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Influence of UV curing on morphology and performance of polysulfone membranes containing acrylates

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ABSTRACT

UV cross-linked polysulfone (PSU) based membranes containing additives with different number of acrylate groups were prepared via UV curing and nonsolvent induced phase separation (NIPS). The resulting membranes had good solvent resistant nanofiltration (SRNF) performance with superior chemical resistance. The impact of the UV irradiation as well as the presence of the acrylate cross-linkers and the photoinitiator with respect to membrane morphology, chemical stability, and SRNF performance was investigated. Membranes with a cross-linker and a photoinitiator in their matrix had a macrovoid-like morphology. By decreasing the membrane wet thickness from 200 to 50 μm to enhance the depth-curing, a sponge-like structure was achieved. The same macrovoid-free structure was found when 150 and 200 μm thick membranes were treated in the reverse order, i.e. first UV irradiated and then immersed in water (UV/NIPS instead of NIPS/UV). Addition of an acrylate cross-linker decreased the contact angle of the membranes (typically from 76° to 61°). Addition of a penta-acrylate cross-linker to the PSU membrane resulted in a 10-fold higher permeance (3.3 L m^{-2} h^{-1} bar^{-1}) in comparison to a reference PSU membrane without acrylate additive with still a 94% retention for Rose Bengal (RB) in IPA. However, after UV curing, the same membrane showed a permeance of only 0.07 L m^{-2} h^{-1} bar^{-1} and a retention of 96%. By reversing the synthesis sequence to UV/NIPS, an increase of permeances up to a value of 1.2 L m^{-2} h^{-1} bar^{-1} and retentions up to 94% were achieved.

1. Introduction

Polymeric membranes are widely used in membrane technology [1–6]. Because of the limitations in their chemical and mechanical properties, they often require an extra cross-linking step, either during synthesis [7–10], or as a post-treatment [11–13]. One of the common cross-linking methods for membrane modifications is a chemical reaction between the membrane forming polymer and a multifunctional reagent, like e.g. between polyimides and diamines [7,8,12,14]. However, such approach cannot be applied to prepare stable membranes from chemically less reactive polymers (like e.g. polysulfones (PSUs) or poly(ether ether ketones) (PEEKs)). Therefore, membranes prepared from these kinds of polymers are very often cross-linked by a more drastic treatment like irradiation (e.g. UV, electron beam, or gamma) [15–17]. Apart from that, another strategy involves the synthesis of polymers from these families that carry functional groups [11,16–18]. This polymer is then turned into a membrane, which is later cross-linked by a physical source (e.g. irradiation [16,17]) or via a chemical reaction [11,10].

As a result of such cross-linking, membranes with improved chemical stability are thus obtained. However, not only the chemical resistance of a polymeric membrane is altered during this treatment, but very often also the membrane performance [8,12,14,19,20] and morphology [9].

As a thermoplastic polymer with high glass transition temperature (T_g) and an absence of reactive groups, PSU seems to be a good candidate for many separation processes that demand a chemically resistant membranes [1]. However, PSU membranes (prepared via phase inversion) are not resistant to many aprotic solvents, and thus are unsuitable for Solvent Resistance Nanofiltration (SRNF) applications in these solvents [1,7,8,12,14]. They are also sensitive to CO_2 plasticization in gas separation applications [21–23]. To be suitable for both applications, a further modification of the PSU membrane is necessary via cross-linking. A high-temperature electron-beam irradiation can be implemented [15], but this technique requires expensive electron-beam equipment and, for PESU only works at high temperatures which might damage the membrane structure.

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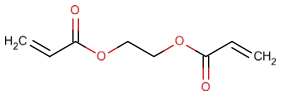
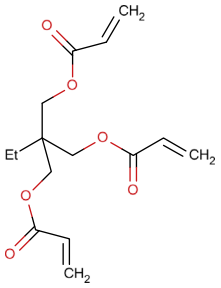
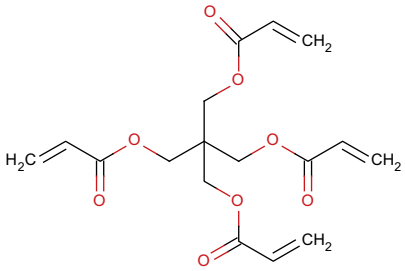
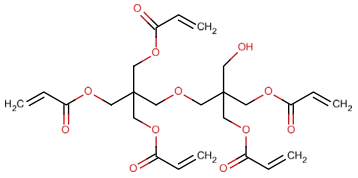
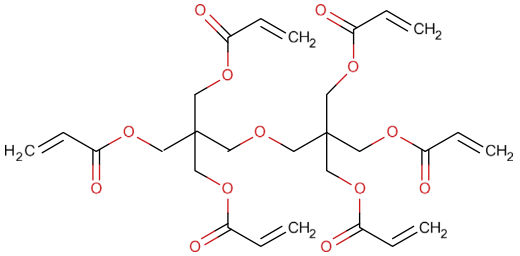
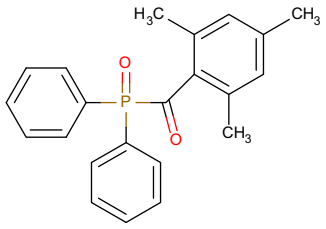
The intrinsic photosensitivity of poly(aryl sulfones) [24,25] provides an opportunity to use UV irradiation as a tool to alter a membrane surface by UV grafting of another polymer chain on top of the PSU membrane [6,26]. Up to now, UV light has mainly been used to modify the surface of PSU membranes in order to decrease membrane fouling [27–30], enhance permeability [31],

Table 1
The cross-linkers and photoinitiator used, as well as their main properties.

Code	Name	Supplier	MW (g mol^{-1})	η^{25} (Pa s)	Purity (%)[a]	Structure [37]
Cross-linker						
Acr2	Ethylene glycol di-acrylate (**EGDA**)	Acros	170.16	NA	90	
Acr3	Trimethylolpropane tri-acrylate (**Sartomer™ SR351**)	Sartomer	296.32	0.08–0.13	> 90	
Acr4	Pentaerythritol tetra-acrylate (**Sartomer™ SR295**)	Sartomer	352.34	0.2–0.5	> 90	
Acr5	Dipentaerythritol penta-acrylate (**Sartomer™ SR399LV**)	Sartomer	524.51	5–9.0	> 90	
Acr6	Dipentaerythritol hexa-acrylate (**Miramer™ M600**)	RAHN	578.56	4–7.0	> 90	
Photoinitiator						
TPO	2,4,6-Trimethylbenzoyl-diphenyl-phosphine oxide (**Darocur™ TPO**)	BASF	348.37	–	–	

[a] All cross-linkers contained a stabilizer (monomethyl ether hydroquinone); NA – not available from the supplier.