

# Membranes based on polymerized ionic liquids

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The term “ionic liquid” (IL) describes salts whose melting points are below 100 °C and which have remarkable properties as low vapor pressures. By the implementation of vinyl groups polymerized ionic liquids (PILs) are possible, which combining the advantages of solid polymeric structures and ionic liquids.<sup>[1]</sup> In membranes, these charged monomers increase the water permeability and show good anti-fouling properties.<sup>[2]</sup> Furthermore, UV initiated polymerization enables to obtain PIL membranes straight out of the casted monomer film. Besides high diversity of ILs based on the synthetic possibilities, this new approach facilitates membrane manufacturing and modification.<sup>[3]</sup>

Challenges are the optimization of long term stability of these neat, free-standing membranes and reproducibility of homogeneous pore size distributions. A high amount of free charges will be of interest to applications in waste water treatment, bio-industrial processes, ion exchange or fuel cell devices.

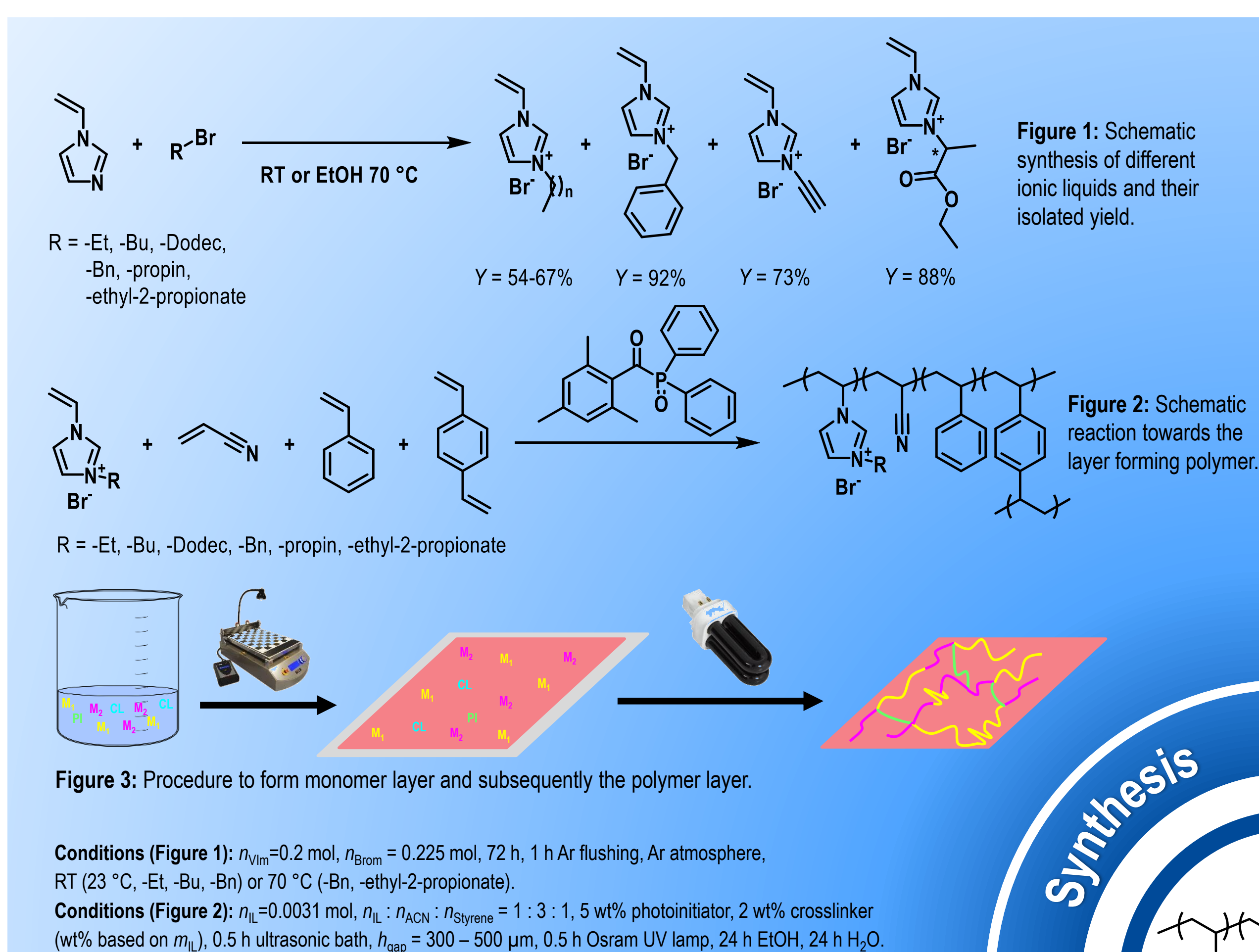
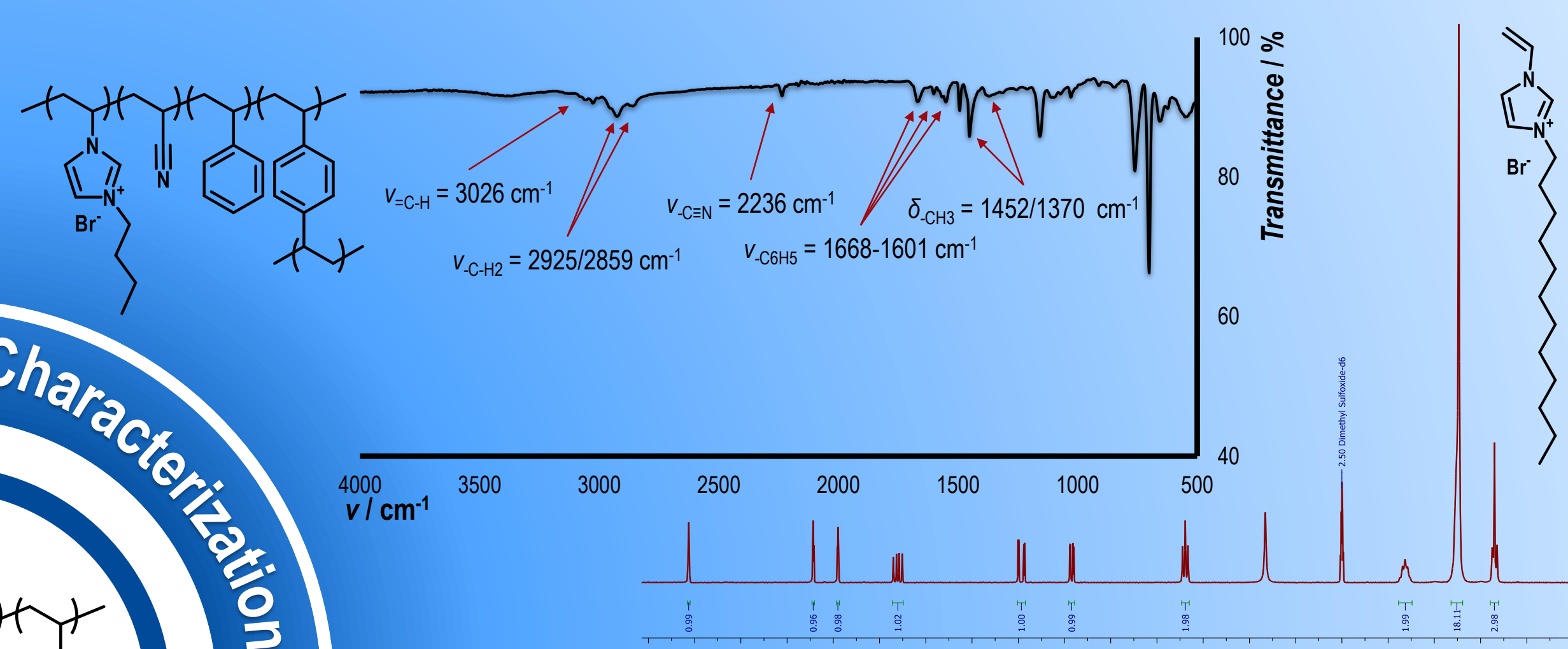
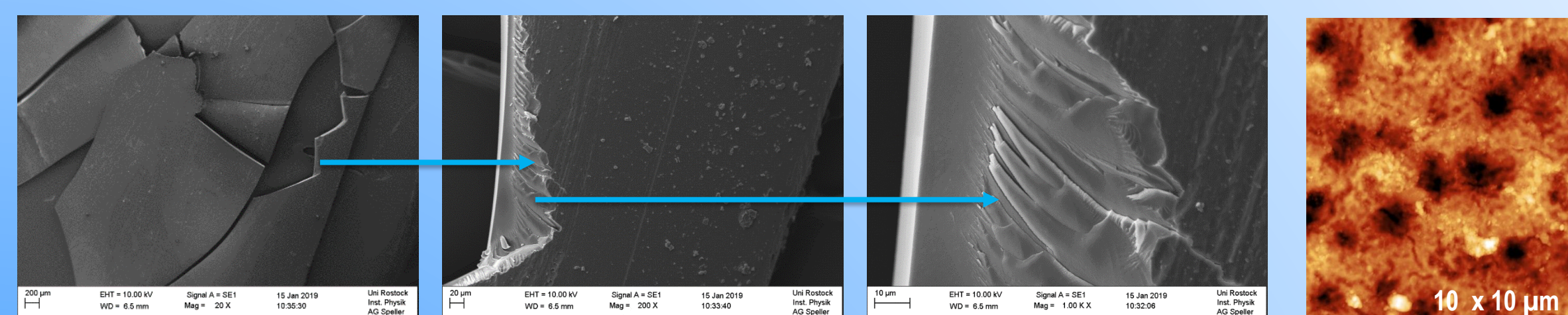


Figure 3: Procedure to form monomer layer and subsequently the polymer layer.

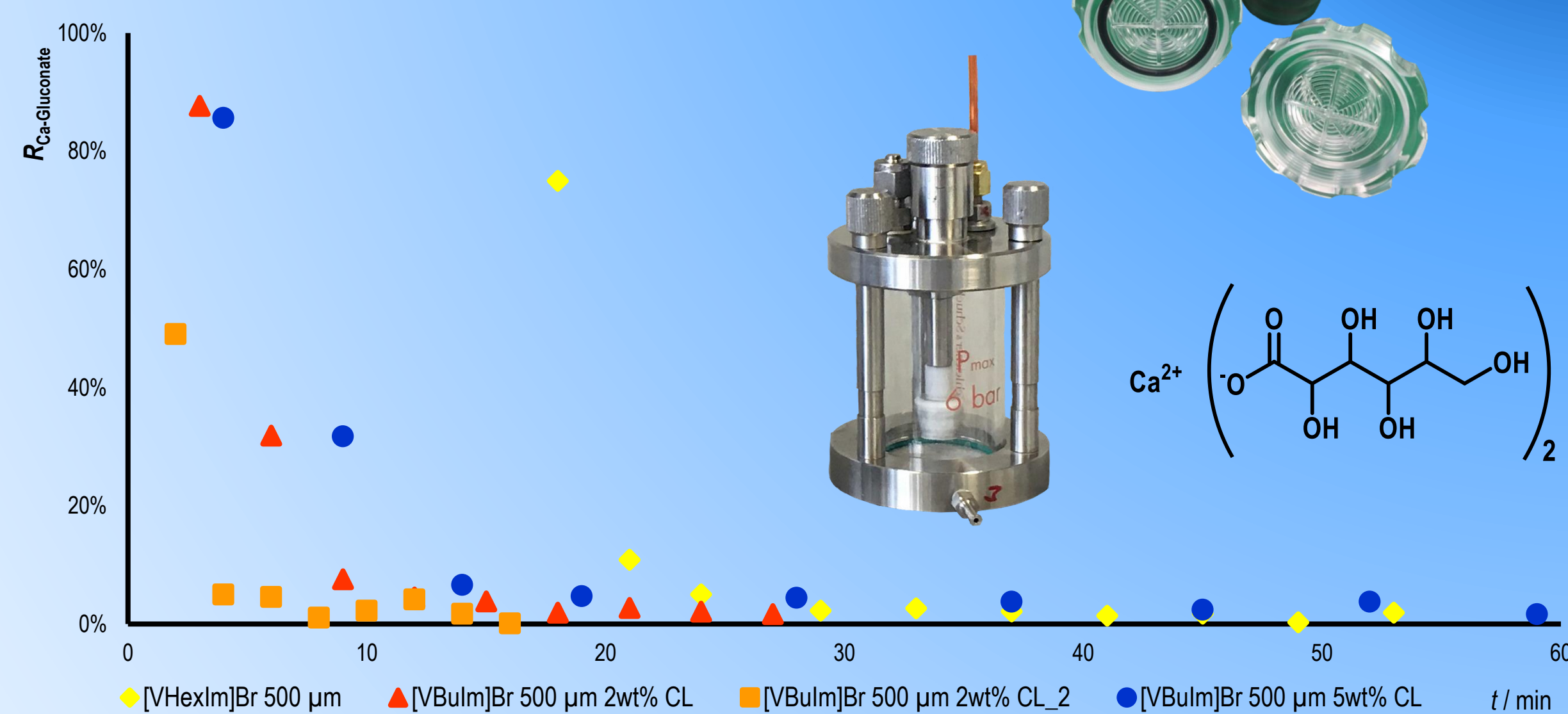
Conditions (Figure 1):  $n_{\text{vin}}=0.2$  mol,  $n_{\text{Br}}=0.225$  mol, 72 h, 1 h Ar flushing, Ar atmosphere, RT (23 °C, -Et, -Bu, -Bn) or 70 °C (-Bn, -ethyl-2-propionate).

Conditions (Figure 2):  $n_{\text{IL}}=0.0031$  mol,  $n_{\text{IL}}:n_{\text{ACN}}:n_{\text{Styrene}}=1:3:1$ , 5 wt% photoinitiator, 2 wt% crosslinker (wt% based on  $m_{\text{IL}}$ ), 0.5 h ultrasonic bath,  $h_{\text{gap}}=300-500$   $\mu\text{m}$ , 0.5 h Osram UV lamp, 24 h EtOH, 24 h H<sub>2</sub>O.

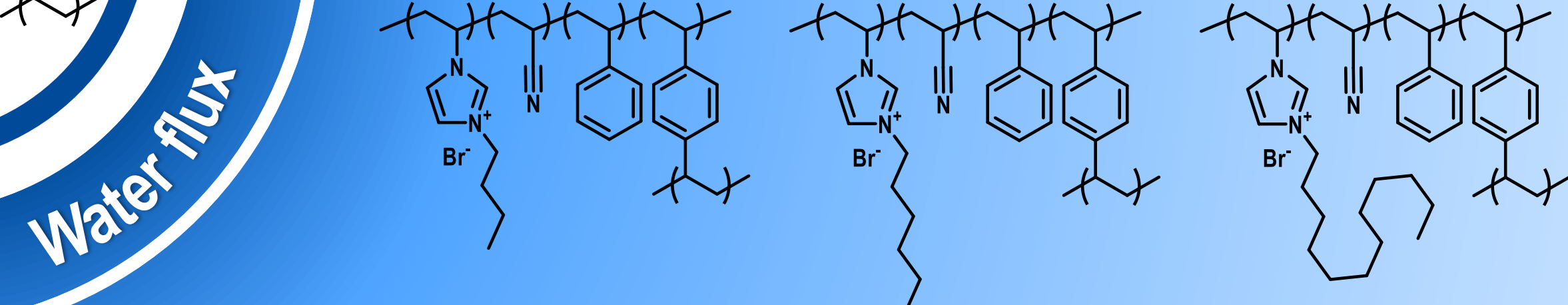
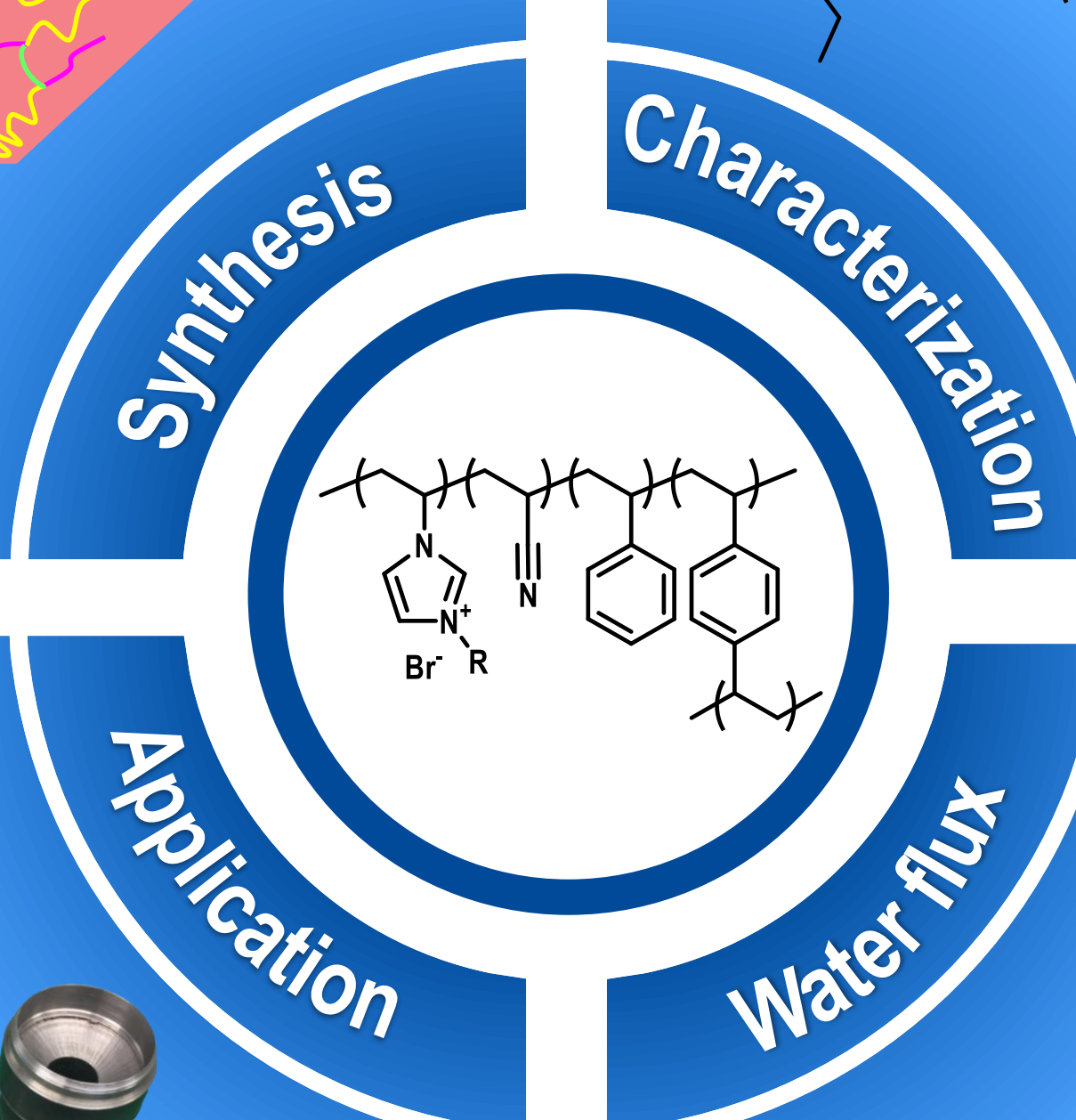
- Structure analysis of polymer layers by NMR, IR, SEM and AFM
- Further effective layer thickness, melting point of substances and mechanical stability



- Calcium gluconate as highly charged sugar as test molecule as aqueous solution
- Retention determined by HPLC measurements of filtrate
- Decreased retention by membrane damages



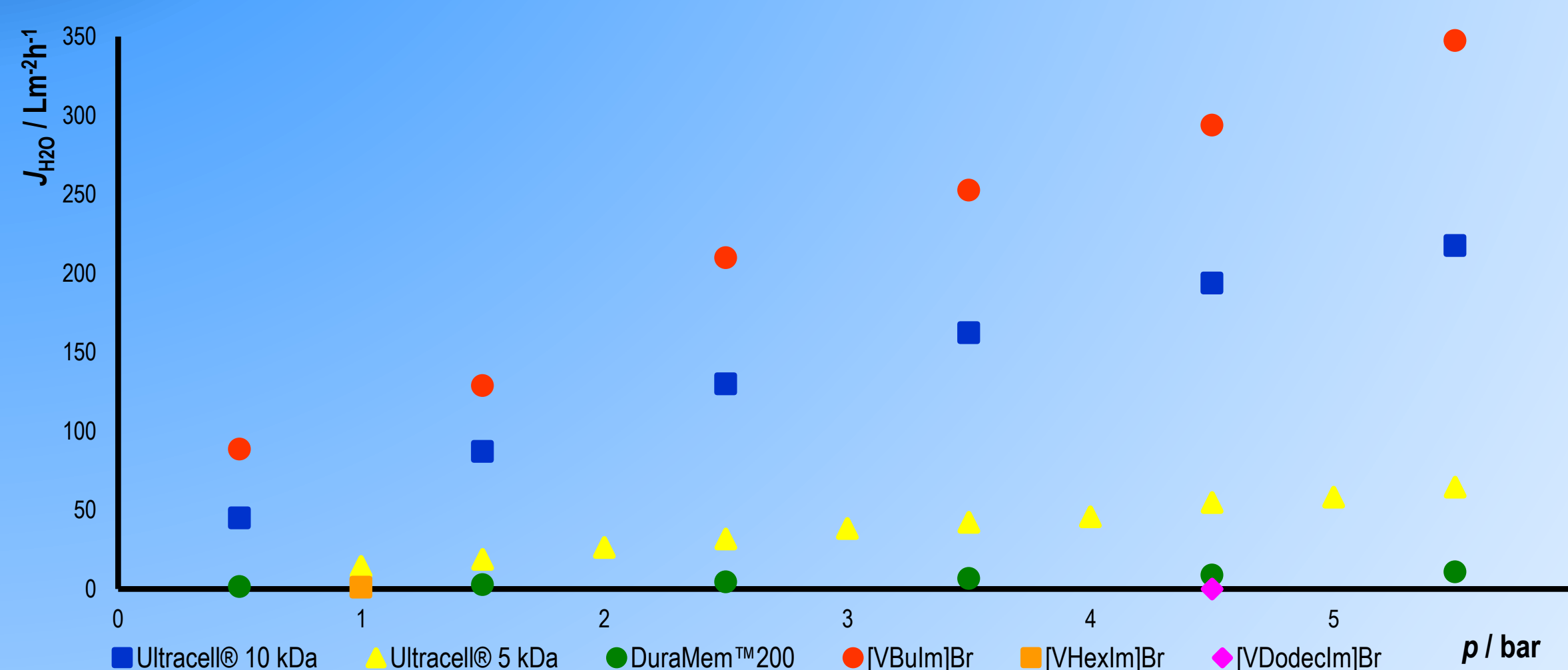
Conditions:  $d_{\text{membrane}}=26$  mm,  $p < 1.35$  bar,  $V_{\text{H}_2\text{O}}=1$  mL  $\cdot$  min<sup>-1</sup>, selfmade dead-end cell,  $n_{\text{IL}}=0.0031$  mol,  $n_{\text{IL}}:n_{\text{ACN}}:n_{\text{Styrene}}=1:3:1$ , 5 wt% photoinitiator, 2 wt% crosslinker (wt% based on  $m_{\text{IL}}$ ), 0.5 h ultrasonic bath,  $h_{\text{gap}}=500$   $\mu\text{m}$ , 0.5 h Osram UV lamp, 24 h EtOH, 24 h H<sub>2</sub>O.



[VBulm]Br:  $74.09 \pm 8.63 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$

[VHexIm]Br:  $5.16 \pm 0.53 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$

[VDodeclm]Br:  $0 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1} > 4.5$  bar



Conditions:  $d_{\text{membrane}}=47$  mm,  $p_{\text{op}}=0.5-5.5$  bar,  $V_{\text{H}_2\text{O}}=25-70$  mL, Schleicher&Schuell stirred dead-end cell,  $n_{\text{IL}}=0.0031$  mol,  $n_{\text{IL}}:n_{\text{ACN}}:n_{\text{Styrene}}=1:3:1$ , 5 wt% photoinitiator, 2 wt% crosslinker (wt% based on  $m_{\text{IL}}$ ), 0.5 h ultrasonic bath,  $h_{\text{gap}}=500$   $\mu\text{m}$ , 0.5 h Osram UV lamp, 24 h EtOH, 24 h H<sub>2</sub>O.

- ✓ Preparation of PILs-membranes by UV polymerization
- ✓ Determination of characteristic data
- ✓ Application in permeation and separation experiments

- ❑ Disclosure of surface structure (pore size, distribution)
- ❑ Evaluating influence of monomer ratios
- ❑ Improve mechanical and long term stability

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References:

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- [2] P. Bengani-Lutz, R. D. Zaf, P. Z. Culfaz-Ermen, A. Asatekin, *J. Memb. Sci.* **2017**, 543, 184–194.
- [3] Z. Zheng, Q. Xu, J. Guo, J. Qin, H. Mao, B. Wang, F. Yan, *ACS Appl. Mater. Interfaces* **2016**, 8, 12684–12692.

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