

Supporting Information

A facile method for grafting functional hydrogel films on PTFE, PVDF, and TPX polymers

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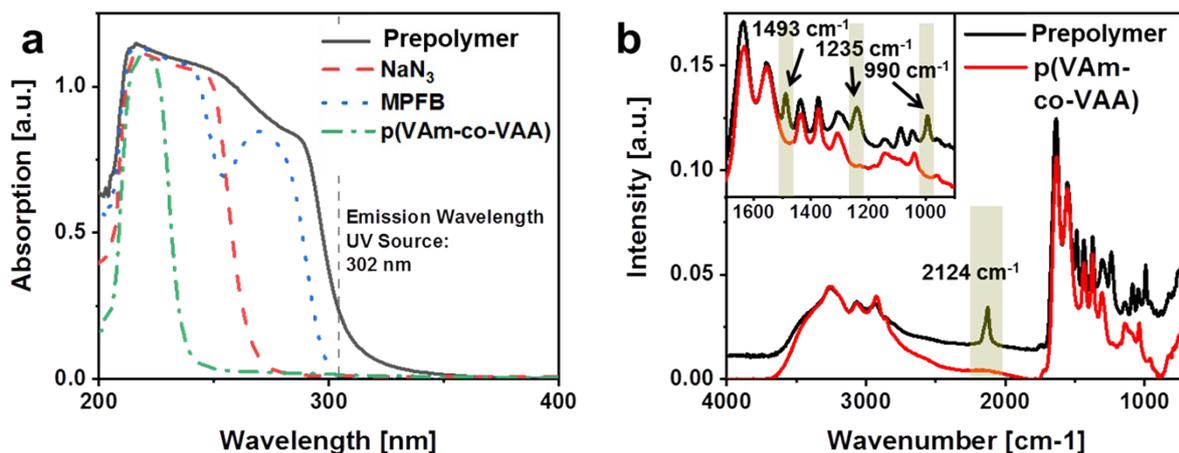


Fig S1. a) UV-Vis spectrum of the starting materials and the prepolymer in water (1 mg mL⁻¹). b) FT-IR spectrum of the prepolymer and P(VAm-co-VAA).

Table S1. The theoretical average number of repeat units between two azides in one polymer (N_{RU}), the theoretical average molecular weight between two azides (M_{aa}), the theoretical average number of azides (N_a) per polymer (based on the number average molecular weight of the polymer obtained by SEC ($5.6 \cdot 10^4$ g·mol⁻¹)) for the theoretical amine/azide ratios, and the experimentally determined azide to amine ratio by IR

| Azide /Amine | N_{RU} | M_{aa} [g·mol ⁻¹] | N_a | Experimental ¹ |
|--------------|----------|------------------------------------|--------|---------------------------|
| 0.1 | ~ 20 | ~ 1270 | ~ 47.2 | 0.1 |
| 0.075 | ~ 30 | ~ 1905 | ~ 31.5 | 0.075 |
| 0.05 | ~ 40 | ~ 2540 | ~ 23.6 | 0.044 |
| 0.025 | ~ 80 | ~ 5080 | ~ 11.8 | 0.028 |

¹To determine the experimental azide/amine ratio the area of the azide vibration is divided by the area of the amide vibration, which was assumed to be constant.

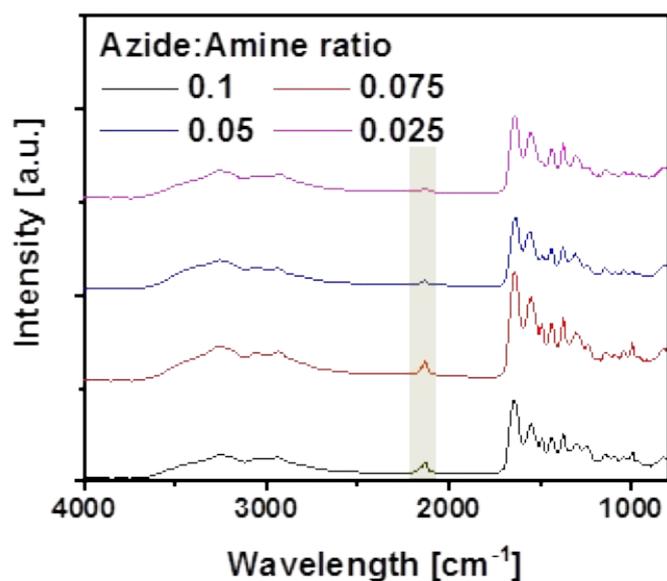


Fig S2. FT-IR spectrum of the prepolymer with different azide contents. The asymmetric azide vibration at 2124cm^{-1} increases with increasing azide content in the crosslinker.

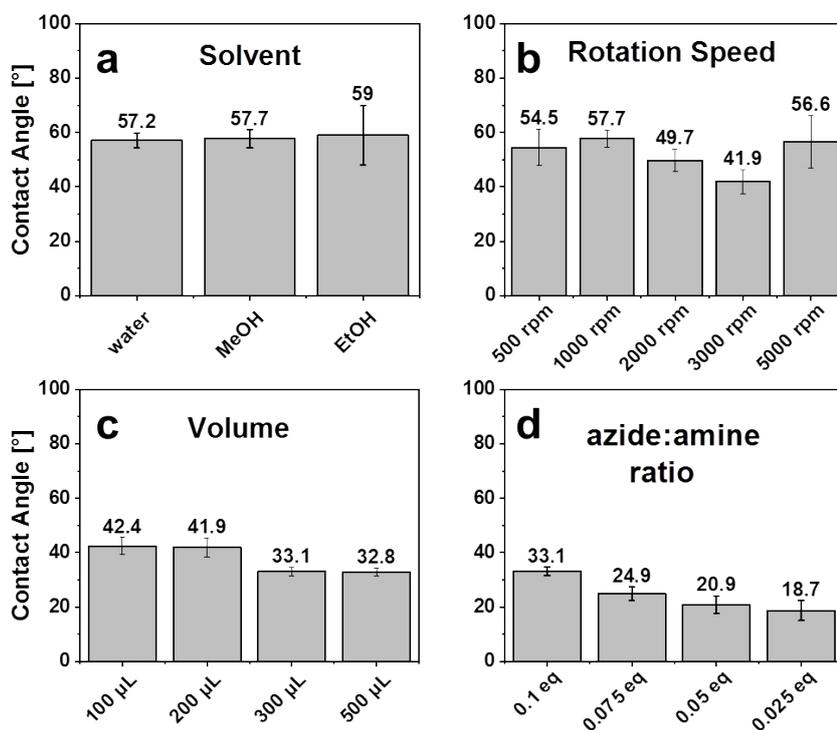


Fig S3. Sessile drop CA (equilibration time: 60 s, $n=5$) of PVDF foils varying a) the solvent (rotation speed 1000 rpm, volume: $200\ \mu\text{L}$, azide:amine ratio: 0.1), b) the rotation speed (solvent: MeOH, volume: $200\ \mu\text{L}$, azide:amine ratio: 0.1), the volume (solvent: MeOH, rotation speed 3000 rpm, azide:amine ratio: 0.1), and the azide:amine ratio (solvent: MeOH, rotation speed 3000 rpm, volume: $300\ \mu\text{L}$).

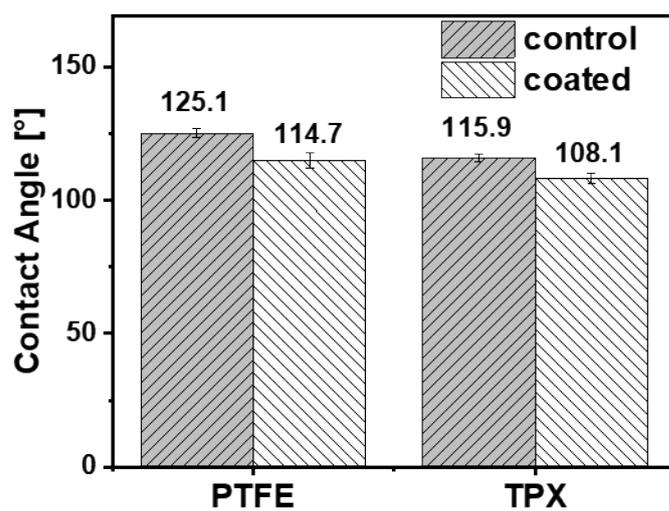


Fig. S4. Sessile drop CA for control and spin-coated (3000 rpm, 5 mg·mL⁻¹, 75 μL·cm⁻², and an azide:amine ratio of 0.025) PTFE and TPX foils.

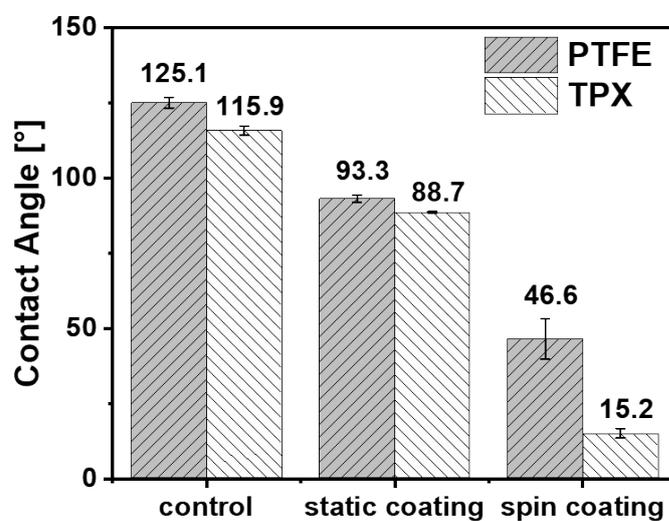


Fig. S5. Sessile drop CA for PTFE and TPX foils after static coating and subsequent spin coating.

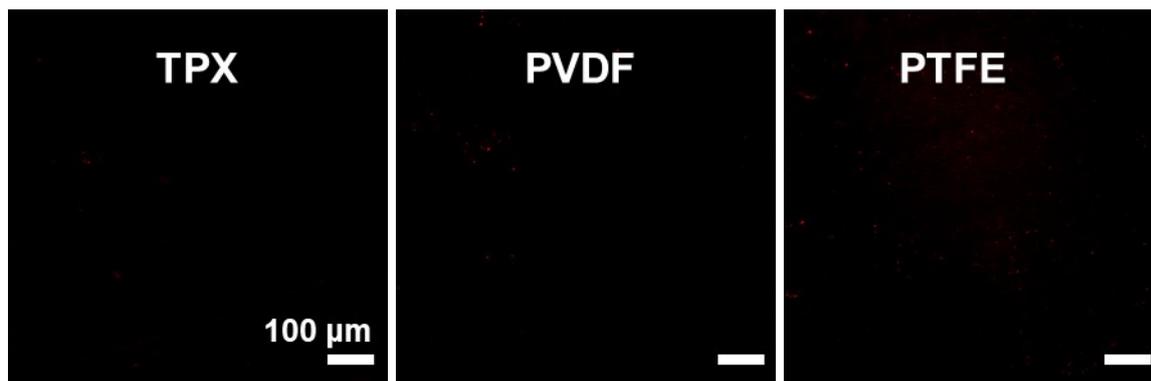


Fig S6. Confocal image of the polymer substrates after UV treating the surface with prepolymer devoid of azide functionality and staining with rhodamine-B-isothiocyanate. The scale bar represents 100 μm

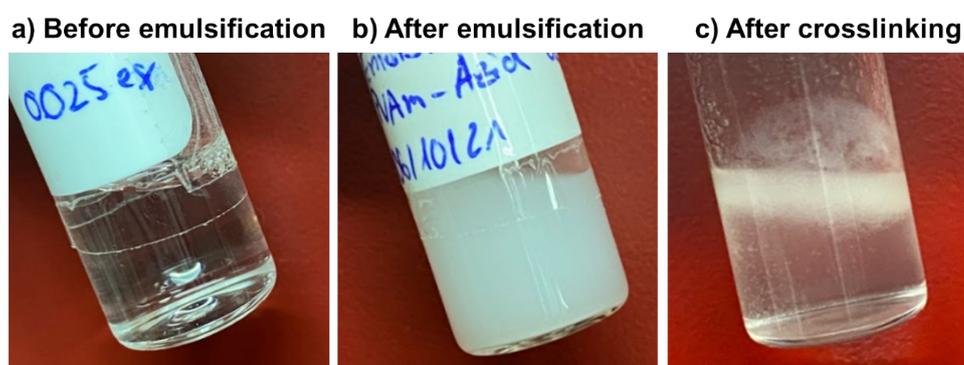


Fig. S7. Photographs of a) 5 wt% of $\text{PFPA}_{0.025}\text{-co-PVAm}$ in water added to Krytox® GPL101, b) after emulsification and c) after crosslinking procedure indicates the formation of a gel-like structure.

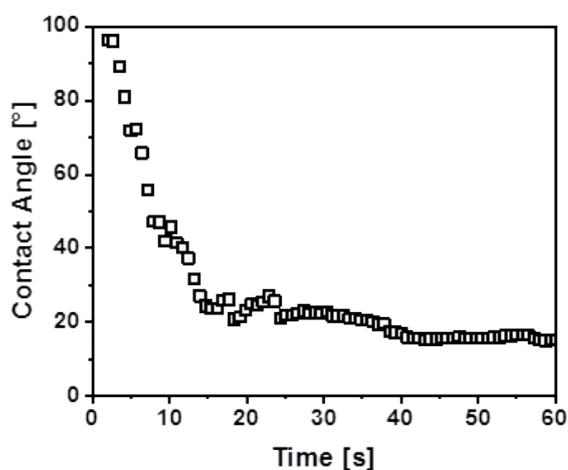


Fig. S8. Sessile drop CA development with time for a TPX membrane.

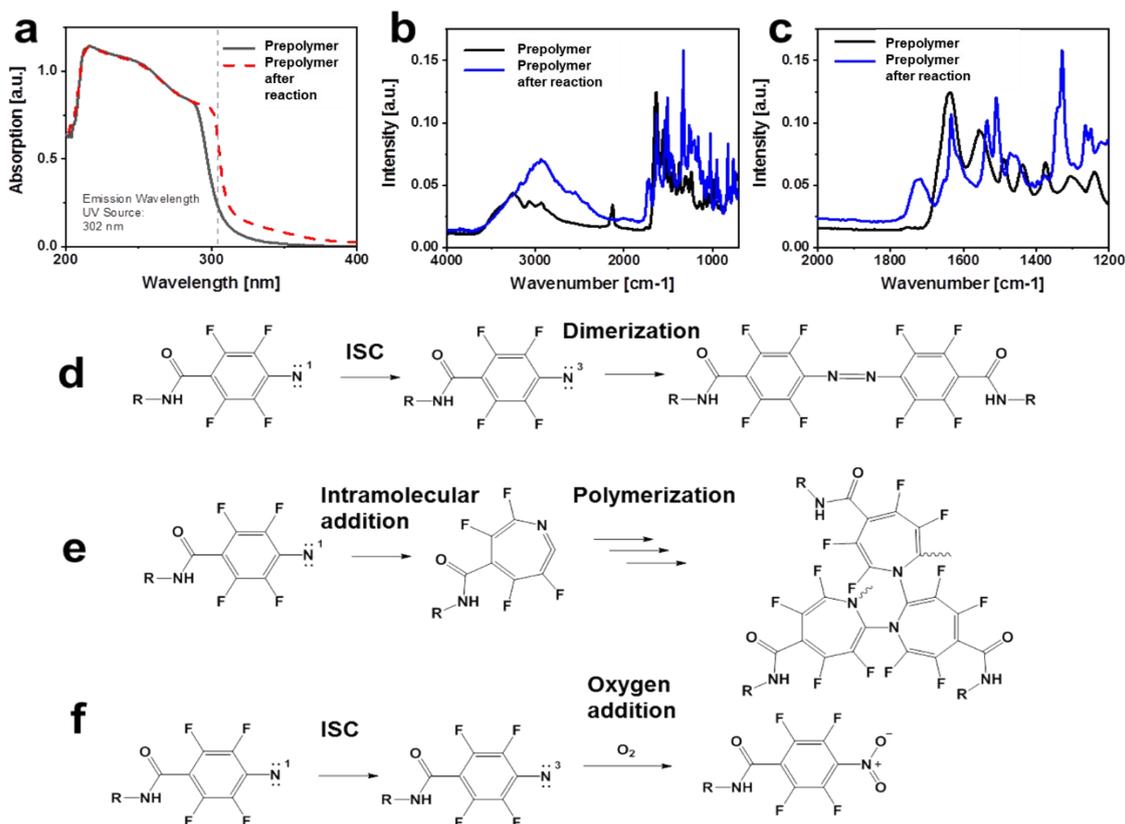


Fig. S9. UV-Vis spectra (a) of the prepolymer and the prepolymer after reaction and their respective IR-spectra (b) and (c). The reaction scheme of ISC to the triplet nitrene with the following dimerization is shown in (d), an intramolecular addition to a ketenimine and the following polymerization is shown in (e), and ISC with subsequent oxygen addition is shown in (f).

Discussion about possible side reactions

UV-treatment of the crosslinker in water leads to a color change from colorless to brownish. In this paragraph, the side reactions are considered, which occur in the aqueous phase. The color change indicates that to some extent the singlet nitrogen underwent ISC to the triplet nitrene which forms azo-compounds. The brownish liquid phase was further analyzed by UV-Vis and FT-IR spectroscopy. In UV-Vis a bathochromic shift is visible which is caused by the azo-compounds. In FT-IR there is a small band at 1411 cm^{-1} , which is related to the N=N stretching of a trans-azo compound. At 1720 cm^{-1} there is a new band, which has been reported by Meijer et al.: The intramolecular addition reaction of the singlet nitrene to the aromatic ring leads to the formation of a reactive ketenimine, which polymerizes to poly-1,2-azepines. The signal was deduced to simultaneous photo-oxidation of the polymer.¹ However, it is noteworthy that the substitution of an alkene with two amine groups can shift the absorbance to higher frequencies. Thus, also the C=C vibration might be responsible for the band.² Furthermore, there are two strong signals at 1510 and 1329 cm^{-1} . These are attributed to the asymmetric and symmetric stretching vibration of nitro-moieties. These are formed by the reaction of triplet nitrene with

molecular oxygen as the water for the reaction was not degassed.³ Furthermore, the amide vibration is changed, i.e. the amide II band is shifted to lower frequencies. This might be attributed to hydrogen bonding.

References

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