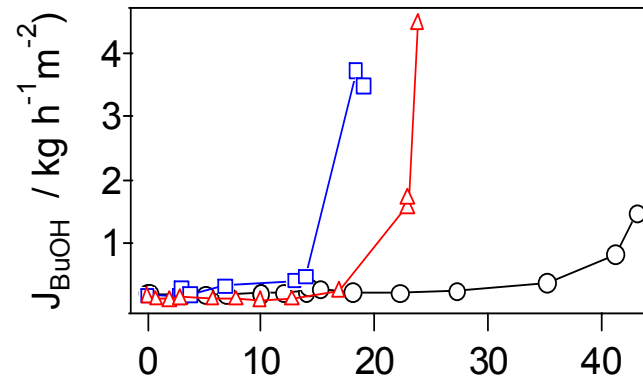
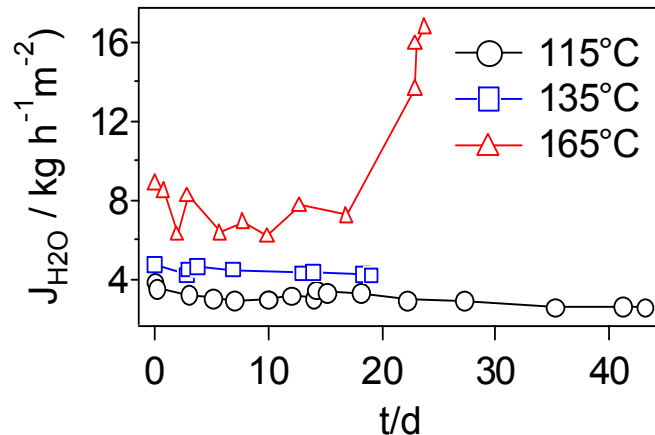


# Industrial performance demands

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

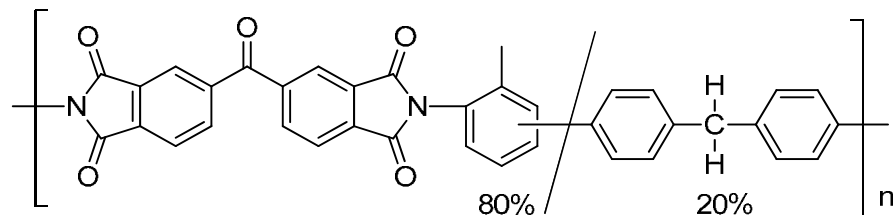
- Fluxes 3-5 kg/m<sup>2</sup>h
- Selectivity > 360 (>95% H<sub>2</sub>O in permeate)
- Life-time 2 - 3 years
- Conditions pH of 2-10, T of 100-150°C

SiO<sub>2</sub> or Me-SiO<sub>2</sub> membranes are not stable

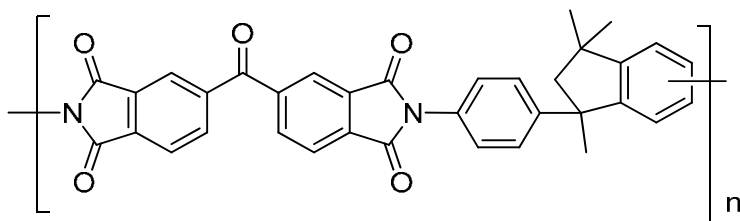


Campaniello et al. *Chem. Commun.* (2004), 834

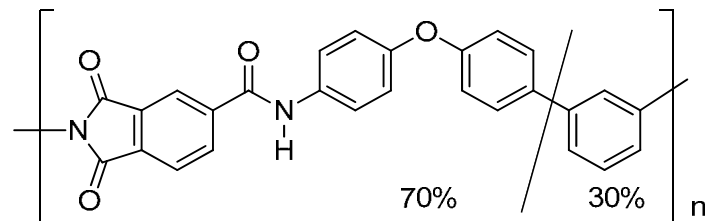
## Polymer types



P84



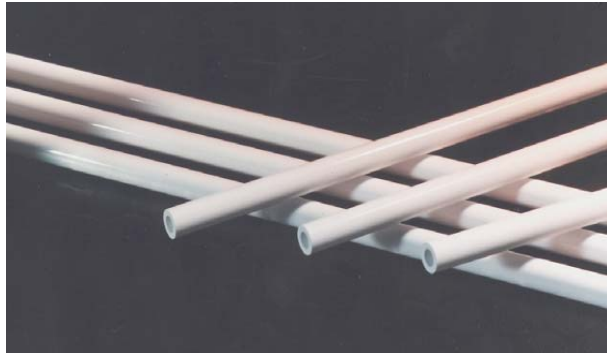
Matrimid



Torlon

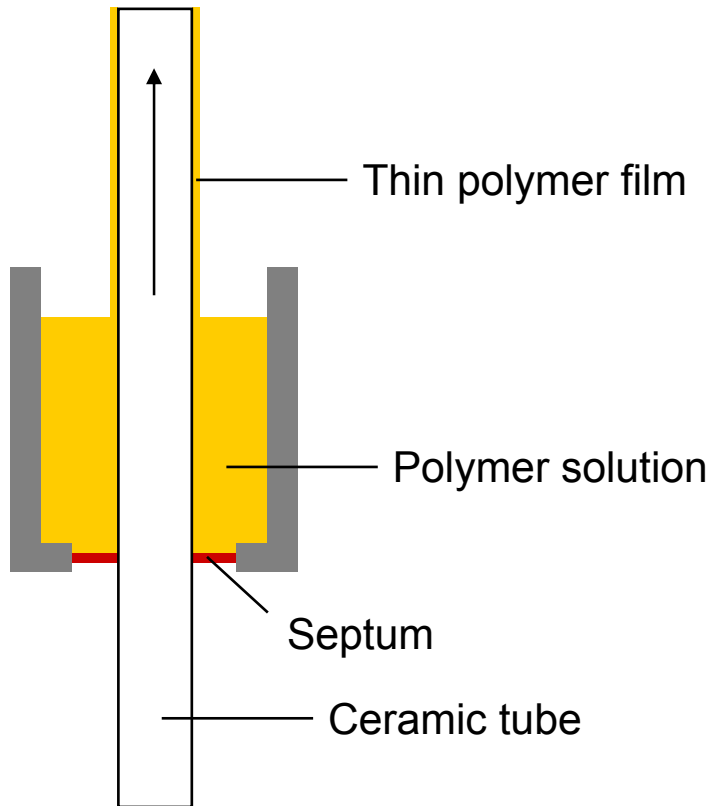
- Temperatures of 60-100 °C**
- F. Zhou, and W. S. Ho *Ind. Eng. Chem. Res.*, 45 (2006), 1787  
 R. Liu, X. Qiao, and T. S. Chung *Chem. Eng. Sci.*, 60 (2005), 6674  
 X. Qiao, T. S. Chung, and K. P. Pramoda *J. Membr. Sci.*, 264 (2005), 176

## Ceramic-supported polymers (CSP)



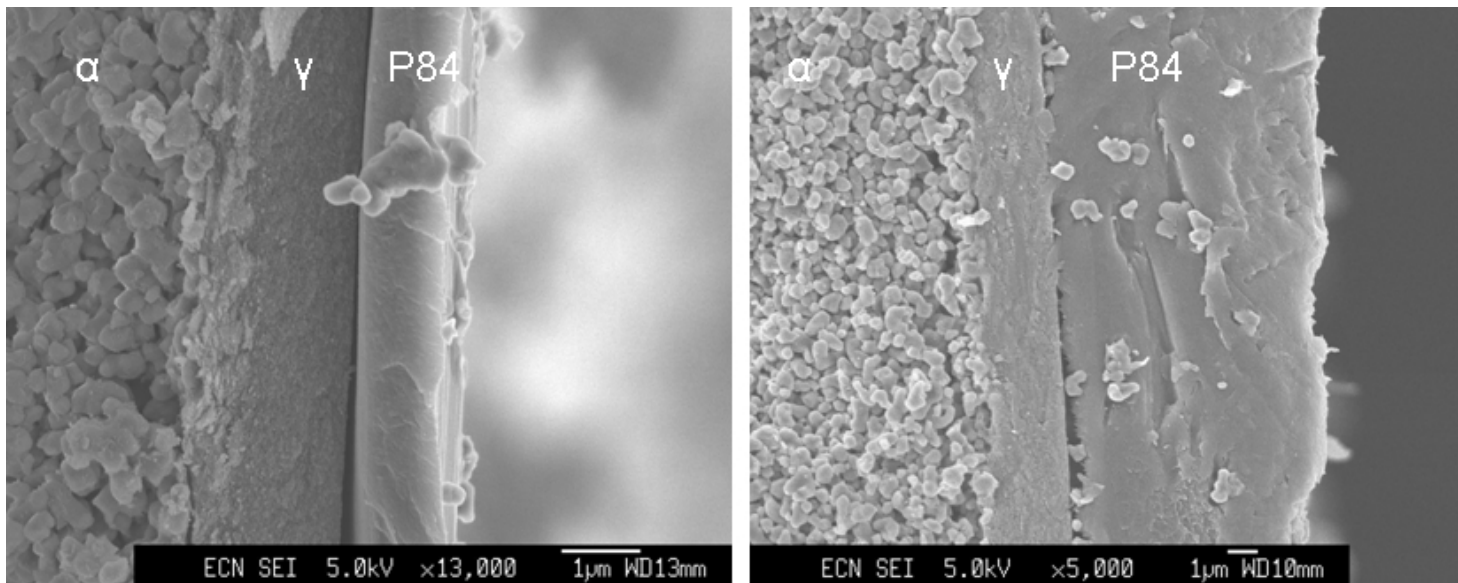
- Mechanically robust
- Highly permeable material
- No flow limitations
- Available technology
- Compatible with existing module and sealing designs

# Film coating of polymer layers



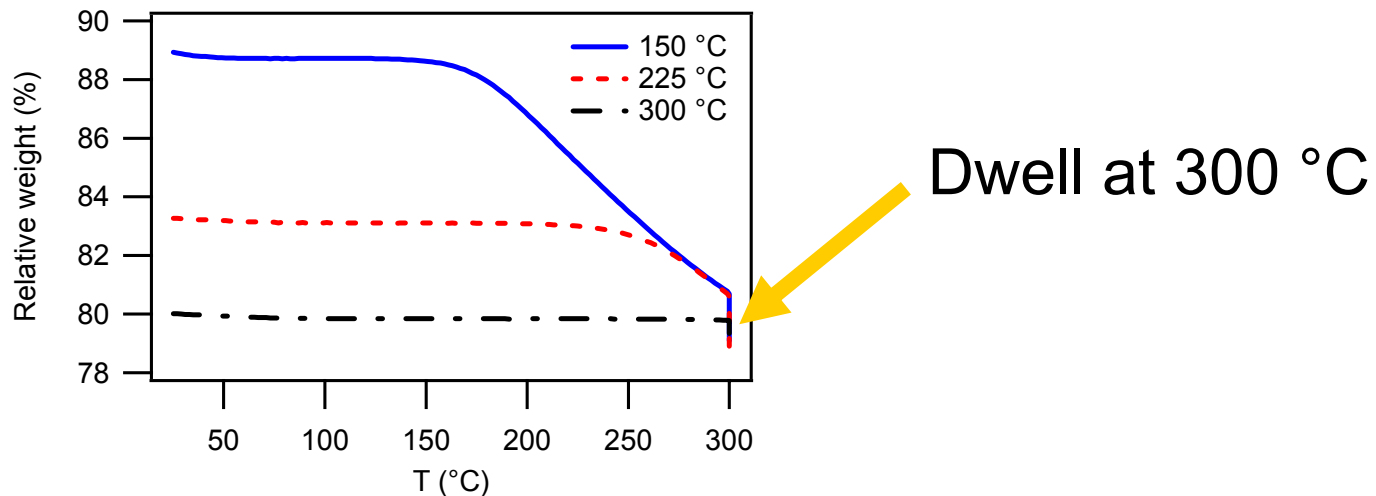
- Around 60 membranes prepared
- 120-400 cm<sup>2</sup> per tube
- Scale-up is possible

## Thickness of polymer layer



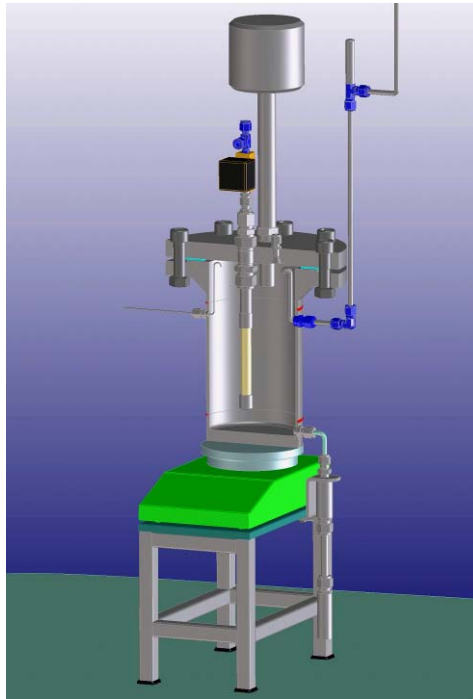
- Concentrations: 1-12 wt% polymer in NMP
- Layer thickness: 1-10  $\mu\text{m}$

## Thermo stability, solvent content (P84)

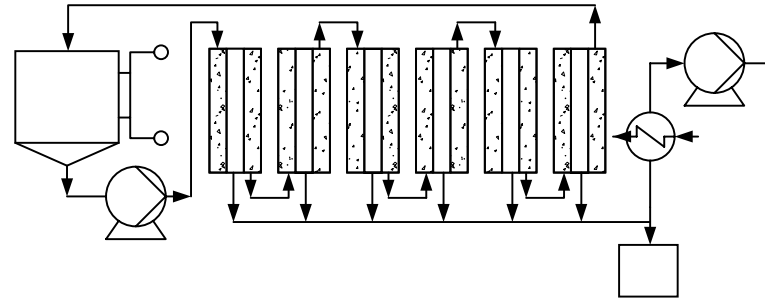


- P84 stable up to ~400 °C in air
- After curing at 300 °C no NMP left

# Pervaporation: test equipment

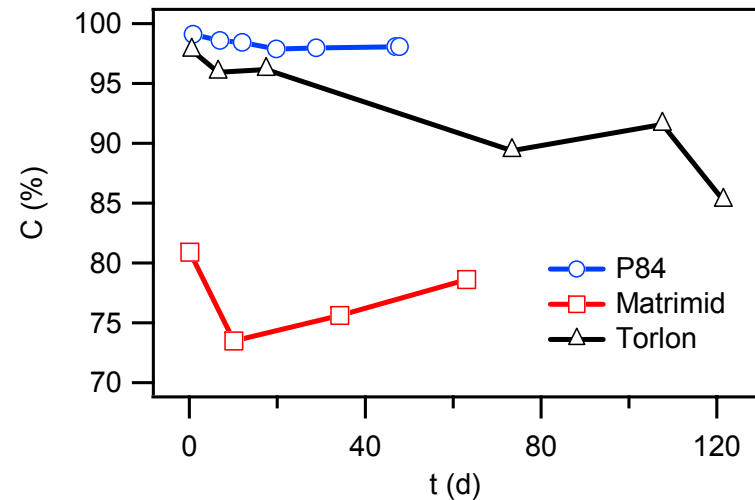
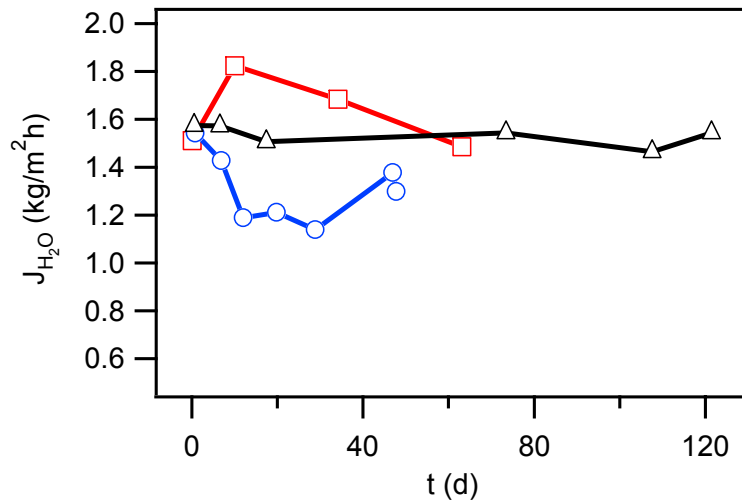


Single tube



Multiple tube

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

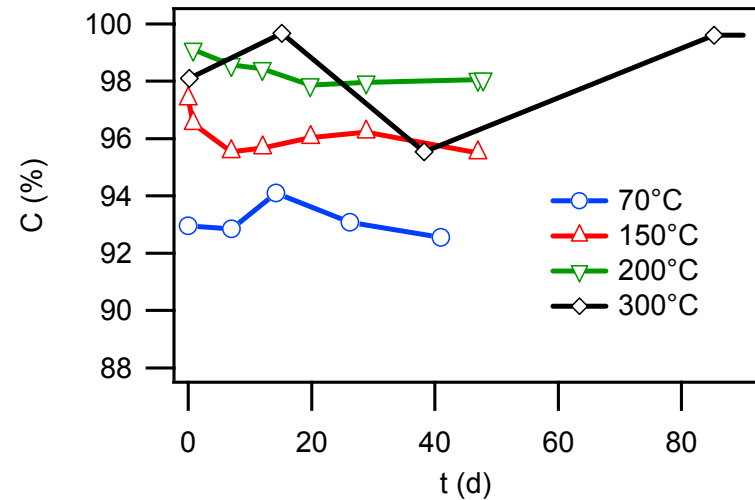
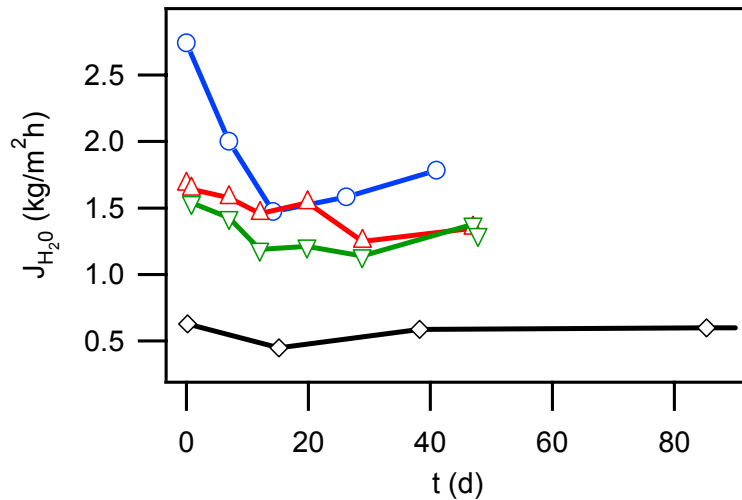


- Fluxes in the same range

- P84 most selective

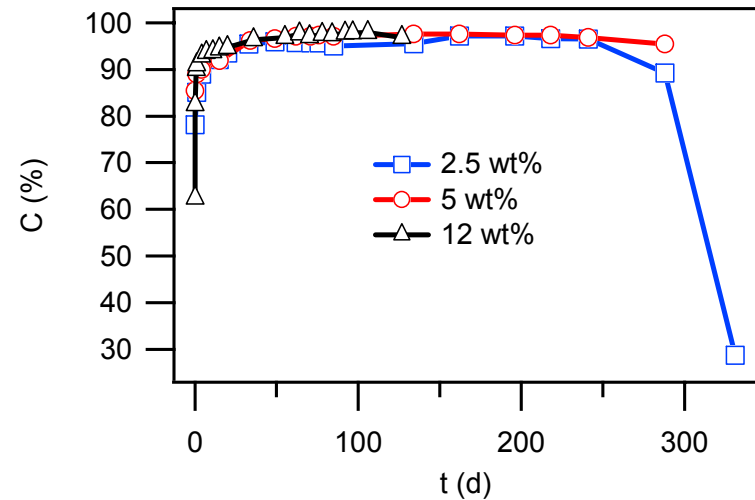
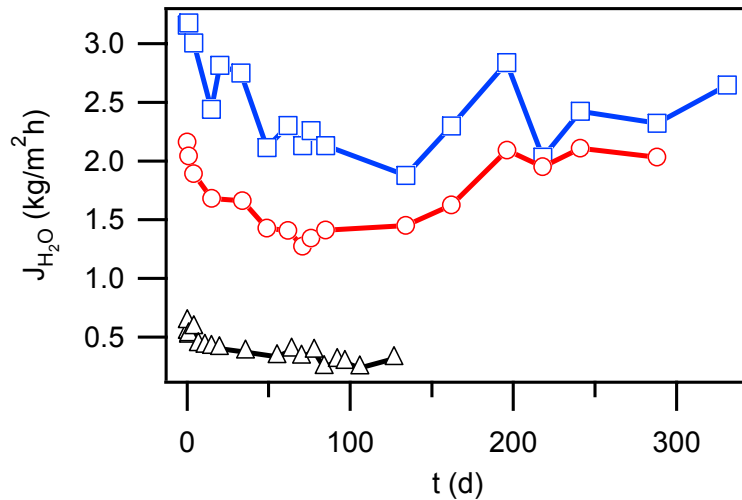
*Selected for further use*

## Effect of curing temperature



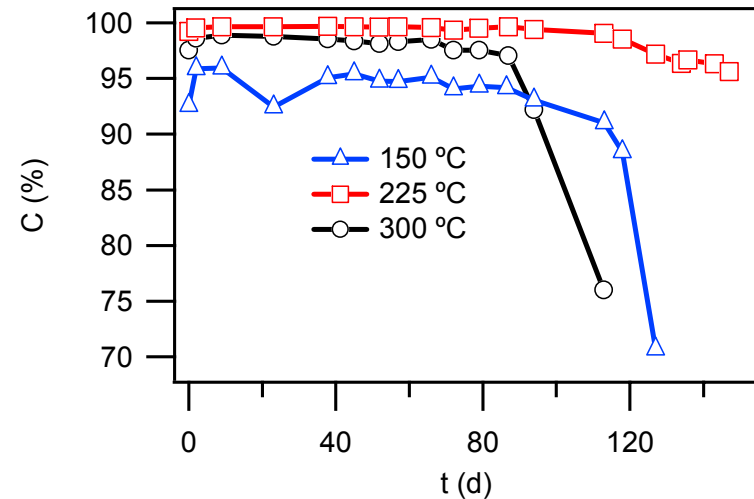
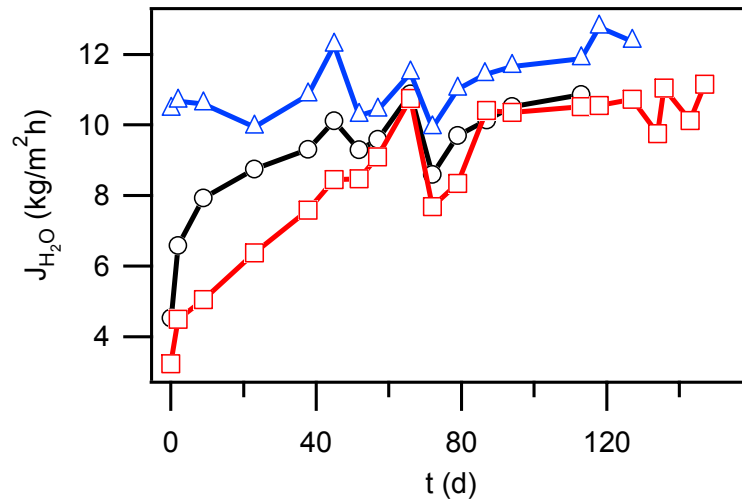
- Flux decreases at higher curing T
- Selectivity increases

## Long term PV at 95 °C



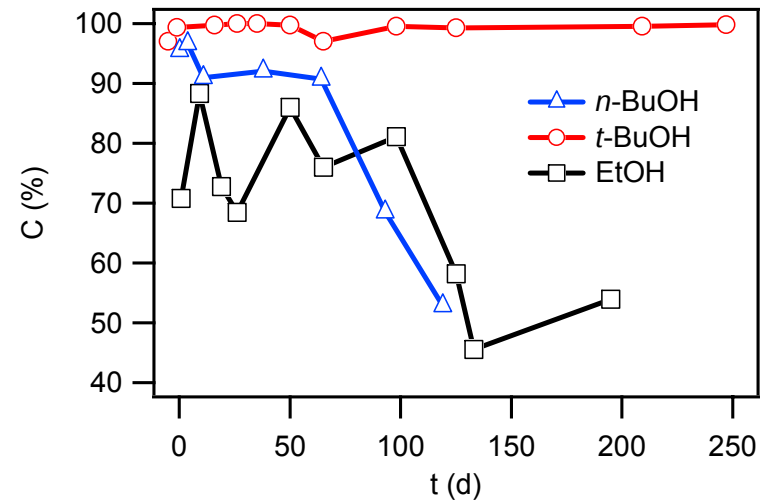
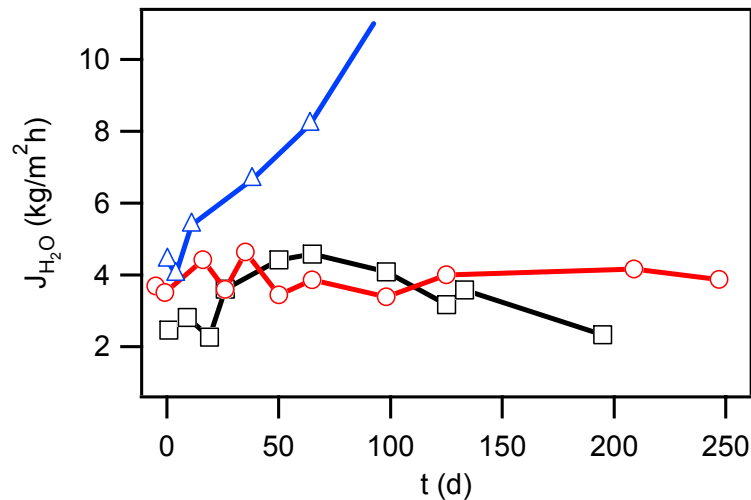
- P84 performs well for at least 300 days
- Thinnest membrane breaks down first

## High temperature PV (150 °C)



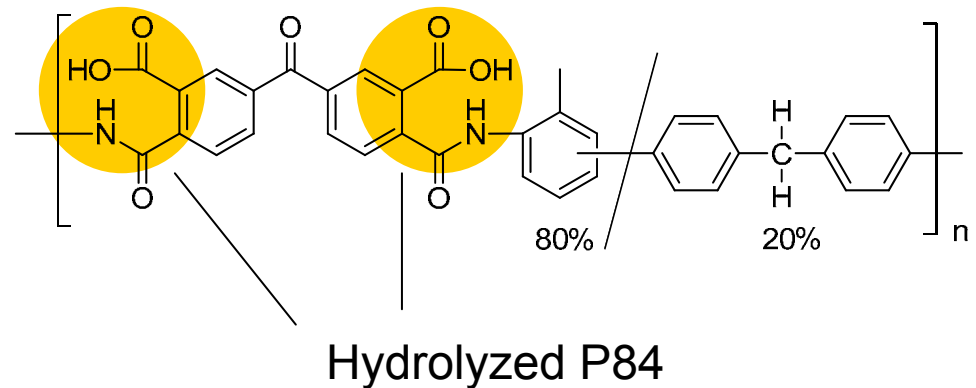
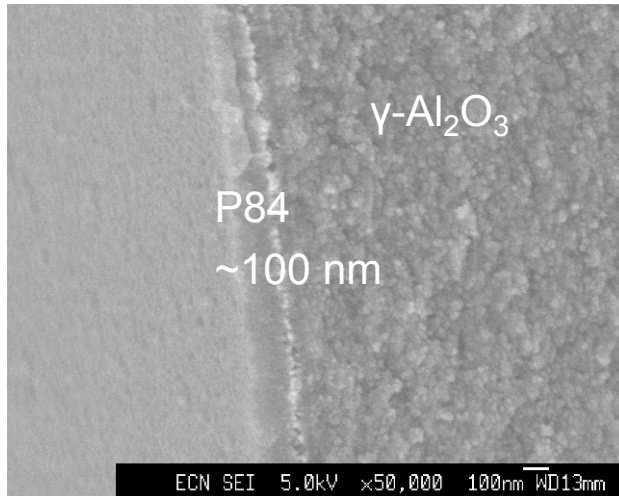
- Life times 80-140 days
- No clear relation with curing T

## 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



- 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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