

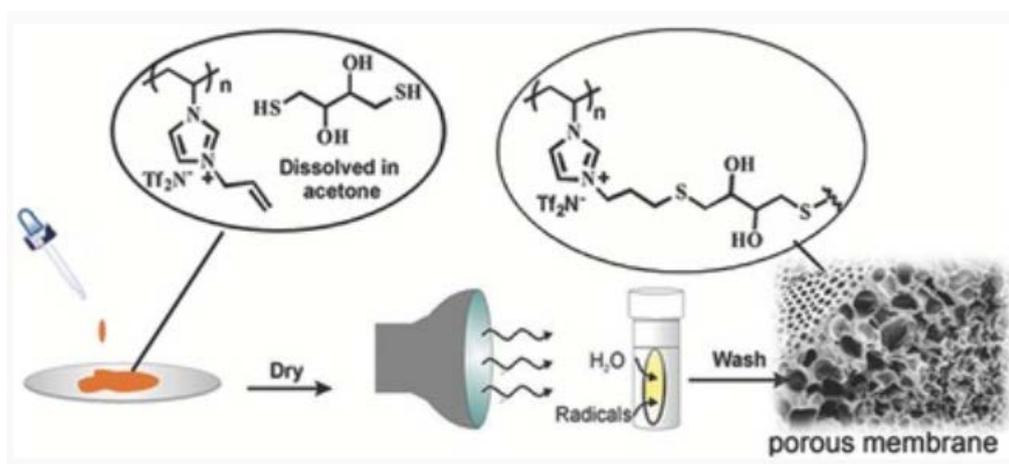


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## Stable Covalently Photo-Crosslinked Poly(Ionic Liquid) Membrane with Gradient Pore Size

Dani, A., Täuber, K., Zhang, W., Schlaad, H., & Yuan, J.



An imidazolium-based poly(ionic liquid) is covalently crosslinked via UV-light-induced thiol–ene click chemistry to yield a stable porous polyelectrolyte membrane, which carries gradients of crosslink density and pore size distribution along its cross-section from top to bottom.

## 1. Introduction

Polyelectrolyte membranes have become an emerging class of materials in the past years.<sup>[1, 2]</sup> They can be made up from one or two different polyelectrolytes, whose charged nature allows for a mutual inter-polyelectrolyte complexation that leads to membrane formation.<sup>[3-5]</sup> Exploiting different kinds of polyelectrolytes it is possible to tune the membrane properties, aiming at various applications, such as separation, sensing, or catalysis.<sup>[6-13]</sup> Moreover, by use of templating agents, layer-by-layer deposition or phase separation mechanism, membranes can be developed in a porous fashion, bearing pores of different sizes and distributions.<sup>[1, 6]</sup> A promising kind of polyelectrolyte membrane is the one based on poly(ionic liquid)s (PILs), in which the ionic liquid moieties along polymer chains can functionalize the membrane and open up routes to a large variety of applications, such as separation, desalination, actuation, pH sensing, and many others.<sup>[14-24]</sup>

The current method used to create porosity in PIL membranes exploits the phase separation from a non-solvent during inter-polyelectrolyte complexation. Since the complexation is triggered by a base (usually ammonia), which penetrates across the membrane in an asymmetrical way, it is possible to achieve a gradient in crosslinking degree and pore size.<sup>[18, 19, 25-28]</sup> Due to the dynamic nature of the ionic bonding, this pore production methodology produces porous membranes that are instable under harsh conditions that are met in applications as corrosion barriers, separation membranes, medical implants, or in electrochemical devices.<sup>[29-31]</sup> In fact, when exposed to high ionic strength solutions, these membranes undergo a partial or full degradation, mainly due to the dissociation of the electrostatic crosslinks. In order to obtain stable polyelectrolyte membranes, covalent crosslinks between polyelectrolyte chains would be preferred over electrostatic crosslinks. Typically, polyelectrolyte membranes are covalently crosslinked by means of a post-treatment

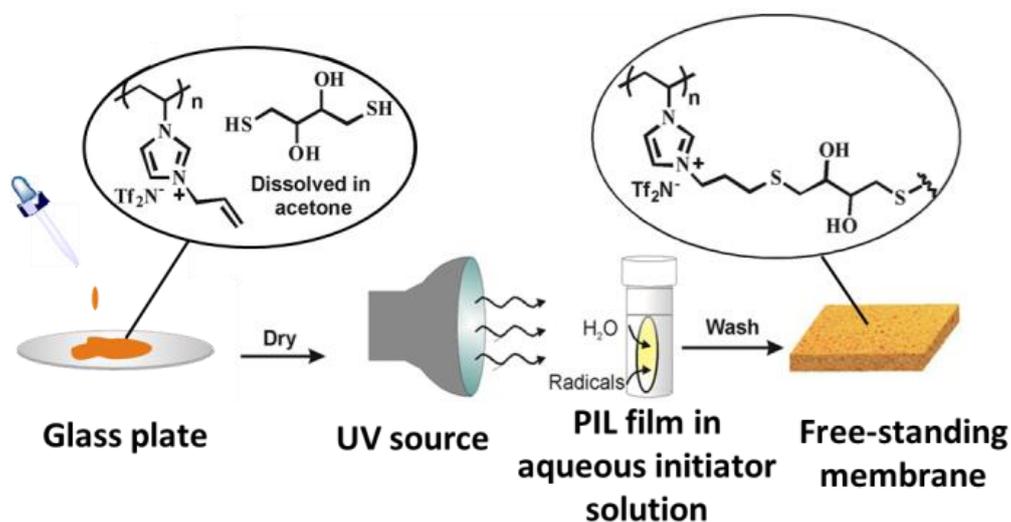
that involves photoreactions, condensation reactions or click-chemistry reactions in order to introduce an additional covalent crosslink on top of the electrostatic one.<sup>[32-36]</sup>

In this communication we describe a direct way to obtain a polyelectrolyte membrane by covalent crosslinking of a single PIL polyelectrolyte, avoiding the use of inter-polyelectrolyte complexation. The covalent crosslinks between the PIL chains were synthesized by a thiol-ene photo-induced reaction in a non-solvent,<sup>[37-39]</sup> resulting in a phase separation that induces porosity in the as-formed membrane. Furthermore, this crosslinking method leads to a pore size gradient along the membrane cross section, producing a stable, covalently crosslinked membrane in a single step procedure.

## 2. Results and Discussion

The fabrication procedure of porous PIL membranes *via* thiol-ene crosslinking is illustrated in Scheme 1. Poly(3-allylmethyl-1-vinylimidazolium bromide) was synthesized according to our previous work,<sup>[40]</sup> and the bromide anion was exchanged to bis(trifluoromethane sulfonyl)imide (Tf<sub>2</sub>N) to obtain a hydrophobic PIL, poly(3-allylmethyl-1-vinylimidazolium Tf<sub>2</sub>N) (PAMVIm-Tf<sub>2</sub>N); experimental details are given in the Supporting Information. To fabricate the porous membrane, PAMVIm-Tf<sub>2</sub>N (103.8 mg, 0.25 mmol of repeating units) and dithioerythritol (DTE; 38.6 mg, 0.25 mmol) were dissolved in acetone (1 mL), and stirred until formation of a homogeneous solution. The solution was cast onto a glass plate (2 cm<sup>2</sup>), and the solvent was evaporated at room temperature overnight. The dry film was then immersed into an aqueous solution of a photoinitiator Irgacure® 2959 (25 mg in 5 mL). The reactor was immediately placed in an ice bath and irradiated with an UV-A light source (225 mW/cm<sup>2</sup>) for 2 hours in ambient atmosphere. A free-standing porous membrane was then peeled off from the glass plate and rinsed with water to remove unreacted DTE and initiator. During the synthesis the initiator radicals in water solution penetrate into the PIL/DTE film triggering the thiol-ene click-reaction. Hydrophobic PAMVIm-Tf<sub>2</sub>N is insoluble in water, hence penetration of water into the polymer film induced a phase separation resulting in the

formation of pores. Moreover, the concurrent thiol-ene reaction crosslinked the polymer chains and stabilized the freshly formed porous structure. The obtained membrane becomes insoluble in acetone, a good solvent for PAMVIm-Tf<sub>2</sub>N, evidencing the successful covalent crosslinking reaction. A control experiment was run in the absence of Irgacure® 2959 photoinitiator, to see whether or not UV light alone would be sufficient to crosslink the PIL.<sup>32</sup> After 2 hours of UV exposure no membrane was formed, and the treated polymer/DTE blend film was easily dissolved in acetone.

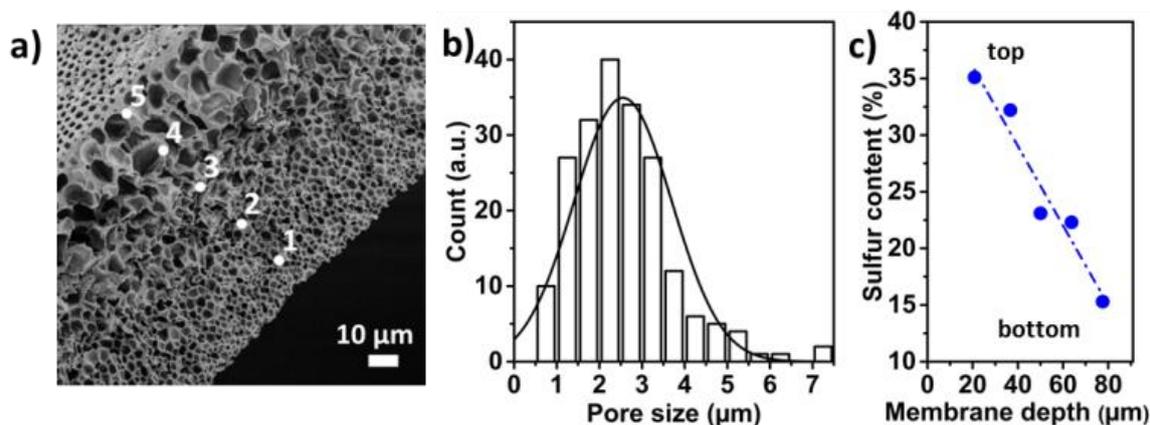


**Scheme 1.** Illustration of the membrane fabrication process. A solution of PAMVIm-Tf<sub>2</sub>N and DTE in acetone was dropped onto a glass plate, after which upon solvent evaporation a dry PIL/DTE blend film was formed and immersed into a solution of radical initiator in water. Irradiation with a UV light source induces crosslinking and pore formation, yielding a free-standing porous membrane.

The porous structure of the thiol-ene crosslinked membrane was investigated by scanning electron microscopy (SEM). As shown in Figure 1a, the pores of micrometer scale are densely packed creating a fully interconnected pore structure across the entire membrane. The porosity gradient, arising from the asymmetric penetration of the photoinitiator across the membrane, is well recognizable in the membrane cross section. The average pore size, calculated by statistical analysis of the SEM image considering all pores along the gradient, is  $(2.5 \pm 1.4) \mu\text{m}$  (see Figure 1b). In contrast, when the PIL film was thermally crosslinked without DTE in the film (details of the synthesis in Supporting Information), the obtained

membrane contained interconnected pores with a much larger size of  $(7.6 \pm 4.1) \mu\text{m}$  (Figure S1). This difference in pore sizes arises from the fact that the kinetics of thermal crosslinking is much slower than phase separation.

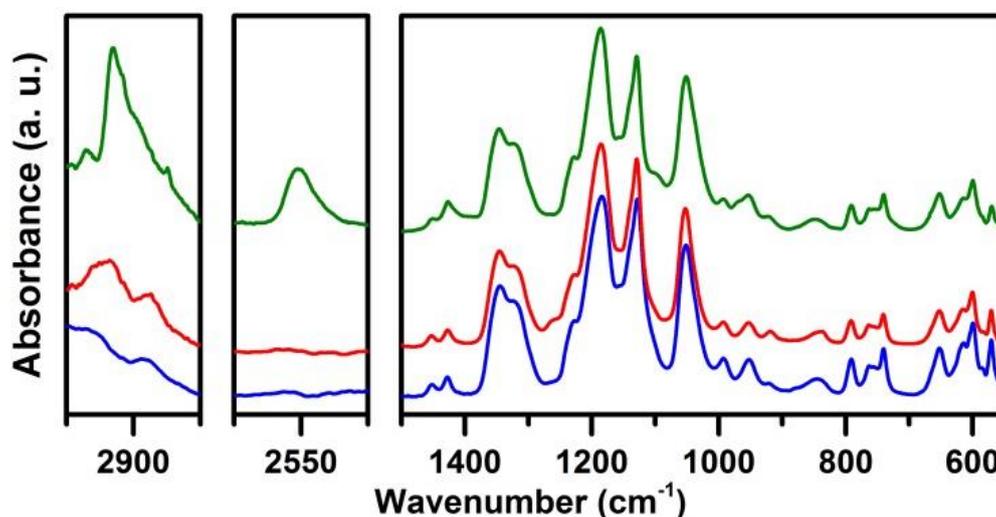
EDX analysis performed along membrane cross section evidences that the content of sulfur decreases progressively from 35.1% on the top to 15.3% at the bottom of the membrane (see Figure 1c and Table S1 in the Supporting Information). These values are related to a decreasing amount of DTE from top to bottom of membrane cross section, related to a decreasing degree of crosslinking over the membrane cross section. It is important to note that the theoretical sulfur contents in DTE and PAMVIm-Tf<sub>2</sub>N are 41.6 wt% and 15.4 wt%, respectively. The EDX analysis shows a little overestimation of sulfur content at a high weight ratio, possibly due to a concurrent self-coupling reaction of DTE in presence of air (see Table S2).



**Figure 1.** (a) SEM image of the porous cross section of the membrane and (b) pore size distribution obtained from statistical analysis on 200 measured pores. (c) EDX analysis of the sulfur content along the membrane depth from the top.

ATR-FTIR spectra of the membrane were collected before and after the thiol-ene reaction on both sides of the membrane. The spectrum collected on the membrane before the thiol-ene reaction, top red curve in Figure 2, is a superposition of the vibrational bands of PAMVIm-Tf<sub>2</sub>N and of DTE; both reference spectra are shown in Figures S2-S3 (Supporting Information). The band related to the C-S stretching of the formed thioether is found in the

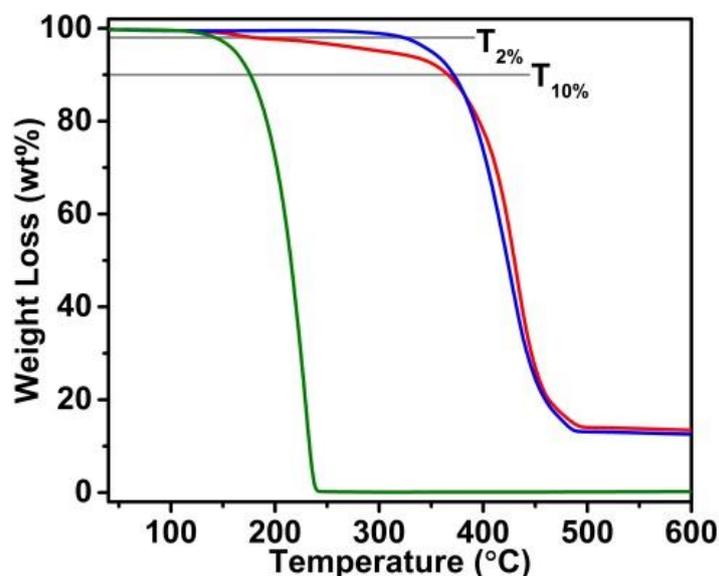
705-570  $\text{cm}^{-1}$  range. However since this band is usually very weak in FT-IR spectroscopy, it is not reliable to use it for monitoring the thiol-ene reaction. Instead, the S-H stretching band of DTE at 2554  $\text{cm}^{-1}$ , is explored, which is visible on the membrane before UV treatment and vanished completely after the reaction.<sup>[41]</sup> Interestingly, the C-H stretching regions are different on the opposite sides of the membrane. The FTIR spectrum from the top side, faced to the UV light source (Figure 2, middle green curve), shows the asymmetric and symmetric C-H stretching bands at 2935  $\text{cm}^{-1}$  and 2872  $\text{cm}^{-1}$ , respectively, ascribable to the thioether methylene group.<sup>[42]</sup> On the bottom side of the membrane (Figure 2, bottom blue curve), these two bands appear weaker indicating fewer thioether bonds and thus a lower degree of crosslinking. Hence, ATR-FTIR analysis qualitatively confirms the successful thiol-ene crosslinking as well as different crosslinking densities along the membrane cross section. All other vibrational features in the low frequency region, assigned to the polymer backbone and the  $\text{Tf}_2\text{N}^-$  anion, are unaltered after the thiol-ene reaction.



**Figure 2.** ATR-IR spectra of the membrane before (green curve) and after the thiol-ene reaction on the top surface (red curve) and the bottom surface (blue curve).

In order to evaluate the stability of the thiol-ene crosslinked membrane, thermogravimetric analysis was performed on the membrane and the two starting components, PAMVIm- $\text{Tf}_2\text{N}$  and DTE (see Figure 3). The pristine PIL is the most thermally stable component showing a 2

wt% mass loss at 323 °C and 10 wt% at 371 °C. On the contrary, DTE is thermally rather unstable, showing a 2 wt% mass loss at 124 °C and 10 wt% at 175 °C. The PIL membrane obtained from PAMVIm-Tf<sub>2</sub>N/DTE shows a small decomposition step at around 180 °C probably ascribable to the decomposition of some DTE molecules in excess. The 2 wt% mass loss is at 179 °C, and the 10 wt% mass loss is at 367 °C. Its decomposition profile resembles the one of the pure PIL. Additionally, the ATR-FTIR spectrum virtually did not change after annealing the membrane sample at 280 °C (Figure S4 in Supporting Information), suggesting that the small weight loss has no impact on the general chemical structure of the membrane.



**Figure 3.** Thermogravimetric profiles of DTE (green curve), PAMVIm-Tf<sub>2</sub>N (blue curve) and the thiol-ene crosslinked membrane (red curve).

### 3. Conclusions

In conclusion, this work describes an easy way to fabricate a covalently crosslinked, porous polyelectrolyte (PIL) membrane having gradient crosslink density and pore size distribution along its cross section. Notably, such a membrane structure has not yet been reported for covalently crosslinked polyelectrolyte membranes. The pore size gradient can be used for an asymmetrical swelling when the membrane is exposed to solvent, resulting in a bending movement. The membrane chemical structure is based on covalent crosslinks and not electrostatic crosslinks, paving the way to create polyelectrolyte membranes bearing freely

adjustable anions, aimed to expanded applications, such as separator in batteries, separations and filtration in different chemical environment.

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author

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Keywords: poly(ionic liquid), membrane, photo-crosslink, nanoporous

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## Supporting Information

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