Recent developments in thin film (nano)composite membranes for solvent resistant nanofiltration

Sanne Hermans, Hanne Mariën, Cedric Van Goethem, Ivo F.J. Vankelecom

Centre for Surface Chemistry and Catalysis, KU Leuven, Kasteelpark Arenberg 23, PO Box 2461, 3001 Leuven, Belgium

Abstract

By separating organic mixtures at a molecular level, solvent resistant nanofiltration is offering a sustainable and reliable solution to many separation challenges in modern process industry. As solvent permeance is usually inversely proportional to the thickness of the selective layer, so-called thin film composite membranes offer great potential. They consist of a thin polymeric top-layer on a support which is generally prepared from another type of polymer. Excellent combinations of retention and permeance have been achieved by the most recent developments in this field. The incorporation of fillers, e.g. metal organic frameworks, in the top-layers has the potential to even further enhance the membrane performances. These solvent resistant nanofiltration membranes in general are expected to play an important role in the future industrial separation of solutes from organic streams.

Keywords

Membranes; Solvent resistant nanofiltration; Organic solvent nanofiltration; Organophilic nanofiltration; Thin film composite; Thin film nanocomposite

Introduction

Solvent resistant nanofiltration (SRNF) (or its synonyms organic solvent nanofiltration and organophilic nanofiltration) is a pressure driven technique to realize membrane separations up to a molecular level in solvent streams. Small solvent molecules will permeate through the membrane, while solutes (with a typical molecular weight in most applications between 200 and 1000 Da) will be retained (Figure 1) [1]. It is a relatively young technology that broke through around the beginning of this century and gained a lot of interest since [2]. According to a recent extensive sustainability assessment, SRNF has a huge potential in becoming the best available technology (BAT) among the separation techniques in organic media [3]. Compared to competing technologies, like e.g. preparative chromatography, distillation, extraction or crystallization, it is generally more energy efficient, mostly does not create extra waste streams and allows for mild operating conditions [3]. SRNF can also very well complement these conventional separation techniques into more efficient hybrid processes. In industry, SRNF may be applied in many solvent-intensive processes, some of them with a large economic impact, such as edible oil refining and degumming, catalyst recovery, solvent recycling in the pharmaceutical industry, solvent dewaxing, polymer fractionation and athermal solvent exchanges.

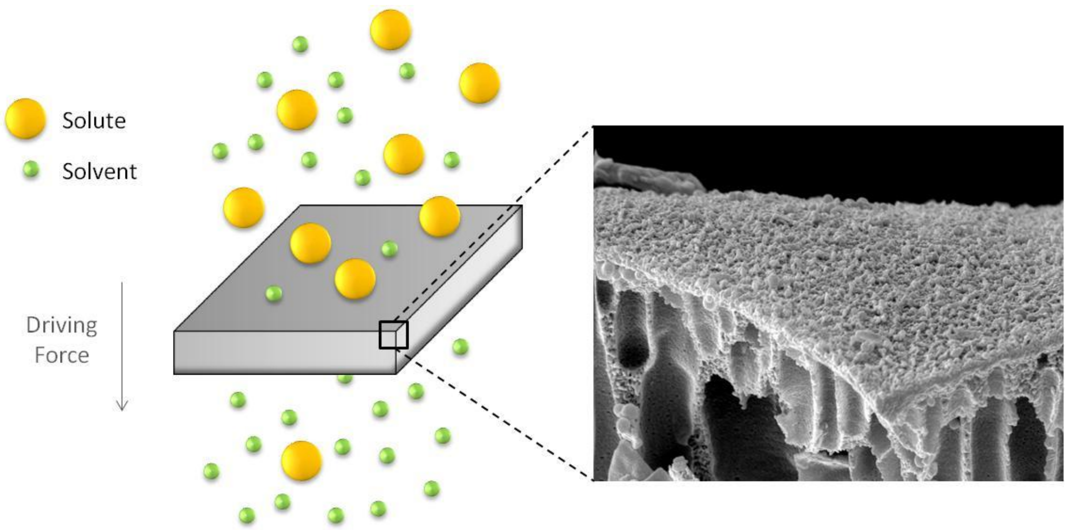

Figure 1: Illustration showing the principle of SRNF, including a SEM image of a thin film composite membrane, consisting of a selective barrier layer on top of a porous support.

An exhaustive review on molecular separations with SRNF was published very recently [4]. It discusses membrane materials (including thin film (nano)composites) and membrane characterization, transport models and process design as well as applications, thus largely updating the very first review in this field published in 2008 [1], while another recent review focuses on the role of SRNF in the pharmaceutical industry [5].

Polymeric membranes are considered to be the most interesting material for SRNF applications. Advantages are the large variety of available polymers, their relatively low price and the ease of fabrication and upscaling of polymeric membranes. An important limitation of polymeric membranes however, is their limited thermal and chemical stability. Interactions between organic solvents and the membrane can cause these membranes to swell extensively (or ultimately even dissolve) resulting in loss of selectivity. The current limited commercial availability of robust membranes with good performance is probably one of the main reasons for the delayed breakthrough of SRNF in industry, together with the general reluctance of the chemical industry to implement new technologies. Reports on successfully implemented SRNF separations at large (or at least pilot) scale could surely help to lower the barrier. Moreover, the transport mechanism through SRNF membranes is much less straightforward than for e.g. aqueous applications. The wide variety of solvents that constitute the feed will all interact in a very different way with the membrane material. This renders a membrane excellent in one solvent and useless in another, even to retain the same solute. Membrane stability in a wide range of organic solvents, combined with excellent and reproducible performances on the long term are thus the main challenge for the further expansion of SRNF.

Due to their specific characteristics (i.e. very thin top-layers), thin film composite (TFC) and thin film nanocomposite (TFN, containing fillers in the selective layer) membranes can be of great value here, complementing the so-called integrally skinned asymmetric SRNF membranes prepared via phase inversion. Polysulfone [6], polyimide [7,8], polybenzimidazole [9], poly(ether ether ketone) [10] and polyaniline [11] have already proven to be valuable polymers for the preparation of integrally skinned asymmetric SRNF membranes via phase inversion, even more so after introducing crosslinking. Since SRNF is a relatively young technique, many materials are yet to be explored for use in this field. This review focuses on the most important developments in TFC and TFN membranes for SRNF applications over the last 5 years.

TFCs for SRNF: general considerations

TFC membranes consist of a very thin, selective layer on top of a porous ultrafiltration (UF) support. Since support and top-layer are synthesized separately, both layers can be independently optimized to achieve a good membrane performance. In general, a TFC membrane comprises three distinct layers (Figure 2): (i) a 'non-woven' fabric, typically made from solvent stable polyester or polypropylene, providing mechanical strength and easy handling of the membrane, (ii) a porous support layer, allowing for a defect-free top-layer formation, and (iii) a thin top-layer, which is the actual selective barrier [12].

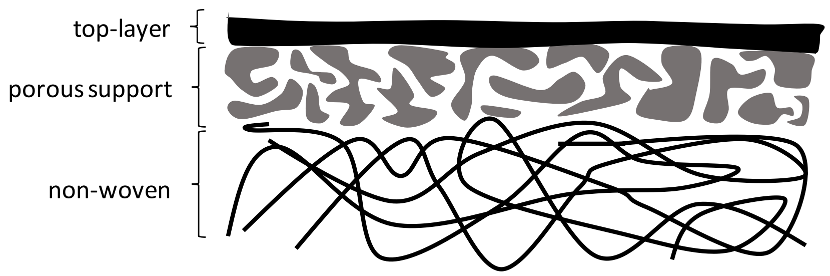

Figure 2: Scheme of a TFC membrane consisting of a non-woven fabric, a porous support layer and a thin, selective top-layer.

The support layer of a TFC membrane is typically prepared via phase inversion, which refers to the controlled transformation of a cast polymer solution from a liquid into a solid state [13]. Crosslinking of the polymer is often required to obtain stability in harsh organic solvents, like dimethylformamide (DMF), and can be done thermally, chemically or by means of UV irradiation [14,15]. The same solvent resistant polymers applied in the synthesis of integrally skinned asymmetric membranes are often used to prepare the porous support for TFC membranes. The most common methods to create a selective layer on top of these support layers are interfacial polymerization (IP) and coating where a polymer solution is contacted with them, mostly at labscale via dip or spin coating. Both IP and coating will be discussed in more detail below. Another method for the preparation of TFCs is plasma polymerization. Ultrathin diamond-like carbon nanosheet membranes were prepared by using a plasma enhanced chemical vapor deposition reactor [16]. Permeation experiments revealed that the selective carbon layer (deposited on porous alumina) had hydrophobic pores of about 1 nm, which allowed ultrafast viscous permeation of organic solvents through the membrane combined with a high retention of organic dyes. Despite the outstanding performance, upscaling of the latter method for membrane preparation is challenging.

TFCs synthesized via IP

In IP, a very thin top-layer is formed on a porous support by the reaction between two monomers at the interface of two immiscible solvents, one impregnated in the support and another present on top of it during reaction. This technique has been widely applied for the synthesis of TFC membranes for aqueous nanofitration and reverse osmosis, in which piperazine (PIP) or m-phenylenediamine (MPD) and trimesoylchloride (TMC) are commonly used as amine and acyl chloride monomers to form a polyamide (PA) top-layer. For aqueous applications, a poly(ether)sulfone support is typically used but due to its limited chemical stability this is less suited for use in solvent applications. As the PA top-layer is stable in aggressive solvents due to its crosslinked nature, most research focused on improving the solvent stability of the support. The membrane performances and feed compositions used in the discussed references are summarized in Table 1. The values reported in this Table are based on the following criteria, taken from [4]: (i) whenever more than one membrane was tested in one single reference, values of the most dense membrane are mentioned; (ii) when multiple solutes were tested, the rejections of the solute with the lowest MW or with a MW that was rejected near 90% are reported.

A PA top-layer prepared from PIP, MPD or hexanediamine (HDA) and TMC was synthesized on top of a crosslinked polyimide (PI) support layer [17]. A tremendous increase in performance was observed after solvent activation. The membranes showed a “molecular weight cut off” (MWCO, a value indicating that solutes (in this case styrene oligomers) with this molecular weight are retained for 90%) value of 200-250 g mol^{-1} in a variety of solvents. To increase the hydrophobic character of the membranes, and thus increase the permeance of apolar solvents, a mixture of triacyl and monoacyl chlorides was used, while free acyl chloride groups, left on the membrane surface after IP, were reacted with hydrophobic molecules. This way, a significant increase in permeance of apolar solvents was achieved [18]. The influence of the applied support was also investigated [19]. In addition, an efficient method for the synthesis of SRNF TFC membranes consisting of PA top-layers on PI supports was developed. Phase inversion, crosslinking and monomer impregnation of the PI support were combined by adding amines to the aqueous coagulation bath of the support [20]. This promising method minimizes the use of materials and makes the SRNF TFC synthesis process significantly greener, faster and more efficient.

A hybrid hydrophilic-hydrophobic selective layer was fabricated on top of a polyacrylonitrile (PAN) support via IP [21]. Hydroxyl terminated trifluoride polydimethylsiloxane (PDMS) was mixed with TMC in the organic phase before being put into contact with the polyethyleneimine (PEI) aqueous solution. The hydrophobicity and thickness of the top-layer increased, but in contrast to the expectations, the flux of apolar solvents decreased compared with the performance using the reference membrane without PDMS. The authors also observed a lower swelling degree of the hybrid TFC in apolar solvents. They claimed that the swelling of either polymer (*i.e.* PDMS in apolar solvents or PEI in polar solvents) is inhibited by the other, resulting in a lower chain mobility, hence lower flux. A PAN support was also chemically crosslinked with hydrazine hydrate, to obtain excellent solvent stability in DMF, and covered with a PA layer via IP using N,N'-diaminopiperazine and TMC as monomers [22]. This approach led to TFC SRNF membranes with an improved performance compared to earlier reported solvent resistant PAN membranes.

Further, hydrolyzed polypropylene was used as a support layer, on which a PA top-layer was formed starting from ethylene diamine and terephthaloyl chloride [23]. A new type of solvent resistant support layer made of polythiosemicarbazide crosslinked with dibromo-*p*-xylene was also reported to be stable in harsh organic solvents (*i.e.* DMF, dimethyl sulfoxide (DMSO) and n-methylpyrrolidone (NMP)) [24]. Compared with integrally skinned asymmetric crosslinked PI membranes, this TFC membrane showed a higher flux for organic solvents combined with a similar MWCO.

TFCs synthesized via coating

In TFC membrane synthesis via coating, a top-layer is formed by applying a polymer, prepolymer or monomer solution onto a porous support layer, followed by evaporation of the solvent and, if required, further polymerization.

A versatile and easy method to prepare excellent SRNF membranes with polypyrrole (Ppy) top-layers was presented by in-situ polymerization on different support layers. The membranes showed a very good selectivity for negatively charged solutes at higher fluxes than commercial membranes [25]. A very promising polymer suitable for top-layer formation in membrane technology in general, is poly(1-(trimethylsilyl)-1-propyne) (PTMSP), a hydrophobic glassy polymer with a very high free volume fraction due to its combination of a rigid backbone structure and bulky side groups. Membranes were made by casting a PTMSP solution on a PAN support [26]. Further, a top-layer synthesis starting from block copolymers which can form arrays of well-defined structures was described [27]. A blend of polystyrene-*block*-poly(ethylene oxide) (PS-*b*-PEO) and poly(acrylic acid) (PAA) was dip or spin coated on various inorganic and organic supports. The resulting TFC membranes showed an array of uniform cylinders perpendicular to the membrane surface. Under the applied conditions, PAA was required in the synthesis process to induce the phase separation of the two blocks in the copolymer. After the membrane formation, the permeance could be clearly increased by removing the PAA from the selective layer, while only minor changes in MWCO were observed.

Another versatile technique is the layer by layer (LBL) assembly of polyelectrolytes (PEs), which are polymers with charged or chargeable groups within the monomer repeating units, on a porous support to form a thin PE multilayer that acts as selective layer. Formation of a PE multilayer occurs via alternate deposition of positively and negatively charged PE layers, in which the number of layers determines the final top-layer thickness [28]. A recently published review describes the preparation and applications of PE multilayers in membrane separations [28]. A common PE combination to produce membranes for SRNF, is poly(diallyldimethylammonium chloride) (PDDA)/sulfonated poly(ether ether ketone) (SPEEK). TFC membranes with a PDDA/SPEEK top-layer on a hydrolyzed PAN support were used for the separation of charged dyes from organic solvents [29]. The addition of NaCl to the PE solutions during preparation increased permeances 10-fold due to the formation of more “loopy” or “tailed” PEs, resulting in thicker but much looser PE top-layers. Recently, the same PE combination was used as top-layer material on a hydrolyzed PAN/Si support [30]. Other PE combinations applied in SRNF are PDDA/polyacrylic acid (PAA) [31], PDDA/poly(sodium styrene sulfonate) (PSS) and PDDA/poly(vinyl sulfate) (PVS) [32]. For PDDA/PAA, increasing the pH from 2 to 4 decreased top-layer thickness, while a thicker top-layer was formed at higher pH values [31]. The retention of membranes synthesized from PDDA/PSS and PDDDA/PVS were clearly higher when the polyanions were used in the H-form compared to the Na-form [32]. A branched PEI/PAA top-layer was synthesized on a polysulfone (PSf) support [33].

A new, very promising class of materials in membrane technology used for top-layer synthesis are polymers with intrinsic microporosity (PIMs), as so far mainly applied in gas separation. Intrinsic microporosity is defined as microporosity that arises directly from the shape and rigidity of component macromolecules [34]. TFC membranes with a 300-800 nm thick top-layer of PIM-1 and PIM copolymers were prepared on a PAN support [35]. After crosslinking the PIM-1 layer, the membrane became stable in aggressive solvents, like THF and chloroform. The PIM-1 top-layer thickness was further decreased down to 35 nm [36]. Unexpectedly, the maximum heptane permeance of 18 L m^{-2} h^{-1} bar^{-1} was achieved with a 140 nm thick top-layer. Decreasing the thickness below 140 nm resulted in a decreased permeance, suggested to be related to packing enhancement of PIM-1.

TFN membranes for SRNF

The performance of polymeric membranes can be limited by declining flux as a function of time due to compaction or physical aging, and the trade-off between permeability and selectivity. One way to overcome this is to incorporate a dispersed phase of particles into the polymeric matrix, forming so-called TFN membranes (Figure 3). These membranes aim at combining the advantages of polymeric membranes (processability, robustness, inexpensive) with the better and more stable separation performance of inorganic materials [37]. Currently, the reports of TFN membranes for aqueous applications are more numerous than for SRNF applications and a wider variety of fillers has already been incorporated [38]. A major challenge for these TFN membranes is to keep the thickness of the selective layer small enough. This implies that nanosized particles need to be used, which seriously complicates the realization of a good dispersion (essential to avoid defect formation).

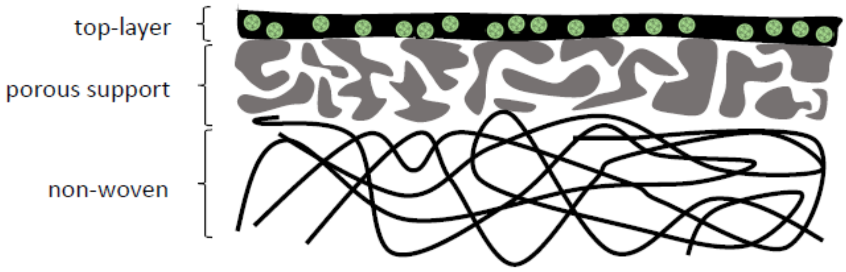

Figure 3: Scheme of a TFN membrane consisting of a non-woven fabric, a porous support layer and a thin, selective top-layer with incorporated fillers.

A nice way to avoid the need for nanosized fillers, but still realize high enough fluxes was through the use of micron-sized hollow spheres. A composite membrane consisting of PDMS coated on a crosslinked PI support showed a good performance for filtrations in IPA, but excessive swelling of the PDMS layer occurred in THF, toluene and ethyl acetate [39]. By incorporating hollow spheres with a zeolitic shell in the top-layer, an increased crosslinking density of the PDMS was obtained. Hereby, selectivities maintained while solvent permeabilities were enhanced due to the presence of large voids inside the incorporated particles.

Different nanosized “metal-organic frameworks” (MOFs), *i.e.* ZIF-8, MIL-53(Al), NH_2-MIL-53(Al) and MIL-101(Cr), were incorporated in PA TFN membranes which showed increased permeability compared to the unfilled PA at little to no expense of rejection [40]. Very recently, a continuous thin film of MOF (ZIF-8) was even fabricated on a polymeric support via an interfacial synthesis method in one cycle [41]. The resulting membranes showed excellent nanofiltration performances in various solvents . Amine and acyl chloride functionalized TiO_2 were also incorporated in a TFN membrane to decrease the swelling degree of the top-layer in organic solvents [42]. In addition, functionalized multiwalled carbon nanotubes (MWCNTs) have been incorporated in PA membranes [43]. Since the inner core diameter of the MWCNTs (30 nm) was much larger than what is needed for SRNF, the authors relied on the PA to develop selectivity and the MWCNTs to enhance the solvent permeability via nanogaps, defined as low-resistance paths for fast permeation of molecules, or disturbed chain packing around the CNT external surface. The resulting TFN membranes showed higher permeabilities at no expense of selectivity. However, a deeper investigation to resolve the exact mechanism behind the improved performance and the influence of the inner core of the MWCNTs should still be done. Incorporation of graphene oxide in polypyrole (PPy)-based TFN membranes resulted in 4-10 times increased alcohol permeability while maintaining rejection [44].

A polyetherimide support, modified with SiO_2 for enhanced stability, was combined with a top-layer containing UZM-5 zeolite nanoparticles [45]. The pores of the UZM-5 nanoparticles presented a preferential flow pattern but the nanoparticles also heavily influenced the PA formation, resulting in a different top-layer morphology, hydrophilicity and thickness. The presence of UZM-5 in the PA selective layer improved both oil rejection and permeate flux under optimal zeolite concentration.

The filler material has also been generated in situ. Silica and titania nanoparticles were incorporated in PA TFN membranes through the in situ reaction of respectively tetraethoxysilane and tetra-n-butyl titanate, catalyzed by the presence of amine groups on PEI [46]. The presence of silica/titania nanoparticles enhanced the thermal and chemical stabilities of the composite membranes by inhibiting the polymer chain mobility. The resulting TFN membranes displayed lower permeabilities but improved rejections and less swelling.

Upon incorporation of noble metal nanoparticles in membranes, photothermal heating of these nanoparticles was exploited to increase the membrane flux significantly by providing extra energy for the permeating molecules to overcome the friction in the selective layer once sorbed in it. This already proven concept for Au nanoparticles in cellulose acetate and PI membranes was recently extended to PDMS TFN membranes. Due to the challenging dispersion of hydrophilic nanoparticles in this hydrophobic matrix, Au^{3+} was reduced in situ through the –Si–H groups of the unreacted PDMS crosslinker [47]. The flux of the membrane was improved without loss of rejection.

A novel TFN synthesis approach was presented by spin coating nanosized polymer particles on a crosslinked PI support [48]. The particles were synthesized by emulsion copolymerization of *N*-isopropylacrylamide and 2-(hydroxy) ethyl methacrylate, and subsequently modified with acrylate moieties to introduce crosslinkable vinyl groups on their surfaces. After spin coating, the nanoparticles were crosslinked by UV irradiation (conversion of methylmethacrylate to polymethylmethacrylate) to stabilize the top-layer. The interstitial spaces between the particles acted as permeation channels. The separation performance could be tuned by simply varying the size of the nanoparticles and thickness of the nanoparticles layer.

Table 1: Overview of membrane materials, feed compositions and performances of references discussed in this review (adapted from [4]).

Membrane type	**Membrane material**	**Solvent**	**Permeance ($L\ m^{-2}\ h^{-1}\ bar^{-1}$)**	**Solute**	**MW Solute ($g\ mol^{-1}$)**	**Rejection (%)**	**Ref.**
TFC via plasma polymerization	DLC/alumina	EtOH	64.4	azobenzene	182	94	16
TFC via IP	PA/crosslinked P84 PI	MeOH	1.5	styrene oligomers	236-1200	98 (236 $g\ mol^{-1}$)	17, 4
		DMF	1.5			91 (236 $g\ mol^{-1}$)	
		THF	1.5			100 (236 $g\ mol^{-1}$)	
		acetone	2.4			95 (236 $g\ mol^{-1}$)	
		ethyl acetate	0.9			85 (236 $g\ mol^{-1}$)	
		toluene	0.1			96 (236 $g\ mol^{-1}$)	
	hydrophobic PA/crosslinked P84 PI	THF	1.5	styrene oligomers	236-1200	98 (236 $g\ mol^{-1}$)	18, 4
		ethyl acetate	3.0			90 (400 $g\ mol^{-1}$)	
		toluene	1.7			97 (236 $g\ mol^{-1}$)	
	PA/PEEK	THF	0.9	styrene oligomers	236-1200	92 (236 $g\ mol^{-1}$)	19, 4
	hydrophobic PA/PEEK	toluene	2.0	styrene oligomers	236-1200	98 (236 $g\ mol^{-1}$)	19, 4
	PA/crosslinked Matrimid PI	EtOH	2.7	rose bengal	1017	100	20
	PA/PAN	IPA	5.0	ethylene glycol oligomers	200-2000	83 (1000 $g\ mol^{-1}$)	21
		ethyl acetate	1.6			84 (600 $g\ mol^{-1}$)	
		n-heptane	1.9			85 (600 $g\ mol^{-1}$)	
		butanone	0.8			81 (600 $g\ mol^{-1}$)	
	(PA/PDMS)/PAN	IPA	3.7	ethylene glycol oligomers		95 (600 $g\ mol^{-1}$)	21
		ethyl acetate	0.5			99 (600 $g\ mol^{-1}$)	
		n-heptane	0.5			99 (600 $g\ mol^{-1}$)	
		butanone	0.4			90 (600 $g\ mol^{-1}$)	
	PA/crosslinked PAN	DMF	0.9	protoporphyrin IX dimethyl ester	591	94	22

	PA/crosslinked PTSC	THF	4.6	rose bengal	1017	100	24
		DMSO	5.2	α-cyclodextrin	973	95	
		DMF	4.8			98	
TFC via coating	PPy/(PSf/SPEEK)	IPA	1.1	rose bengal	1017	98	25
	PPy/PAN-H	IPA	2.7			99	
		THF	28.6			99	
		DMF	0.05			91	
	PPy/PSf-acid	IPA	0.7			95	
	PPy/PI-acid	IPA	0.03			95	
	PPy/PSf	IPA	2.4			82	
	PTMSP/PAN	MeOH	7.7	remazol brilliant blue R	627	90	26
		EtOH	4.8			90	
		aceton	17.2			85	
	(PS-*b*-PEO/PAA)/alumina	MeOH	0.1	ethylene glycol oligomers	200-900	82 (420 g mol^{-1})	27
		DMF	0.02			78 (420 g mol^{-1})	
		DCM	0.05			91 (370 g mol^{-1})	
		acetone	0.04			90 (370 g mol^{-1})	
	(PDDA/SPEEK)/PAN	IPA	0.2	rose bengal	1017	98	29
		THF	27.5			100	
	(PDDA/SPEEK)/(PAN-H/Si)	IPA	0.1	rose bengal	1017	99	30
		DMF	0.07			89	
		THF	10			99	
	(PDDA/PAA)/PAN-H	IPA	0.07	rose bengal	1017	99	31
		THF	12			99	
	(PDDA/PSS)/PAN-H	IPA	0.06	acid fuchsin	586	99	32
	(PDDA/PVS)/PAN-H	IPA	1.0			100	
	(PEI/PAA)/PSf	IPA	29.6	anthracene	178	68	33
	PIM-1/PAN	EtOH	3	hexaphenylbenzene	535	78	35
		MeOH	6			73	
		n-heptane	7			92	
			4.0	styrene oligomers	200-1200	90 (<200 g mol^{-1})	
	(PIM-1/PEI)/PAN	EtOH	1.4	hexaphenylbenzene	535	85	
		MeOH	3.6			91	
		n-heptane	1.0			97	
		acetone	2.8			94	
		chloroform	3.7			90	
		THF	2.0			95	
		toluene	1.3			95	
			3.1	styrene oligomers	200-1200	90 (430 g mol^{-1})	
	PIM-1/PAN	n-heptane	18	hexaphenylbenzene	535	86-90	36
TFN	(PDMS/silicalite hollow spheres)/PI	THF	2.8	bromothymol blue	624	76	39
		toluene	1.2			97	
		ethyl acetate	1.4			100	
		IPA	1.0	rose bengal	1017	100	
	(PA/MOFs)/crosslinked P84 PI	MeOH	3.9	styrene oligomers	236-1200	96 (236 g mol^{-1})	40
		THF	11.1			92 (236 g mol^{-1})	
	ZIF-8/PES	EtOH	3.2	rose bengal	1017	86	41
		IPA	0.4			94	
	(PA/TiO_2 nanoparticles)/Matrimid PI	MeOH	25.2	crystal violet	408	93	42
	(PA/MWCNTs)/PP	MeOH	6.3	brilliant blue	826	91	43
	(PPy/GO)/PAN-H	IPA	3.2	rose bengal	1017	99	44
	(PA/UZM-5)/(PEI/modified SiO_2)	MEK/toluene	0.9	lube oil		96	45
	(PA/SiO_2 nanoparticles)/PAN-H	IPA	1.8	ethylene glycol oligomers	200-2000	80 (200 g mol^{-1})	46
	(PA/TiO_2 nanoparticles)/PAN-H	IPA	1.0		200	98	
	PDMS/ gold nanoparticles	IPA	0.04	methyl orange	327	100	47
	P(NIPAM-HEMA)/crosslinked PI	toluene	0.6	styrene oligomers	236-1200	90 (220 g mol^{-1})	48
		acetone	1.3			90 (220 g mol^{-1})	

Conclusions

Both TFCs and TFNs clearly show the potential for excellent performance in SRNF applications. A large variety of chemical compositions can be used for the synthesis of the selective layer, hence the formation can be optimized as a function of the specific solvent application.

According to the generally accepted contribution of the solution-diffusion mechanism to the overall SRNF transport mechanism, a good affinity of the polymer for the permeating solvent is indeed required, but without inducing excessive swelling which would lose all selectivity. This might require a radical change in polymerization chemistry for the TFCs prepared via IP, which is now still largely copied from the well-known membranes currently worldwide applied in water treatment.

In addition, simple actions, like immersing IP membranes in certain solvents, or like using the right conditioning agent to conserve membranes for extended periods, seem to increase fluxes by even an order of magnitude sometimes, while leaving selectivities intact. Such phenomena should certainly still be further exploited and better understood to maybe even allow still more spectacular post-synthesis performance enhancements. Also for instance the sometimes observed non-reciprocal proportionality between selective layer thickness and flux, indicates SRNF transport is ruled at a level where subtle polymer rearrangements and molecular, maybe even atomic, interactions dominate.

When considering the life cycle analysis of polymeric membranes, an important aspect still to be addressed is the use of less harmful organic components during their synthesis; in fact not only for SRNF but for all membrane applications. Nowadays, toxic solvents like DMF and hexane are often used to prepare polymer (or monomer) solutions. Although the awareness in the membrane community is currently growing, this topic should be further addressed in future research.

The steadily increasing interest in SRNF, by academia as well as by potential industrial end-users, shows that this young technology is becoming a valuable and versatile part of the separation specialist's or process engineer's toolbox. Literature on development of novel SRNF membranes and processes has strongly been increasing over the past 5 years and more and more industries, being confronted with the limitations of conventional separation processes are picking up the technology, mainly because of the more favorable energy consumption, absence of thermal effects on the feed, the modular character of membrane separations and the low waste generation. The current limited commercial availability of a broad enough spectrum of good SRNF membranes for the wide variety of solvent/solute combinations is still often a drawback, just like the absence of full-scale success stories in the open literature and a too limited set of commercial membrane suppliers.

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