

Membranes based on UV-polymerized vinylimidazolium 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 feasible, which are combining the advantages of solid polymeric structures and ionic liquids.^[1] Furthermore, UV initiated polymerization makes it possible to obtain PILs membranes straight out of the casted monomer film. In addition to various synthetic possibilities, this new approach facilitates membrane manufacturing and modification.^[2,3]

Herein, we present the casting of vinylimidazolium ionic liquids in the formation of membranes and their surface characterization by AFM. In application, these free-standing polymer membranes were able to withhold calcium gluconate, a charged sugar derivate, significantly for several hundred hours of filtration.^[4]

Formation of PILs layers

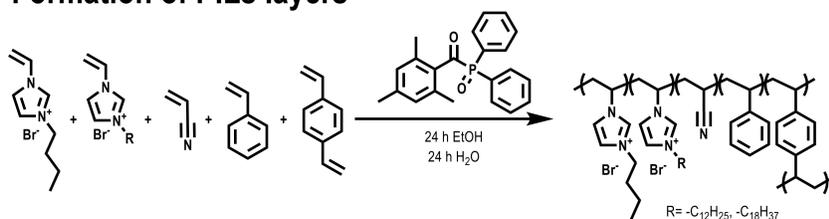


Figure 1: Reaction scheme of the UV initiated polymerization. **Conditions:** $n_{IL} = 0.0093$ mol, $n_{IL} : n_{ACN} : n_{Styrene} = 1 : 3 : 1$, 5 wt% photoinitiator, 2 wt% crosslinker (wt% based on m_{IL}), 0.5 h ultrasonic bath, $h_{gap} = 300$ μ m, 0.5 h Osram UV lamp ($\lambda = 250-300$ nm), 24 h EtOH, 24 h H₂O.

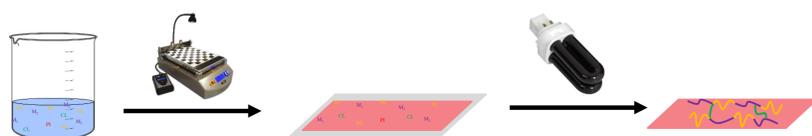
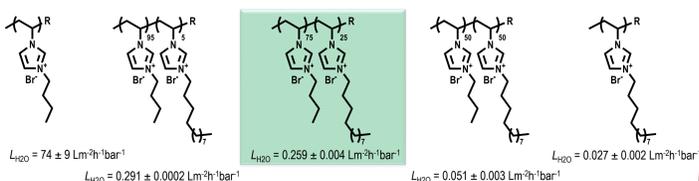


Figure 2: Procedure to form monomer layer and subsequently the polymer layer.



- Mechanically stable **over 700 process hours**
- Performance dependent on retentate concentration and agglomerations on membrane surface decreasing flux (**Figure 2**)
- Calcium gluconate **withhold up to 94%** while charges are crucial for performance

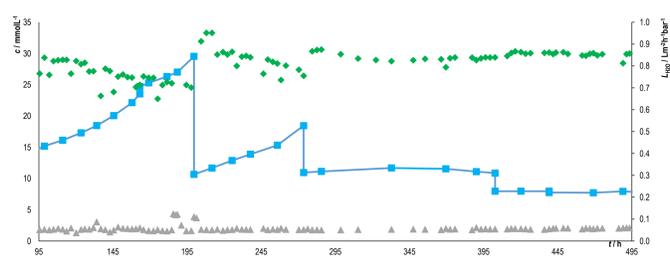


Figure 4: Concentration of calcium gluconate in dead-end filtration experiments. **Conditions:** $d_{membrane} = 43.35$ mm, $p_{air} = 6$ bar, Schleicher&Schuell stirred dead-end cell, $n_{VinylImBr} = 0.00465$ mol, $n_{VinylDodecImBr} = 0.00155$ mol, $n_{IL} : n_{ACN} : n_{Sty} = 1 : 3 : 1$, 5 wt% PI, 2 wt% CL (wt% based on m_{IL}), 0.5 h ultrasonic bath, $h_{gap} = 300$ μ m, 0.5 h UV lamp, 24 h EtOH, 24 h H₂O.

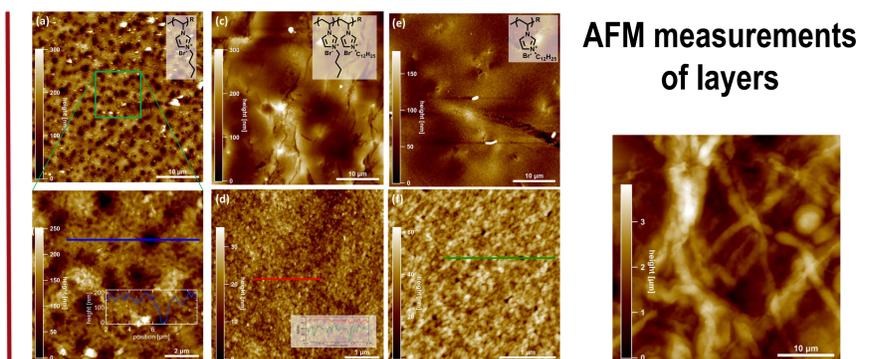
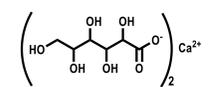


Figure 3: Morphology of membrane surfaces (at top sides) obtained by AFM. Bright (dark) colors correspond to large (small) heights. The left column (a,c,e) contains overview images while the right column (b,d,f) shows higher resolved images of the fine structure of three samples, i.e., (a,b) PILs B, (c,d) PILs BD2, (e,f) PILs D. Line profiles are shown as insets, taken at locations indicated by straight lines in the images (b,d,f). Right: Top side topography after being used for filtration with calcium gluconate.

- Mixture of ILs influences manifestation of the **grainy structure**, the formation of **pores and trenches on the surface**

- Higher and bigger holes correspond to increased flux data
- Dominant liquid flux channels assigned to presence of hollow channels between grains

- Experimental setup enables **pressures up to 80 bar**
- Cross-flow filtration improves retention** under similar conditions
- Decreased permeability by setup



Filtration of charged sugar

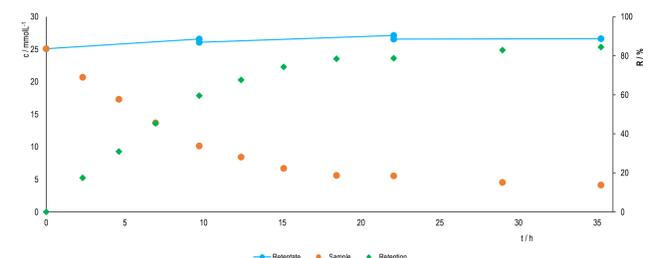
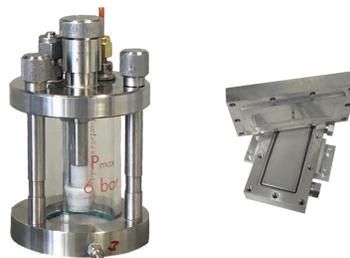


Figure 5: Concentration of calcium gluconate in cross-flow filtration experiments. **Conditions:** $A_{membrane} = 25.5$ cm², $p = 20-80$ bar, homemade cross-flow cell, $n_{VinylImBr} = 0.00465$ mol, $n_{VinylDodecImBr} = 0.00155$ mol, $n_{IL} : n_{ACN} : n_{Sty} = 1 : 3 : 1$, 5 wt% PI, 2 wt% CL (wt% based on m_{IL}), 0.5 h ultrasonic bath, $h_{gap} = 300$ μ m, 0.5 h UV lamp, 24 h EtOH, 24 h H₂O.

- ✓ To our knowledge, first time **two IL containing layer** in filtration
- ✓ Correlation between retentate surface structure and performance
- ✓ **Longtime stable** application of PILs layers in filtration experiments
- ✓ Significant **retention of charged sugars**

- ☐ Scale-up towards continuous processes
- ☐ Expansion to further charged compounds
- ☐ Overcome decreased flux due to agglomerations of charged sugars in filtration

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References:

- [1] J. Claus, F. O. Sommer, U. Kragl, *Solid State Ionics* **2018**, *314*, 119–128.
- [2] Z. Zheng *et al.*, *ACS Appl. Mater. Interfaces* **2016**, *8*, 12684–12692.
- [3] J. Guo *et al.*, *ACS Appl. Bio Mater.* **2019**, *acsabm.9b00619*.
- [4] F. O. Sommer, J. S. Appelt, I. Barke, S. Speller, U. Kragl, **2019**, *in preparation*.

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