

Advanced routes towards PIL membranes

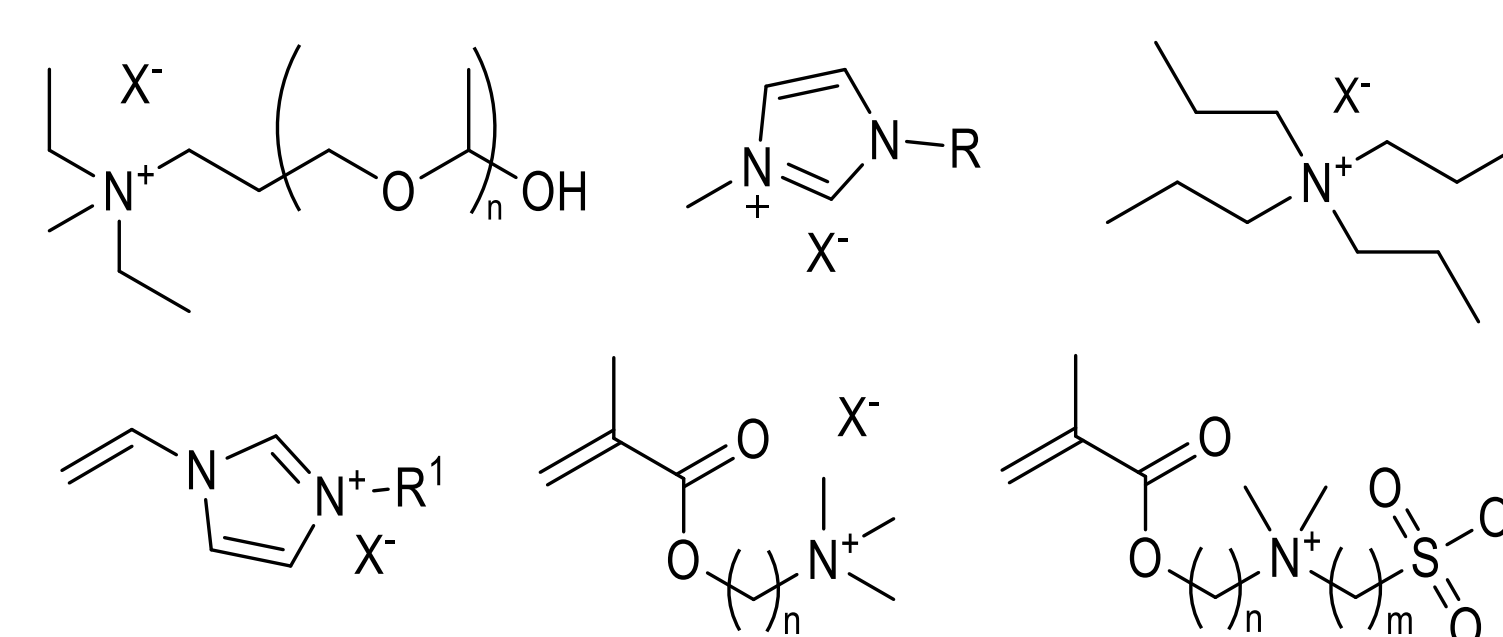
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Introduction

The term "ionic liquid" (IL) describes salts whose melting points are below 100 °C and which have remarkable properties as low vapor pressures or non-flammability. ILs are also named "designer solvent" due to their synthetic variety making them attractive for example in the area of synthesis and extractions. By the implementation of vinyl groups polymerized ionic liquids (PILs) are possible and combining the advantages of both, solid polymeric structures and ionic liquids. **Figure 1** shows some general structures of ILs (top) and polymerizable ionic liquids (bottom).^[1]

Membranes based on ionic liquid monomers describes an upcoming class of materials. Integrating copolymers of charged and uncharged monomers show a high water permeability and good anti-fouling properties making them applicable in fresh water treatment or bioindustrial purification steps. Due to self assembling pores only have diameters of 1 nm which correspond to a molecular weight cut off (MWCO) near 1 kDa. Compared to commercial available membranes with same MWCO porous supported PILs membranes show a higher water flux.^[2] Furthermore, UV initiated polymerization enable to obtain PILs membranes straight out of the casted monomer film. Besides high diversity of ILs based on the synthetic possibilities, this new approach facilitates membrane manufacturing.^[3]

New challenges are the optimization of long term stability and reproducibility of homogeneous pore size distributions. Opposite to supported membranes or uncharged monomers in the polymer, a high amount of free charges will be of interest to applications in ion exchange or fuel cell devices.



R¹: Alkyl, -CHO, -NR²R³, -SO₃H
X⁻: Cl⁻, Br⁻, PF₆⁻, TFSI⁻, NTf₂⁻, ClO₄⁻, B(CN)₄⁻, ...

Figure 1: General form of ionic liquids (upper structures) and polymerizable ionic liquids (bottom structures)

Experimental Setup & Results

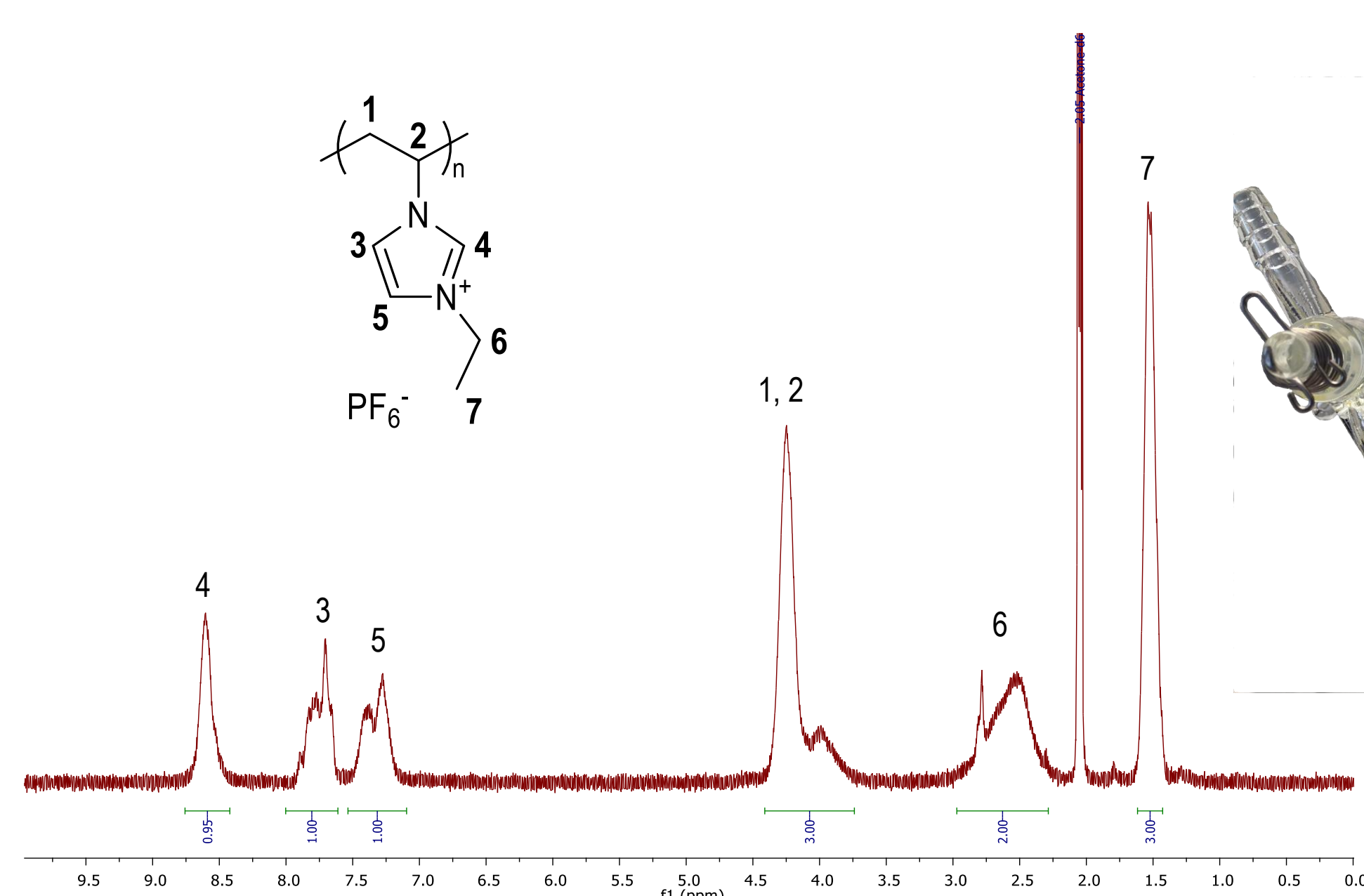


Figure 2: Flask with poly(vinylethylimidazolium) hexafluorophosphate and ¹H-NMR spectra of it.

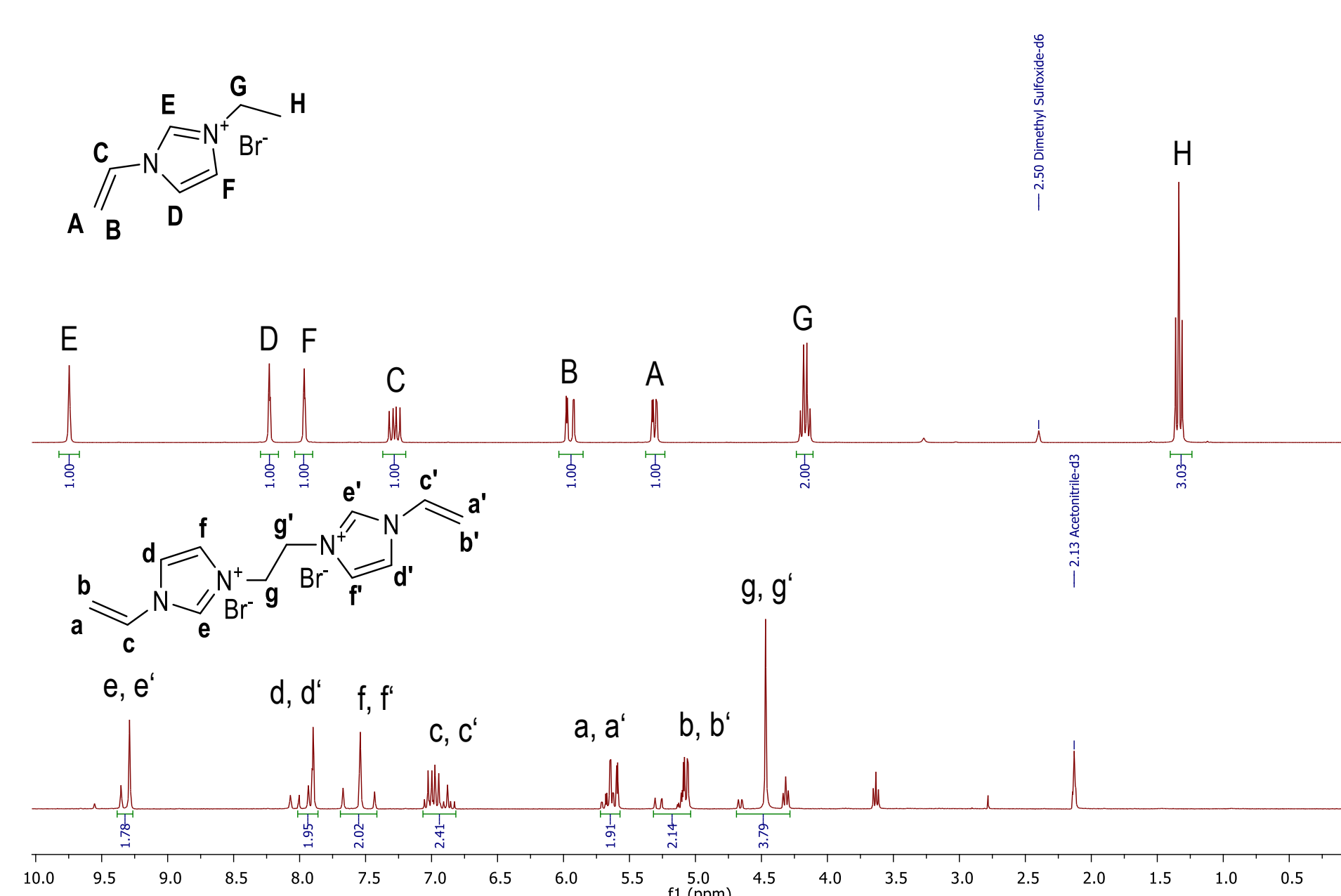


Figure 3: ¹H-NMR spectra of vinylimidazolium bromide and a divinylimidazolium crosslinker with the solution for photocrosslinking.



Figure 4: Casting device.

To precipitate the polymer film an anion exchange is necessary. Typically used anions are e.g. hexafluorophosphate (PF₆⁻), perchlorate (ClO₄⁻) or trifluoromethylsulfonyl imide (NTf₂⁻) which make polyvinylimidazoliums water-insoluble.^[4]

The homogenous casting solution (**Figure 5**) is based on a water miscible solvent, as acetonitrile or dimethylacetamide, and is casted onto a glass or teflon surface. Despite, the different solubilities of all components, only a solid polymerfilm retains after an aqueous precipitation bath (**Figure 7**).



Figure 5: Casting solution.

Additives may be added to adjust solution properties as viscosity in the casting step or influence the pore size development in the precipitation process. Likewise, different heights of the casting knives gap and casting speed affect the properties of the resulting membranes. Additionally, the device (**Figure 4**) can be heated up to evaporate solvents.

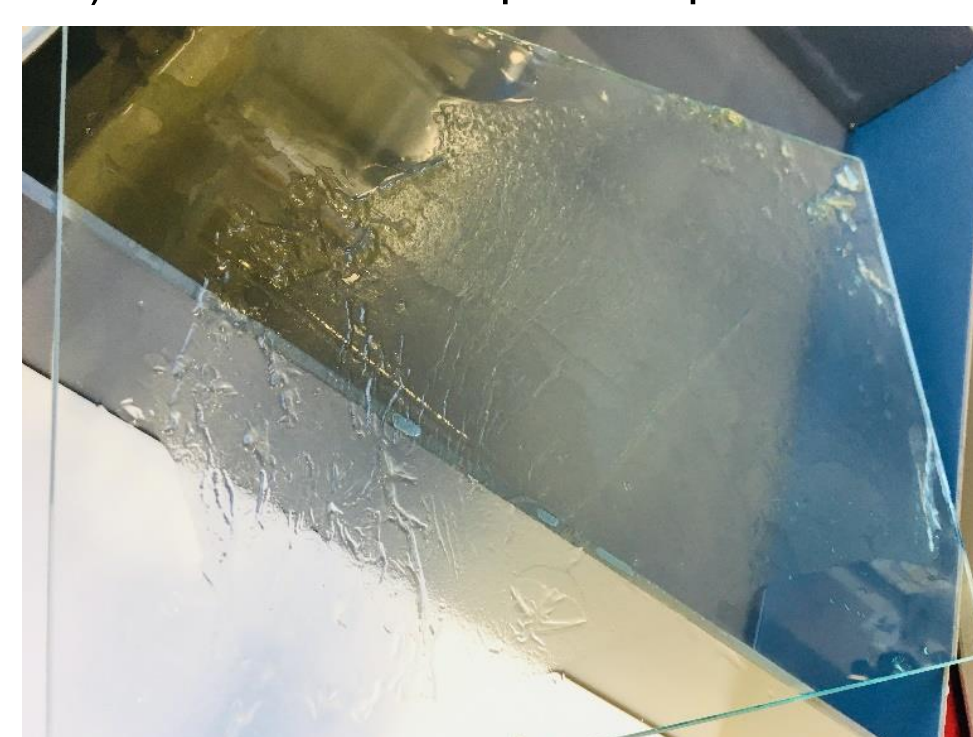


Figure 7: Polymerfilm obtained by precipitation.

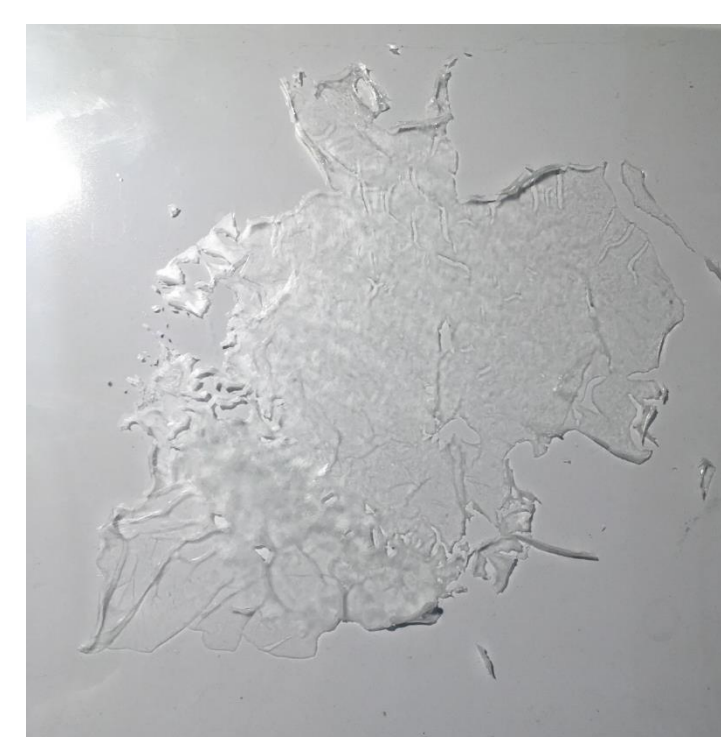


Figure 8: Photocrosslinked polymerfilms.

A homogeneous mixture containing the monomers, crosslinkers and a photoinitiator is obtained by ultrasonic treatment (**Figure 3**). The solution is casted onto a glass surface, subsequently exposed up to an hour to UV light (**Figure 6**) with wavelengths appropriate to the initiator. The resultant polymerfilm (**Figure 8**) shows a high stability over several days in water and alcoholic coagulation baths.



Figure 6: UV-lamp.

Summary & Outlook

A new opportunity to obtain neat polymerized ionic liquid membranes is given by either casting of solved polymers or the crosslinking of casted monomer solutions. Furthermore different IL monomers and crosslinkers were investigated in both casting process which lead to potential polymerized ionic liquid membranes.

Studies concerning the stability, water permeability and separation performance as well as enhanced analytical results will follow.

Further projects

Free positions for Bachelor and Master thesis are available! Feel free to contact under fridolin.sommer@uni-rostock.de or 0381-498 8994.

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References:

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