

Understanding and guiding the phase inversion process for synthesis of solvent resistant nanofiltration membranes

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ABSTRACT: Since its introduction in membrane technology in the 1960's, phase inversion by means of immersion precipitation has been widely studied for the preparation of membranes to be applied in the fields of microfiltration (MF) and ultrafiltration (UF). However, much less knowledge is available about this process in terms of integrally skinned asymmetric nanofiltration membranes, especially for more hydrophobic polymers applied in solvent resistant nanofiltration (SRNF). This review focuses on the preparation aspects of integrally skinned asymmetric membranes to be applied in the field of SRNF via phase inversion. It starts with the explanation of the basic principles of the phase inversion process, covering both thermodynamic and kinetic aspects. Further, it summarizes the parameters that significantly influence final membrane performance and morphology, including polymer type and concentration, casting solvent, additives, evaporation time, and temperature, humidity, membrane thickness, composition, and temperature of coagulation bath and post-treatment. Literature contained within this review constitutes the core references in the field of SRNF, but also several references on preparation of MF, UF, aqueous NF, and reverse osmosis (RO) membranes have been included to better clarify or illustrate certain aspects of the process. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42130.

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INTRODUCTION

Solvent resistant nanofiltration (SRNF) is a relatively new (since \pm 2000) and rapidly growing technology. Alternative nomenclature regularly found in the literature and referring to the same type of materials and processes is organophilic nanofiltration (ONF) and organic solvent nanofiltration (OSN). SRNF is a liquid-phase pressure-driven process where separation occurs at molecular level and mutual interactions between solute and solvent, solvent and membrane as well as between solute and membrane play a role. The influence of these rather complex membrane/solvent/solute interactions is to a certain extent even more significant than the molecular size. The applied pressure at the feed stream required to create the necessary driving force for SRNF is usually between 5 and 40 bar. SRNF membranes have molecular weight cut-off (MWCO) values in the range from 200 to 1000 Da.¹ SRNF-performance can generally be considered as reasonable when rejection of a marker compound is more than 90% and permeance is above 1 L/(m² h bar), even though these numbers are very much application dependent. Also, when the membrane gets "tighter" (i.e., with lower MWCO), the flux gets lower as well; however, it can still remain acceptable.

So-called integrally skinned asymmetric membranes prepared via the phase inversion process and applied in SRNF, are the focus of this review. "Integrally skinned asymmetric" refers to the presence of a dense layer, responsible for the actual separation of the molecules, on top of a porous substructure, constituted by the same kind of polymer. Such structures are essential to allow molecular separations, while still realizing sufficiently high fluxes through these membranes. Since solvent-membrane interactions are so important in SRNF, it is clear that other polymer types have to be used than in aqueous NF. With all organic solvents being less polar than water, those polymer types are by preference more hydrophobic, which makes this class of membranes largely distinct from those applied in NF or RO. As phase inversion involves use of a so-called nonsolvent for the polymer, it is obvious that the tools to prepare those more hydrophobic SRNF-membranes also become quite different from those known in the field of aqueous NF.

In general, when making and optimizing SRNF-membranes, it is noticed that it always comes down to trial and error, hence there is clearly a lack of fundamental understanding in this field. Therefore, the insight in the real effects of the synthesis

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parameters on the phase inversion process for SRNF-membranes is very important.

This review starts with the explanation of the basic principles of the phase inversion process, which is known to be governed by both thermodynamic and kinetic aspects. Further, it summarizes the parameters that significantly influence final membrane performance and morphology, including polymer type and concentration, casting solvent, additives, evaporation time and temperature, humidity, membrane thickness, composition and temperature of coagulation bath and post-treatment. Literature references that this review is based on constitute the core of the SRNF field; however, some references from MF, UF, aqueous NF, and RO have been included for better clarification or illustration of certain aspects of the process.

Broader Perspective on SRNF

Different models have been developed to describe membrane transport in SRNF. In the case of SRNF-membranes, three kinds of mathematical models can be distinguished. A first group of models originate from irreversible thermodynamics, where the membrane is treated as a black-box. The other groups of models take into account membrane properties. SRNF occupies the transient zone between the two extremes of solution diffusion (as expected from nonporous membranes) and pore flow or convective flow (as expected from porous membranes).¹

Being a new technology, large-scale applications are basically still under development, but SRNF-membranes are definitely finding their way into (petro) chemical,² pharmaceutical,³ food,^{4,5} and fine chemicals^{6,7} industries for the recycling of solvents, purification of drug precursors, fractionation of oligomers, recovery of natural oils from their extraction solvents.¹ These processes involve a variety of organic solvent streams making the chemical resistance of the membrane material as its most critical property in addition to its selectivity and permeability.⁸ In comparison with conventional separation techniques, like distillation, extraction, crystallization, and preparative chromatography, which are energy and solvent intensive, SRNF can be considered as an environmentally friendly technology as it

does not create waste streams and needs only pressurization of the liquid feed, which requires only moderate energy consumption. It was for instance demonstrated that SRNF uses 25 times less energy per volume of recovered solvent when compared to distillation for solvent recovery from crystallization mother liquors.⁹

Various polymeric and ceramic membranes have been studied for use in organic solvents. Ceramic membranes are more robust due to their higher chemical and thermal stability, compared with polymeric membranes. They do not deform under applied pressures, nor swell and are easier to clean. On the other hand, they are much more expensive, brittle and are difficult to be prepared for the very low MWCO range.¹ Ceramic membranes are usually made from materials like silica, alumina, zirconia, or titania.¹⁰ Chemically rather stable polymers that are most typically used to synthesize SRNF-membranes are polyimides (PI),^{11–18} polyamides (PA),^{19,20} polyacrylonitrile (PAN),^{1,21,22} polydimethylsiloxane (PDMS),^{23–25} polysulfone (PSf),^{8,26–30} and polyelectrolyte complexes (PEC).^{31–33} Both amorphous and semi-crystalline polymers can be applied. Amorphous polymers are generally of preference for the preparation of nonporous membranes, as they are more permeable compared to semi-crystalline polymers. By incorporation of inorganic particles (like zeolites, metal organic framework, or carbon molecular sieves)^{33–39} into the polymeric matrix, it is possible to synthesize so-called mixed matrix membranes (MMMs).⁴⁰ Compared to the existing pure polymeric membranes, they have the potential to achieve higher rejection and permeance or both by the addition of inorganic particles with inherently superior separation characteristics.⁴¹ Examples of suppliers of commercial SRNF membranes, their products and the stability ranges of their membranes are given in Table I.

Most membranes applied in the field of SRNF are synthesized via the phase inversion process. Only some, like the PDMS-, PA-, and PEC-based membranes, are formed as thin-film composite (TFC) materials. TFC membranes most often consist of an ultra-thin top-layer on a porous sub-layer, made from other materials. The top-layer (in the submicron range) is the actual

Table I. Suppliers of Commercial SRNF Membranes and Their Products (as in January 2015)^{42–45}

Company	Membrane	Material	Stability range	MWCO (Da)
Evonik MET (Germany)	DuraMem® PuraMem®	Lenzing P84® polyimide (*nonstandard DuraMem®) Lenzing P84® polyimide	AC, EtOH, MeOH, THF, DMF*, DMSO*, DMAc*, IPA, ACN, MEK, EtAc and more TOL, HEP, HEX, MEK, MIBK, EtAc and more	150–900 280–600
SolSep (The Netherlands)	SolSep UF SolSep NF	Diverse (unspecified) Diverse (unspecified)	Alcohols, aromatics, esters, ketones, chlorinated solvents MeOH, EtOH, PRO, AC, EtAc, HEX, TOL, CHB	10–20 k 300–750
Borsig Membrane Technology (Germany)	GMT-oNF	PDMS-based composites	alkanes, alcohols, aromatics, ethers, esters, ketones	Unspecified
Inopor® (Germany)	Inopor®nano	TiO ₂ , SiO ₂	Unspecified	450–750

AC, acetone; ACN, acetonitrile; CHB, chlorobenzene; DMAc, *N,N*-dimethylacetamide; DMF, *N,N*-dimethylformamide; DMSO, dimethylsulfoxide; EtAc, ethyl acetate; EtOH, ethanol; HEP, heptane; HEX, hexane; IPA, isopropanol; MEK, methylethylketone; MeOH, methanol; MIBK, methylisobutylketone; PDMS, polydimethylsiloxane; PRO, propanol; THF, tetrahydrofuran; TOL, toluene.

selective layer. The porous UF or MF sub-layers provide a smooth surface for the synthesis of a defect-free top-layer. Both integrally skinned asymmetric and TFC membranes are often prepared on a nonwoven support that provides the mechanical strength. The biggest advantage of TFC membranes over integrally skinned asymmetric membranes is that each layer can be tuned independently to obtain a membrane with desired properties and performance. The ultra-thin top-layer can be obtained via simple solution casting (like spin coating, dip coating or spray coating) or polymerization (interfacial polymerization (IP), *in situ* polymerization, plasma polymerization, or grafting).⁴⁶

THE PROCESS OF PHASE INVERSION

Introduction

The phase inversion process was first introduced in membrane technology by Loeb and Sourirajan⁴⁷ in the 1960's and is the base for the synthesis of most commercially available membranes. During the phase inversion process, a thermodynamically stable polymer solution is transformed from a liquid into a solid state in a controlled manner. This solidification is preceded by a liquid–liquid demixing. A certain time after initiation of the demixing into a polymer-rich and a polymer-lean phase, the phase with the highest polymer concentration will start solidifying through processes like gelation, vitrification, or crystallisation. The polymer-lean phase will lead to the pores in the solidified material, while the polymer-rich phase will lead to the solid membrane matrix. This demixing may be induced by:

- immersion precipitation (immersion in a nonsolvent bath);
- controlled evaporation (evaporation of the volatile solvent from the polymer solution, consisting of a solvent/nonsolvent mixture);
- thermal precipitation (lowering temperature) or

- precipitation from the vapor phase (placing the cast film in a vapor phase consisting of nonsolvent).^{10,48}

Among the ones aforementioned, immersion precipitation is the most often used technique, as membranes can be prepared from a wide variety of polymers. And the only requirement of this technique is that the polymer must be soluble in a solvent or a solvent mixture. In general, the type of polymer does not limit the preparation technique.

Basic Principles

During the phase inversion process, both thermodynamic and kinetic aspects play a role, making it difficult for this quite complicated process to be fully understood. Moreover, the whole process is often finished in few milliseconds only, making it challenging to follow *in situ*.

Thermodynamic Considerations. The thermodynamic behavior of immersion precipitation can be best represented in a ternary polymer/solvent/nonsolvent phase diagram [Figure 1(a)]. This is in fact just a simplified image of the common reality where often much more than three components can be present in the casting solution and the coagulation bath. The initial polymer casting solution is located in the stable monophasic region outside the binodal i.e., the region between the polymer/solvent axis, the solvent/nonsolvent axis and the binodal. As a result of the contact with nonsolvent, the composition of the polymer solution moves to the right side of the diagram (pathways A and B). There are two possible pathways for the polymer solution to phase separate. Separation can occur either by binodal demixing or spinodal decomposition. Following binodal demixing (pathway A), the polymer solution will end up at the metastable region between binodal and spinodal. Here, the polymer solution will phase separate into a polymer-lean phase (the composition of which is reflected in point A'' on the graph) and a polymer-rich phase (with composition reflected in point

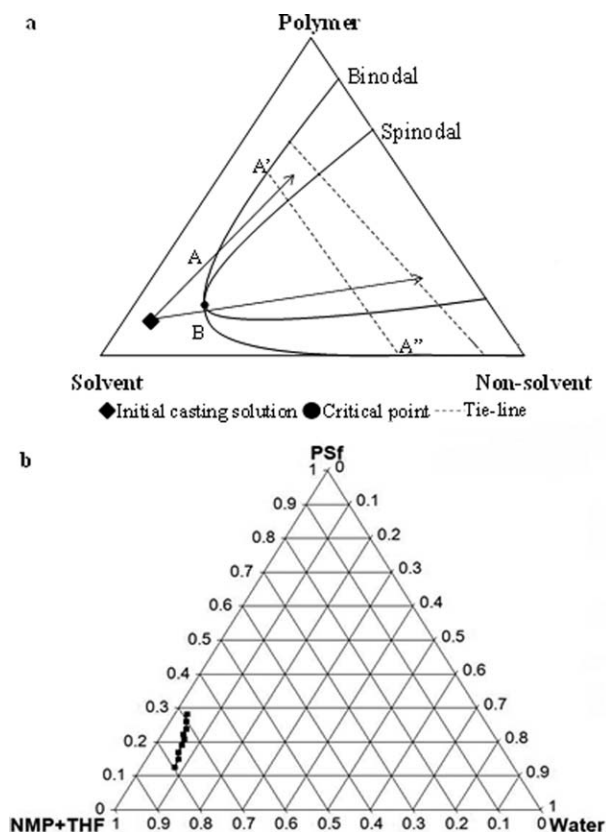


Figure 1. (a) Idealized ternary phase diagram: schematic representation of the mechanism of phase separation during membrane formation (adapted from Ref. 10); (b) Cloud point measurements, as obtained by the titration method, plotted in the ternary phase diagram of PSf using a THF/NMP solvent system and water as nonsolvent (Adapted from Ref. 27).

A') according to the nucleation and growth mechanism. These compositions are indicated on the phase diagram by the ends of the so-called tie-lines which connect points A' and A''. These tie-lines on the phase diagram join phases at equilibrium with each other. Spinodal decomposition (pathway B) occurs when the polymer solution crosses the zone between the bi- and the spinodal without leaving enough time to start demixing and ends in the thermodynamically unstable zone inside the spinodal either directly or via the metastable region. Here again, two different phases appear, but instead of developing well-defined nuclei, initially two cocontinuous phases develop, which might finally also transform into nuclei.^{1,10,49}

Literature describes procedures on how to construct a phase diagram.^{50–52} The most direct and simplest approach to define the thermodynamics of the system is by determining the cloud point curve, often also referred to as the precipitation curve [Figure 1(b)]. The cloud point curve forms the border between the compositions that are completely stable and the compositions that are meta- or unstable. In a truly ternary system (in which the polymer is monodisperse), the cloud point curve coincides with the binodal. In a quasi-ternary system (in which the polymer is polydisperse), the polymer becomes fractionated at equilibrium between two phases. The lower-MW fractions have preference for the polymer-lean phase, while the higher-

MW fractions are primarily present in the polymer-rich phase. This causes the polymer-rich phase, in equilibrium with phases leaner in polymer, not to lie exactly on the binodal. The polymer-lean phase will also not be located exactly on the binodal.⁵³ Experimentally, cloud points, the points that form the cloud point curve, can be determined by visual observation of the turbidity change of the polymer solution while titrating it with nonsolvent, provided sufficient difference in refractive indexes. The determination of the spinodal is connected with the difficulties of realizing metastable states of low stability and can be performed by the extrapolation of some property (isothermal compressibility, heat capacity, diffusion coefficient). The changes in behavior of these properties characterize a system moving from a stable homogeneous state into a metastable state, situated beyond the binodal. Any phase in the region of its stable existence is stable relative to arbitrary changes in the internal parameters of both finite and infinitesimal size. Behind the spinodal the probability of spontaneous formation of a competing phase is determined by the value of the free energy barrier, which the system must overcome to begin the phase transition. The value of the free energy barrier is a measure of the stability of the metastable system relative to finite perturbations.⁵⁴ Determination of the position of the spinodal on the phase diagram can be performed via Pulsed Induced Critical Scattering Technique (PICS).⁵⁵ PICS enables the measurement of the concentration fluctuations that signal in the homogeneous and metastable states the path to phase separation in polymer solutions by extrapolation. When the concentration fluctuations appear in the system, the free energy of the system increases remarkably. Because of this increased free energy, any kind of aggregation of polymer molecules (due to their random motions in the solution) is immediately suppressed as the polymer molecules diffuse back to the regions with a lower concentration. This ensures a relatively even distribution of polymer molecules over the solvent. The free energy of the system can be lowered by bringing the polymer solution into the metastable region (region between binodal and spinodal), i.e., by lowering the pressure at constant temperature or by lowering the temperature at constant pressure. The applied changes to the system can result in a slower suppression of concentration fluctuations. In such a case, regions of higher polymer concentration get formed in the solutions and become surrounded by polymer solutions with lower concentration. The polymer solution thus gets less "homogeneous." When putting a beam of light through such a solution, part of it will be scattered as it comes across regions with different refractive index (as a result of these concentration fluctuations of the polymer solution). If to lower the pressure (or temperature) further, these regions of higher polymer concentration grow in size, so the light becomes even more scattered.

Kinetic Considerations. The kinetic aspect of phase inversion by immersion precipitation is mostly related to the exchange rate of solvent out and nonsolvent into the casting solution, i.e., the mass transfer during coagulation. The driving force for the components of the system is the chemical potential gradient of the solvent or nonsolvent over both phases. Upon first contact with the coagulation bath, these chemical potential differences

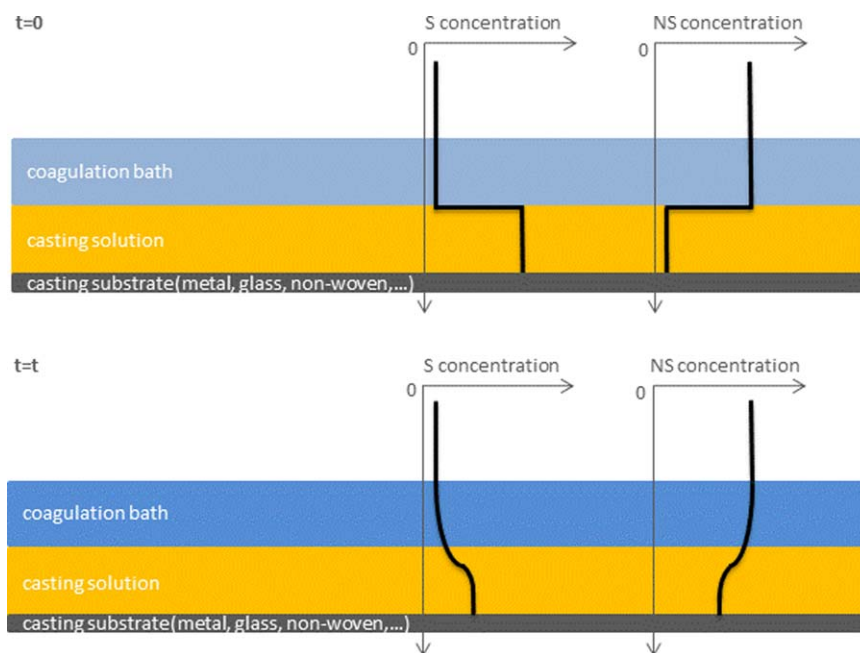


Figure 2. Concentration profiles of solvent (S) and nonsolvent (NS) during immersion precipitation, immediately after immersion in the nonsolvent (top) and after a time t (bottom) for a casting solution that contains some NS (Adapted from Ref. 27). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

are the largest near the contact surface between the polymer solution and the nonsolvent, rendering the exchange rate here the fastest. However, as the diffusion of components progresses with time, the exchange rate slows down since the concentration profiles level out as presented in Figure 2. At the same time, a top-layer with reduced permeability is formed which also limits mass transfer. The proportionality factor related to the exchange rate covers features, like size of the molecules that diffuse in and out, and also the viscosity of the media that the molecules travel through.^{27,56}

Liquid–liquid demixing takes place after contact of the cast polymer film with the nonsolvent. It is possible to distinguish between the two different types of demixing depending on the exchange rate. There are two possible pathways (Figure 3). When the membrane pores are formed very quickly after immersion in the nonsolvent bath, the demixing is referred to as “instantaneous” demixing. When the membrane pores are formed only after a sufficiently long period of time, i.e., when more nonsolvent has entered the film, it is referred to as “delayed” demixing.⁴⁸ Literature does not provide the exact time boundaries for “instantaneous” and “delayed” demixing. “Instantaneous” demixing results in membranes with a relatively porous skin-layer, with macrovoids (big tear-like or finger-like pores) in the sub-layer. In contrast, “delayed” demixing leads to membranes with a relatively dense skin-layer, without macrovoids (Figure 2).⁵⁷ Therefore, membranes obtained via “delayed” demixing are expected to show lower permeances and higher rejections. Above theoretical considerations, which mainly originate from investigations on PSf- and cellulose acetate (CA)-based MF- and UF-membranes,⁴⁸ are not in line with the results obtained for PSf-based SRNF-membranes when changing polymer concentration and evaporation time as phase

inversion parameters.²⁷ With increasing polymer concentration in the casting solution, the time before precipitation got longer. Highly concentrated polymer solutions were thermodynamically less stable (less nonsolvent was needed to realize precipitation), but slowed kinetics (due to increased viscosity) markedly delayed the membrane formation process. All obtained PSf-membranes showed macrovoids; however, some morphological changes were observed with increased polymer concentration: the number of macrovoids decreased and their shape changed from finger-like to pear-like. In the case of varied evaporation time, macrovoids got suppressed only for very long evaporation times (more than 100 s). The data showed that linking macrovoid appearance with delayed demixing did not seem to be correct, as the measured times before precipitation were similar for the highest polymer concentration and the longest evaporation time.

It cannot be neglected that during the phase inversion process, precipitation kinetics provides important fundamental information regarding the membrane formation process. Basically, two different experimental methods can be applied to define the precipitation kinetics: optical microscopy, introduced by Strathmann *et al.*⁵⁸ and light transmittance, introduced by Reuvers and Smolder.⁵⁹ “Delayed demixing” is the term commonly used in membrane preparation to refer to a low precipitation rate, whereas “instantaneous demixing” refers to a high precipitation rate.^{60–62}

Macrovoids. A very specific phenomenon in membrane technology, directly following from the phase inversion process, is the formation of macrovoids. Macrovoids are generally considered as unwanted for pressure driven membrane process, since they are assumed to create weak spots where the selective layer might collapse at elevated pressure. Selective layer can be either

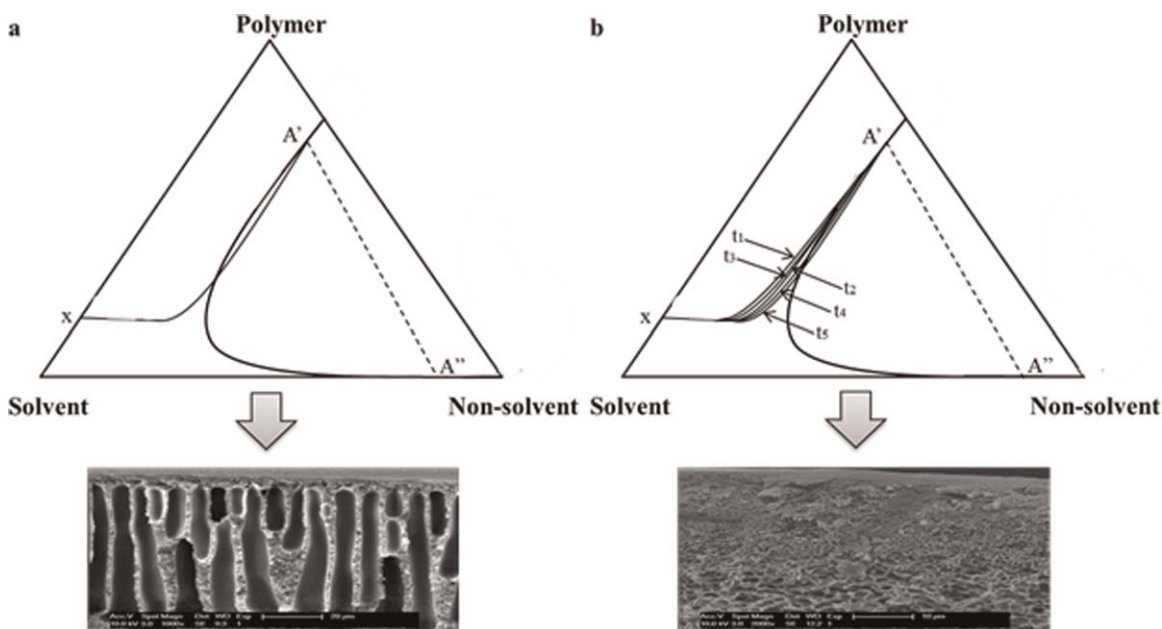


Figure 3. Idealized ternary phase diagram: schematic composition paths of the cast film at a certain moment t after immersion. For each subsequent moment, a different decomposition path will exist as the result of the diffusion exchange between solvent and nonsolvent from and into the cast film. Instantaneous demixing is represented in diagram (a), while the diagram (b) represents delayed demixing. In the case of instantaneous demixing, the binodal is crossed already at the time t and the demixing will start directly. In the case of delayed demixing, all positions in the film are still situated in the thermodynamically stable zone. Demixing will start only after a while when more nonsolvent has diffused into the polymer solution so that the binodal can be crossed^{1,10} (Adapted from Ref. 10). T_1 , t_2 , t_3 , t_4 , and t_5 represent decomposition paths at different times for delayed demixing. These paths are a visualization for a reader to facilitate understanding the difference between instantaneous and delayed demixing. The time t increases in the following order $t_1 < t_2 < t_3 < t_4 < t_5$. Below the diagrams: different morphologies following the different types of demixing.

applied afterwards when phase inversion is used to prepare a support layer, or the skin of an integrally skinned phase inversion membrane to be used as such. According to Frommer and Lancet, macrovoid formation is related to fast precipitation of the polymer in the coagulation bath and a high mutual affinity between the solvent and the nonsolvent.⁶³ A strong tendency of mutual mixing is expressed in a high heat of mixing. The greater the heat of mixing, the higher thus the possibility of macrovoid formation. Frommer and Messalem postulated that convective flows are responsible for the macrovoid formation in the cast polymer film upon immersion in the nonsolvent coagulation bath.⁶³ The term “convective flows” used here refers to currents of low MW fluids. These fluids flow into the zones with low polymer concentration. The term “convective flows” should not be mistaken with the motion caused by density gradients due to temperature changes. The appearance of convective flows is related to the high tendency of the nonsolvent to either penetrate or mix with the solvent that was used to prepare the solution. The main driving force for the initiation and formation of convective flows is then the surface tension of the different phases involved.^{64–69} After initiation, the formation of convective flows can be either enhanced or suppressed by e.g., changes in concentration, temperature, viscosity. A sufficient supply of nonsolvent thus has to be in contact with the cast film for the convective flows to appear. Guillen *et al.*⁷⁰ confirmed, using direct microscopic observations and kinetic analyses, that macrovoids are indeed formed by convective flows of the nonsolvent in the cast film. The formation mechanism of a

PSf/N-methyl-2-pyrrolidone (NMP)- and a PSf/DMF-based membranes was investigated: a membrane cast from an NMP solution resulted in macrovoids, whereas the one cast from a DMF-solution had a sponge-like structure. These results were recently confirmed³¹ and are thus in contrast with the earlier more general statements that macrovoids can be found in membranes prepared from DMF/water, NMP/water, and DMAC/water systems, regardless the chosen polymer.⁴⁸ It is often

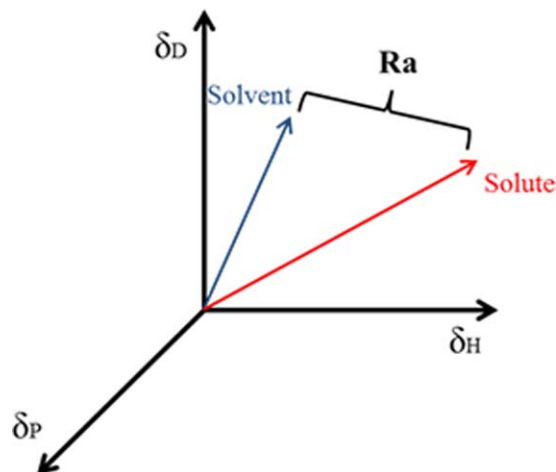


Figure 4. Schematic presentation of a solubility parameter distance. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

believed that the appearance of macrovoids in NMP-based PSf systems is due to high mutual affinity between NMP and water. However, if to consider the miscibility of three different solvent systems: NMP, DMAc, and DMF with water using the solubility parameter difference $\Delta\delta_{S-NS}$, DMF has the highest mutual affinity with water. The $\Delta\delta_{S-NS}$ -values of NMP, DMAc, and DMF with water are 35.38, 32.44, and 31.14 MPa^{1/2} respectively. The solubility parameter difference $\Delta\delta_{S-NS}$ between the solvent system of the casting solution and the nonsolvent system of the immersion bath is a first indication of their mutual affinity. A lower value for this parameter corresponds to a higher affinity of either liquids (or liquid mixtures) for each other, hence a better miscibility. The postulated link between macrovoids and high solvent/nonsolvent affinity thus cannot be confirmed. The mutual affinity of a solvent/nonsolvent system is thus probably not the only property that defines the macrovoid formation, as the kinetics of the phase inversion process can also play a significant role. The study of mass transfer phenomena through the liquid interfaces implies that it is related to the formation of convective flows at the interface. Already in 1959, Sternling and Scriven offered some requirements that should be fulfilled in order to initiate "interfacial turbulence." These requirements are in fact the exact description of polymer precipitation during membrane formation by phase inversion method. "Interfacial turbulence is usually promoted by: (1) solvent transfer out of the phase of higher viscosity, (2) solvent transfer out of the phase in which its diffusivity is lower, (3) large differences in kinematic viscosity and solvent diffusivity between the two phases, (4) steep concentration gradients near the interface."⁶⁷

The formation of macrovoids can be suppressed by lowering the ability of the nonsolvent to percolate in the cast film, e.g., by increasing the viscosity of the casting solution or by creating a thick gel layer on top of the cast film. Actions that can be taken to lower the ability of the nonsolvent to percolate in the cast film include (1) lowering the temperature of the coagulation bath; (2) addition of salt to the coagulation bath, in order to lower the activity of nonsolvent; (3) changing the nonsolvent with one of lower ability to mix with the solvent; (4) changing the solvent with one of lower ability to mix with the nonsolvent. On the other hand, actions that can be taken to increase the viscosity of the casting solution or to create a thick gel layer on top of the cast film include (1) lowering the casting temperature and the precipitation temperature; (2) increasing the polymer concentration in the casting solution; (3) increasing the evaporation time or temperature prior to immersion in the coagulation bath.⁶³

Synthesis Parameters Influencing Membrane Performance and Morphology

In general, the pore size and the overall porosity of a membrane mostly depend on the rate of out-diffusion of the solvent from a cast film and of in-diffusion of the nonsolvent from the coagulation bath to the cast film. The diffusion rates can be controlled via the manipulation of the composition of the casting solution, casting conditions and/or precipitation conditions.

The physical and chemical properties of the synthesis system thus influence the final structure of the integrally skinned SRNF membranes obtained by phase inversion. This kind of casting

solutions minimally consist of polymer, solvent and nonsolvent, but often also of different types of additives and cosolvents. Extensive research has been carried out so far to investigate the factors influencing the final membrane morphologies and performances of membranes synthesized via phase inversion, especially for membranes applied in MF and UF. Much less generic knowledge has been gathered for NF, and surely for SRNF.

The final membrane morphology and performance both depend on an immense number of experimental parameters. These include composition of the casting solution (like polymer concentration, the type of solvent, the ratio of cosolvent/solvent, the content of nonsolvent), the type of support material (glass, polymer, metal, and nonwoven), the thickness of the cast polymer film, the speed of casting, temperature of casting, controlled air flow, the time and temperature of the evaporation prior to immersion, relative humidity while casting and during the applied evaporation time, the composition and temperature of the coagulation bath and the post-treatment.^{10-15,27-30,48}

Composition of the Casting Solution. The most important factors among those mentioned above are the type of polymer and the choice of solvent, which is linked to the former as it has to allow full dissolution of the polymer. The solvent used to prepare the casting solution has to be at least partly miscible with the nonsolvent used in the coagulation bath in order to accomplish the phase inversion process by means of immersion precipitation.

Polymer. In SRNF, the chemical resistance of the membrane is defined by the polymer structure and is obviously of prime importance. The polymers applied in the field of SRNF are mostly hydrophobic. Commercially available polymers were so far commonly used, due to their easy accessibility and possible upscaling later on. However, the main problem with such kinds of polymers is that not many detailed specifications are communicated by the company. As they are often prepared for a totally different, mostly large-scale application, like insulating materials for semi-conductors or even construction materials, they often contain many additives (e.g., flame retardants), which obviously will affect the phase inversion process and the properties of the resulting membranes. Being industrially produced, the polydispersity (PDI) of these polymers is also often very high. Moreover, some of the polymer producing companies modified the polymer production for other (bigger) clients, without even notifying the membrane producers. Fortunately, with the growing market of membrane separations, it is more and more common for polymer producing companies to start to offer polymers specifically recommended for membrane preparation.

- Polymer pretreatment

To work with well controllable base products in the phase inversion process, a proper pretreatment of commercially available polymers is thus often very important. Examples of such pretreatment might be washing of the polymer in different solvent systems (dissolving followed by reprecipitation)⁷¹ or fractionation of a polymer solution using MF-membranes with different MWCO. Recently, it was proven that molecular weight and PDI, but especially the purity of the membrane forming polymer are

the properties that significantly influenced membrane performance of PSf-based SRNF-membranes.²⁸ A set of 10 different PSf samples were purified by means of repeated washing. Purification of the starting membrane polymer lowered the polydispersity of the polymer (from 4.2 to 2.2), obviously changed its composition (removal of contaminating compound) and its physico-chemical properties (e.g., for the same concentration of the casting solution (21 wt %) viscosity changed from 0.8 to 1.4 Pa s, as a result of increased MW of the membrane forming polymer), as well as the performance of the final membrane. Such simple polymer purification via washing caused a remarkable increase of both permeances and rejections (all permeances increased up to a factor of 5 and rejections sometimes changed from 65 to 94%). Applying purification as an additional step is thus an easy approach to significantly improve membrane performance.

- Polymer structure

The polymer structure is another property that cannot be neglected. For instance, increased fluxes can be achieved by use of branched polymers in membrane synthesis because the distance between their chains is higher, thus creating more free volume. For aromatic PAs⁷² and poly(amide-hydrazine)s (PAHs),⁷³ decreased fluxes were observed for para-substituted rings due to the higher symmetry and more compact structure. For these rather rigid polymers, higher MWs might cause a decrease in fluxes and increase in rejections due to the establishment of more hydrogen bonds between the imino and carbonyl groups in longer chains.

- Polymer concentration

The polymer concentration is one of the most studied membrane synthesis parameters in each membrane application. In general, by increasing the initial polymer concentration in the casting solution, membranes with thicker and denser skin-layers are formed. Because of the increased polymer concentration at the polymer/nonsolvent interface, the in-diffusion of nonsolvent and out-diffusion of solvent are slowed down as the consequence of the increased viscosity of the casting solution. This results in higher selectivities and lower permeabilities, as has been demonstrated for e.g., PI¹⁴ and PSf.²⁷

Casting solvent. The choice of solvent is logically limited by the polymer type and determines on its turn the crucial interaction with the nonsolvent in the coagulation bath. Depending on the affinity between solvent and nonsolvent, more porous or more dense membranes can be obtained.⁴⁸ Typical solvents that dissolve polymers applied in SRNF well are NMP, γ -butyrolactone (GBL), DMAc, DMF, DMSO, THF, and dichloromethane (DCM).

- Theoretical description of solvent-polymer interactions

The Hansen solubility parameters (HSP) can be of use to facilitate the choice of solvent. These parameters were developed to predict whether one material would dissolve in a certain solvent to form a homogenous solution. The basic concept of the theory is that “like dissolves like.” Each molecule is given three

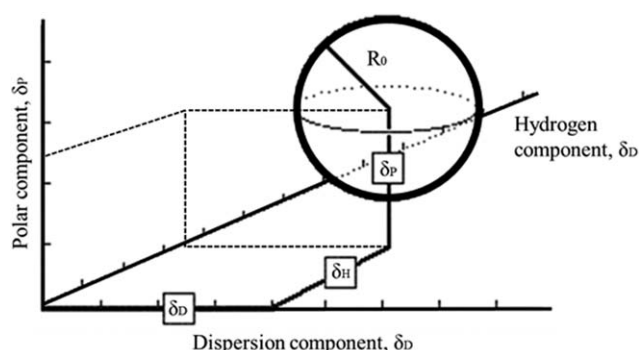


Figure 5. Schematic presentation of a Hansen solubility parameter sphere for a given component (adapted from Ref. 79).

HSPs (δ_D , δ_P , δ_H) quantitatively account for the cohesion energy density arising from atomic dispersion type interaction (D), dipolar interactions (P), and hydrogen bonding interactions (H).⁷⁴

The group contribution method can be used to calculate the solubility parameters of the polymer.^{57,75–77} However, polymer solubility parameters can also be estimated experimentally by using swelling experiments (the swelling coefficient reaches a maximum when the solubility parameter of the solvent nearly matches that of the polymer) or the intrinsic viscosity (which is an indirect measure of the individual chain conformation: polymer chains are most expanded in the best solvent).⁷⁸

The total solubility parameter is the geometric mean of the three components given by eq. (1):

$$\delta = (\delta_D^2 + \delta_P^2 + \delta_H^2)^{1/2} \quad (1)$$

These three parameters can be regarded as co-ordinates of a point in a three-dimensional space, often referred to as the Hansen space. The closer two molecules are situated to each other in the Hansen space, the more likely they are to form a homogenous solution. To calculate the solubility parameter distance (R_a) between 2 points in the Hansen space, the following formula [eq. (2)] is used:⁵⁷

$$R_a = [4(\delta_{D2} - \delta_{D1})^2 + (\delta_{P2} - \delta_{P1})^2 + (\delta_{H2} - \delta_{H1})^2]^{1/2} \quad (2)$$

For polymer solutions, R_a is a measure of affinities between polymer (1) and solvent (2). To determine whether the parameters of these two molecules are close enough to allow miscibility, a value called the “radius of the Hansen solubility sphere” (R_0) is given to the substance being dissolved. The center of the Hansen solubility sphere is the point that has the three Hansen parameters as coordinates (Figure 5). The relative energy difference,⁵⁷ RED, is therefore equal to R_a/R_0 . The RED value should not be higher than 1 if solubility is expected. Solubility increases when the RED value approaches 0.

Additives. Other components can be added to the casting solution, like cosolvents,^{11,14} nonsolvent,^{12,14} particles or polymeric additives.^{80–93} These additional components can either constitute a dispersed phase^{94,95} or can be fully dissolved, being of organic or inorganic nature. Nonsolvent power, viscosity, volatility, and additive concentration are the decisive properties

effecting the final membrane structure and performance. Taking into account all these above mentioned effects, it is very difficult to find general links between additive properties and membrane performances and/or morphologies.

- Inorganic additives

A: Inorganic salts

At first, research was concentrated in the 1960s on the use of inorganic salt additives. It was found that salt ions influenced interactions between polymer chains and influenced the solution quality by sometimes even rendering a nonsolvent into a solvent for a certain polymer. KF , KBr , KCl , KI , KSCN , KMnO_4 , NaIO_4 , $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$, $\text{Mg}(\text{ClO}_4)_2$, ZnCl_2 , MgF_2 , $\text{MgI}_2 \cdot 8\text{H}_2\text{O}$, $\text{Mg}(\text{SCN})_2 \cdot 4\text{H}_2\text{O}$ were for instance all studied in CA-based RO systems.⁹⁶ After the phase inversion process, which typically took place in aqueous medium, the salts were leached out from the formed membrane and left pores behind. LiCl for example suppressed macrovoid formation in poly(vinylidene fluoride) PVDF due to competing effects of thermodynamics and kinetics on the phase inversion process. LiCl is a nonsolvent for the polymer system, thus it reduces the thermodynamic stability of the casting solution, therefore enhances the liquid-liquid demixing. On the other hand, it also causes an increase of the polymer solution viscosity, thus delaying the diffusivity between solvent and nonsolvent and as a result delaying phase separation.^{97–100} The influence was found to be solvent-dependent and for instance, less strong if cast from NMP. The solvent-salt interaction as well as the salt-polymer interaction is of importance. Other frequently used inorganic salt additives are ZnCl_2 , $(\text{NaPO}_3)_6$, Na_2SO_4 , Na_2CO_3 , NaCl , and NaF .^{101–103} It should be mentioned that most of the reports focused on the effects of the added cations on the phase inversion process, while a systematic study of the anion effects often remains absent.

B: Metal oxides

Interestingly, metal oxides can be used to reduce macrovoid formation and therefore improve mechanical strength of polymer membranes. Soroko *et al.* prepared TiO_2 containing PI-membranes for SRNF-applications.¹⁰⁴ Macrovoids present in the unfilled membranes were suppressed by increasing loading of TiO_2 nanoparticles, and eventually disappeared completely at a TiO_2 loading above 3 wt %. TiO_2 nanoparticles significantly enhanced viscosities of the casting solutions due to their high specific area and high surface energy.¹⁰⁵ Increasing viscosity actually works as a void-suppressing factor: it slows down the exchange rate of solvent and nonsolvent, causing a shift of phase inversion from instantaneous into delayed demixing. Similar observations have been made by Yang *et al.* for polysulfone ultrafiltration membranes.¹⁰⁶ Also, Aerts *et al.* observed that an increase in ZrO_2 nanoparticle content in polysulfone membranes caused decrease in macrovoid formation due to a higher viscosity of the casting solution.^{95,105}

C: Noble metal nanoparticles (NPs)

Separation of compounds with very low MW requires very dense membranes, which generally have very low fluxes. This can be to a certain extent compensated by use of NPs, e.g., gold, silver, and copper, as they exhibit unique and tunable

optical properties as a result of their surface plasmon resonance. They thus possess photothermal heating properties, which allows them to convert light into heat.¹⁰⁷ Vanherck *et al.* prepared PI- and CA-based SRNF membranes containing gold nanoparticles (GNPs). Synthesis of membranes with localized heating increased membrane fluxes by a factor as high as 4, without lowering selectivity.¹⁰⁸ Morphologically, macrovoids are less pronounced for higher concentrations of GNPs added to casting solution, macrovoid walls become more porous and a dense skin-layer is no longer visible. Similarly, Yanbo *et al.* synthesized PDMS-based SRNF membranes.¹⁰⁷

- Organic additives

Afterwards, the studies focused more on the use of organic additives. Low MW additives like glycerol (GLY), alcohols, diols,¹⁰⁹ and dicarboxylic acids¹¹⁰ are often used, while polyvinylpyrrolidone (PVP)⁸² and polyethylene glycol (PEG)^{80,81} are the most frequently used high MW additives. A particular additive can either suppress or induce macrovoid formation, depending on its concentration in the casting solution. Following systems were found to suppress macrovoid formation (upon increasing the additive concentration in the casting solution): CA/1,4-dioxane (DIO)/water,¹¹¹ PI/NMP/THF/water, PI/NMP/THF/IPA, PI/NMP/THF/AC, and PI/NMP/THF/1-hexanol,¹⁴ PI/DMF/DIO,¹¹ polyetherimide (PEI)/NMP/diethylene glycol dimethyl ether (DGDE)¹¹² and PI/NMP/DGDE.¹¹³ On the other hand, addition of DIO, DGDE, AC, and GBL to PSf/NMP solutions promoted macrovoid formation.¹¹⁴ The structure of the top-layer right above these macrovoids changed. DIO, DGDE, and AC caused formation of denser and thicker top-layers, whereas GBL formed a more porous, sponge-like structure. A PSf/DMAc-based system with 71 different low MW additives was investigated via chromatography to study molecular interactions.¹¹⁵ Most of the screened additives formed hydrogen bonds with the solvent, thus changing the PSf supermolecular structure. Following low MW additives were tested in preparation of SRNF-membranes from PSf/NMP-, PSf/DMF-, PSf/DMAc-, and PSf/DMSO-based systems: DIO, diethylene glycol diethyl ether (DGDE), dimethyl phthalate (DMPH), poly(ethylene glycol) dimethyl ether 250 (PEG-DME250), IPA, AC, 2-butanol (BUT), GBL, acetic acid (AA), and GLY.³⁰ It was proven that use of an additive was absolutely required in order to synthesize membranes from the PSf-based systems that possess SRNF properties (i.e., a high enough rejection). Increasing the concentration of any of these additives in the casting solution, therefore coming to theta conditions, always caused an increase in viscosity of the casting solution. Volatility of the additive was found to be a nondecisive factor to direct the membrane performance for the PSf/NMP system.

Literature provides some examples of polymeric additives that were found to suppress macrovoid growth: polyetherimide (PEI)/DMAc/PEG (600),⁸³ PEI/NMP/PEG (200, 400, and 600),⁸⁴ PEI/NMP/PEG 600,⁸⁵ PSf/DMAc/PEG (400, 6000, and 20,000) and PSf/NMP/PEG (400, 6000, and 20,000),⁸¹ PSf/NMP/PEG (600, 2000, 6000),⁸⁶ polyethersulfone (PES)/NMP/PVP^{87,88} and PAN/DMSO/PVP.⁸⁹ Examples of the systems that induced macrovoid formation on the other hand were: CA/NMP/PEG

Table II. The Effects of Additives on Macrovoid formation for Different Systems

Macrovoids	Additive	Polymer system	Effects on performance	
			P	R (solute)
Formed	AC	CA/DIO ¹¹¹	Not studied	Not studied
	DIO	PSf/NMP ¹¹⁴	Not studied	R↑ (PEG 35 k)
	DGDE	PSf/NMP ¹¹⁴	Not studied	R↑ (PEG 35 k)
	AC	PSf/NMP ¹¹⁴	Not studied	R↑ (PEG 35 k)
	GBL	PSf/NMP ¹¹⁴	Not studied	R↑ (PEG 35 k)
Suppressed	Water	CA/DIO ¹¹¹	Not studied	Not studied
	Water	PI/NMP/THF ¹⁴	P↓	R↑ (RB)
	IPA	PI/NMP/THF ¹⁴	P↓	R↑ (RB)
	AC	PI/NMP/THF ¹⁴	P↓	R↑ (RB)
	1-hexanol	PI/NMP/THF ¹⁴	P↓	R↑ (RB)
	DIO	PI/DMF ¹¹	F↓	R↑ (PS)
	DGDE	PEI/NMP ¹¹²	F↓	R↑ (PEG 600)
	DGDE	PI/NMP ¹¹³	Not Studied	Not studied
	PEG 600	PEI/DMAc ⁸³	Not Studied	Not studied
	PEG (200, 400, and 600)	PEI/NMP ⁸⁴	F↑	R↓ (PEG 600)
	PEG 600	PEI/NMP ⁸⁵	No Effect	No effect
	PEG (400, 6k and 20k)	PSf/DMAc ⁸¹	F↑	R (BSA) regardless the pH max for PEG 6000
	PEG (400, 6k and 20k)	PSf/NMP ⁸¹	F↑	R (BSA) regardless the pH max for PEG 6000
	PEG (600, 2k, 6k)	PSf/NMP ⁸⁶	F↑	R↓ (PEG 12000 and 35000)
	PVP	PES/NMP ^{87,88}	Not studied ⁸⁷ F↓	Not studied ⁸⁷ no effect
	PVP	PAN/DMSO ⁸⁹	PVP Mw 10K: F↑ PVP Mw 46K: F↓ PVP Mw 360K: F↓	R↓ (dextran) R↑ (dextran) R↑ (dextran)

AC, acetone; BSA, bovine serum albumin; CA, cellulose acetate; DGDE, diethylene glycol dimethyl ether; DIO, 1,4-dioxane; DMAc, *N,N*-dimethylacetamide; DMF, *N,N*-dimethylformamide; DMSO, dimethyl sulfoxide; F, flux; GBL, γ -butyrolactone; IPA, isopropanol; NMP, *N*-methyl-2-pyrrolidone; P, permeance; PAN, polyacrylonitrile; PEI, polyetherimide; PEG, polyethylene glycol; PES, polyethersulfone; PI, polyimide; PS, polystyrene; PSF, polysulfone; PVP, poly(vinylidene fluoride); R, rejection; RB, rose Bengal; THF, tetrahydrofuran.

400,⁹⁰ PES/DMF/PEG (200, 400, and 600),⁹¹ PSf/sulfonated poly(etheretherketone) (SPEEK)/DMF/PEG 600⁹² and PSf/DMF/PVP.⁹³

Much less studied is the role of high MW additives in the preparation of SRNF-membranes. Following high MW additives were tested in the preparation of SRNF-membranes from PSf/NMP/THF-based system: nine different PEGs, two different PVDFs, one type of PVP, PES, polyacrylonitrile (PAN), CA, and cellulose triacetate (CTA).²⁹ For PEG as an additive, performance results as well as SEM studies showed an important change around a PEG MW of 10,000 Da. An initial decrease in rejection was then turned into an increase, due to the realized leaching out of the additive from the membrane after the synthesis. For the higher MWs, an increased viscosity of the casting solutions and increased level of polymer chain entanglement hindered the leaching out and at the same time delayed the demixing process, leading to denser membranes. SEM observations showed that increasing the MW of PEG or increasing its concentration caused creation of a thicker layer with increased density on top of the macrovoid containing layer.

Table II summarizes the influence of various additives on macrovoid formation and their impact on performance for different systems.

Casting Conditions. Evaporation time and temperature. Introduction of an evaporation step is a commonly used procedure to obtain less porous membrane surfaces when volatile solvents or cosolvents are present in the initial casting solution.¹⁴ An evaporation step causes a selective loss of the volatile (co-)solvent from the cast film. As a result, a so-called “skin-layer” is formed with a locally increased polymer concentration. Upon immersion in the coagulation bath, that “skin-layer” is a kind of resistance barrier between the bulk of the membrane and the coagulation bath. The in-diffusion of nonsolvent and the out-diffusion of solvent are thus hindered and demixing gets delayed.^{1,10}

Recently, a kind of volcano plot was observed for rejections of PSf- and PEEK-based SRNF-membranes with extended evaporation time. A possible explanation could be the initiation after a certain time of polymer precipitation at the membrane skin

before the actual immersion in a nonsolvent coagulation bath.⁷¹ Especially, at relatively high humidity level in the synthesis lab, water could condense on the membrane surface where the endothermic cosolvent evaporation locally lowers the temperature of the cast film. Recently, it was also claimed that the partial evaporation of a volatile cosolvent prior to immersion in a nonsolvent bath is unnecessary to form a selective “skin-layer” on a PI-based SRNF-membrane, and that it even should be avoided, as it worsens the flux without significantly effecting rejection.¹² However, a study with another type of PI-based SRNF-membranes, showed that an increased evaporation time did increase rejections while decreasing permeances.¹⁴

It is obvious that the higher the evaporation temperature, the more solvent will evaporate.^{1,10} This was for instance shown to cause increased rejections and decreased fluxes for PAH membranes.¹¹⁶

Relative humidity (RH). RH is an important parameter in the membrane synthesis process, but difficult to investigate in a lab-scale atmosphere, as it is mostly not easy to properly control it.^{12,117} For both PEEK and PES, a certain critical RH was found below which the RH did not play a role.^{117,118} For SRNF casting solutions, this parameter might be even much more critical, as they are closer to instability already at the moment of coagulation, for instance due to increased polymer concentration, and especially after applying extended evaporation times (see above) or use of additives with nonsolvent properties.

Membrane thickness. The effect of membrane thickness has often been overlooked and not considered as important, but some studies did find that the thicker the membrane (when comparing wet coating thicknesses for (PAN/DMF) ranging from 11.9 to 213 μm), the more macrovoids are formed.¹¹⁹ Changing the membrane morphology into a spongy structure via a mere decrease in thickness is extremely interesting when trying to avoid macrovoid formation.¹²⁰ From a more fundamental point of view, these results raise questions. Indeed, formation of macrovoids or spongy structures has always been explained as a consequence of either having delayed or instantaneous demixing, which obviously is determined by in- and out-diffusion at the upper surface of the cast film. Possibly, this has to do with different ways on how polymer conformation changes in the solidifying film and accompanying tensions that are built up in the solidifying film can still be spread to lower, still more mobile parts of the cast film.

Also, thinner casting layers can implement considerable savings in the production process, less contamination of the coagulation bath by leaching compounds or solvents, and different intrusion into the (non-)woven support. Moreover, when membranes are post-treated with e.g., UV or electron beam radiation, the beams need to penetrate over the whole depth of the membrane, thus a reduced thickness of the layer would be really favorable.¹²¹ Depending on a number of parameters (such as e.g., the roughness of the support, the viscosity and surface tension of the casting solution), polymer coating of less than 100 nm thick can industrially be applied easily.

Precipitation Conditions. Composition and temperature of the coagulation bath. Composition^{82,109,122–125} and temperature^{100,126,127} of the coagulation bath are parameters that are easy

to control and with a very strong influence on the resulting membrane, as already proven for MF, UF, aqueous NF, and also for PI-based systems in SRNF. The exchange rates of solvent and nonsolvent are very important in the membrane synthesis via phase inversion by means of immersion precipitation and can be easily accelerated through elevated temperatures. If the mutual affinity between solvent and nonsolvent is high, the miscibility between them is high, thus the exchange rate of both is supposed to be high and the demixing will be more instantaneous, resulting in more porous membranes with macrovoids in the sub-layer. This theoretical statement is not always in line with experimental results, as already discussed above in the basic principles of the phase inversion process. Addition of solvent to the nonsolvent coagulation bath is a procedure to delay demixing process, but there are two competing phenomena occurring. Presence of solvent in the coagulation bath lowers the “pure” nonsolvent activity, as well as the exchange rate with the solvent during the membrane formation process (more delayed demixing). On the other hand, it also lowers the polymer concentration at the (cast film)/(nonsolvent bath) interface since more solvent remains, thus rather causing instantaneous than delayed demixing.^{1,57}

Support material. The type of support material has an impact on the speed of the demixing process of the casting solution during membrane fabrication, especially in the preparation of flat sheet membranes via phase inversion by means of immersion precipitation.¹²⁸

Industrial production of flat sheet membranes most often takes place on nonwoven polymeric supports,^{27–30} whereas in lab-scale experiments, mica,¹²⁸ glass,¹²⁹ metal,¹²⁸ or polymer plates, are commonly used in addition to these woven and nonwoven support materials. When the supporting materials during the synthesis are impermeable, the nonsolvent can obviously only penetrate from the top into the cast film. Also permeable woven or nonwoven supports are often well fixed to another impermeable substrate, typically a metal or glass plate to allow handling at lab scale,^{128,129} hence also preventing nonsolvent infiltration from the bottom side of the cast film and thus slowing down the precipitation of the full structure. It should be noticed that wetting from the bottom side will in principle not influence the properties of the selective skin of the membrane, but might modify the supporting structure, hence e.g., the possible formation of macrovoids.

During immersion of the cast film in the coagulation bath, wetting phenomena are combined with polymer solidification.¹³⁰ Solidification is often reflected in shrinkage of the cast film. Membranes cast on rigid backing materials are only able to shrink in thickness, as lateral shrinkage is hindered by the adhesion of the membrane to the rigid support.¹³¹ This restricted relaxation of the membrane polymer can lead to tensions in the cast film, finally resulting in presence of larger pores.

When casting membranes at industrial scale by means of continuous casting machines using highly porous nonwoven or woven supports, the back side of the membrane is immediately in contact with the coagulation liquid and, if the support is wettable, the solidification process can start from both sides nearly without

delay. Wettability of the support is a function of its average pore size, the polymer material it is made from, possible surface treatments that were applied, and so on. A very broad variety of nonwoven and woven supports is industrially available as they are commonly used for completely other large-scale purposes, like e.g., in electronics, construction, automotive, or hygiene.¹³²

Vapor phase induced phase inversion (VIPS). Coagulation by immersion precipitation has by far been the most popular method to synthesize integrally skinned membranes. VIPS (also referred to as precipitation from the vapor phase) is generally said to give similar results as phase inversion by immersion.^{133,134} During the precipitation from the vapor phase, the cast polymer solution is placed in a vapor consisting of a nonsolvent, sometimes saturated with the solvent used for the preparation of the casting solution to slow down the precipitation. During VIPS, phase separation occurs due to the diffusion of nonsolvent that is first absorbed onto the cast film.⁴⁸ The resulting membrane structure is more symmetric and more microporous compared to membranes obtained by immersion precipitation.¹³⁵

Post Treatment. Post-treatments and conditioning procedures are not only used to increase the performance of asymmetric membranes, but also to increase their long term stability and practical handling. Synthesized membranes can be further post-treated by annealing (dry or wet), solvent exchange, solvent treatments, crosslinking or use of conditioning agents.^{1,10} The paragraphs below will explain in more detail in which direction a particular post-treatment method can affect membrane performance. In some cases, the impact of these post treatments on performance is extremely strong, often overruling much of the fine-tuning that can be done via optimization of the actual phase inversion parameters discussed earlier.

Annealing. Annealing is a very effective way to densify membrane structures, as it causes shrinkage of voids between nodule aggregates and the spaces between intra-molecular chain segments. Both amorphous and semicrystalline polymers can be annealed. In case of amorphous polymers, annealing causes more efficient chain packing, whereas in case of semi-crystalline polymers, it might cause increased crystallization.^{136,137}

Thermal annealing is typically performed in a water bath at 70–90°C. It is a very effective way to densify membrane structures, as it causes shrinkage of voids between nodule aggregates and the spaces between intramolecular chain segments.¹³⁸ As the consequence, the membrane performance is often largely affected by thermal annealing.

Asymmetric CA-based RO membranes were annealed in water baths at different temperatures.¹³⁹ NaCl rejections increased significantly (from 15 to 82%) and permeances dropped [from 0.9 to 0.27 L/(m² h bar)] with increasing temperature of the water bath from 20 to 95°C. The same happened for PAN-based UF membranes in a water bath at 80°C or PAN-based NF membranes at 70–96°C.^{139,140} As annealing causes void shrinkage, it can also be a promising approach to ultimately increase the selectivity of prepared SRNF-membranes.

Drying via solvent exchange and use of conditioning agents. Porosity and surface structure of membranes can be preserved

by (multiple) liquid exchanges. A first step of the procedure is to exchange the residual nonsolvent in the membrane after synthesis with another liquid. This liquid has to be miscible with the nonsolvent and should obviously not dissolve the polymer. Afterwards, this liquid can be replaced with a second more volatile liquid. Volatility of the second liquid makes it more easy to get it removed through evaporation in order to obtain a dry membrane that can be handled well and for instance be put in modules more easily.^{1,10}

However, in a multistep solvent exchange, residual DMF and water were removed from PI-based membranes by immersion in IPA, then in toluene and finally in a bath containing mineral oil.¹⁴¹ During phase inversion, membranes are normally precipitated in water, while they are during the actual SRNF mostly contacted with apolar organic feeds. It is therefore needed to pretreat them with appropriate liquids to allow full pore wetting during operation. Mineral oils are used to prevent the membrane pores from drying out and hence avoid membrane pore collapse, which is often irreversible and would reduce membrane fluxes drastically. Lube oils, GLY, and long chain hydrocarbons can be used to further enhance the performance of synthesized membranes,^{141,142} possibly due to induced polymer rearrangements. Increased toluene fluxes of PI membranes were for instance found via addition of lube oil to a second solvent exchange bath containing MEK and toluene.¹⁴²

Solvent treatment. Presoaking of polymeric membranes often increases the flux, which is related to polymer swelling and wetting of microscopic defects in the membrane. Such swelling loosens chain–chain interactions and increases chain-spacing and chain flexibility, resulting in increased permeation through the polymer matrix.

Presoaking of dry aromatic polyamide RO-membranes in aliphatic alcohols resulted in a significant increase in water flux.¹⁴³ Similarly, presoaking of commercially important aromatic polyamide based RO-membranes, such as CPA2 and SWC1, with acids (hydrofluoric and hexafluorosilicic) and aliphatic alcohols (IPA) also caused a significant increase of water flux.¹⁴⁴ For PA- and PI-based membranes (Desal-DK and STARMEM 228), AC, MeOH, and TOL pretreatment significantly influenced the membrane performance, but not that much for PDMS-based membranes (MPF-50).¹⁴⁵ The insignificant influence of pretreatment on MPF-50 might be due to the fact that this membrane has a nonporous structure.¹⁴⁶ Recent work reports two different approaches to pretreat a new generation of SRNF membranes (TFC membranes synthesized via IP).²⁰ Impregnation of a UF support with polyethylene glycol resulted in increased fluxes, while treatment with so-called “activating solvents” (DMF or DMSO) before filtration resulted in a significant improvement of solvent fluxes without negative effect on retentions. These “activating solvents” dissolve partly the loose polyamide top-layer, without affecting the cross-linked polyimide support.

Crosslinking. To improve the chemical stability and performance properties of asymmetric membranes, the phase inversion can be followed by a crosslinking step, i.e. via thermal, UV or chemical crosslinking.

For instance, phase inversion polystyrene asymmetric membranes can be photo-crosslinked. A first partial crosslinking was realized before actual immersion in the nonsolvent bath, containing MeOH and benzoin as radical initiator, by exposing the cast films to UV-lamp for 24 h. The crosslinking was finalized after the phase inversion process via an additional UV-treatment, which also took 24 h.¹⁴⁷ Recently UV-treatment was also found to be successful for PSF and PI systems by creating semi-interpenetrating networks with polyfunctional acrylates.¹⁴⁸ On the other hand, chemical crosslinking is a more precise tool to control the crosslinking degree as the chemical reactions that occur tend to be more specific.^{149,150} Chemical crosslinking was so far most often studied for PI systems, where two kinds of cross-linker can be used: diamines and diols. In the case of diols, polymer chains should contain free carboxylic acid groups, in order to form ester bonds. Amines on the other hand break up imide bonds, thus forming intermolecular amides. To perform chemical crosslinking of PI-based membranes with diamines, the membrane first has to be put in a solution of crosslinker (e.g., most often diamines in MeOH), so that the membrane structure swells and crosslinking agent can enter it.¹⁵¹ Interestingly, immersion precipitation and crosslinking can be performed simultaneously via addition of the crosslinking agent to the coagulation bath.^{17,152,153}

CONCLUSIONS

Key parameters during the synthesis of integrally skinned asymmetric phase inversion membranes to be applied in the field of SRNF were reviewed and complemented with important data and insights obtained earlier for the already much more studied MF-, UF-, NF-, and RO-membranes for aqueous applications. The complete picture of what is happening in the membrane synthesis system when changing a parameter requires consideration of both thermodynamic and kinetic aspects of the demixing and solidification process, which makes full prediction of membrane morphologies and their link to the membrane performances often very difficult. To increase the further insight, more frequent construction of phase diagrams to describe the system's thermodynamics, as well as a determination of the system's precipitation kinetics would be helpful. In SRNF, the chemical resistance of the membrane forming polymer is very important and the proper selection of polymer candidates to ensure this chemical resistance is not obvious. The choice of casting solvent but also the selection of appropriate additives, essential for the synthesis of a membrane with attractive performance, can be facilitated via the HSP approach. Often overlooked in the past are the exact properties of the starting polymer material (i.e., MW, PDI, purity, etc.), which becomes probably more important in the preparation of dense membranes, like for SRNF, than for porous membranes.

It is of note that the fundamental interpretation of the phase inversion process for the synthesis of SRNF membranes has so far been very limited, due to the fact that the synthesis parameters have only been linked to performance of membranes and only seldomly to morphology studies, and surely not to the synthesis process itself. Therefore, insight in the real effects of the synthesis parameters on the kinetics and thermodynamics of the phase

inversion process for SRNF-membranes is still highly needed. Synthesis parameters that have so far not received sufficient attention, but often have drastic impact on the final membrane, which are e.g., the composition and the temperature of coagulation bath (probably because preferentially kept at ambient conditions at production scale), polymer purity, relative humidity (often difficult to control at lab scale), and membrane thickness. Changing membrane morphology from macrovoids into spongy via mere change of the thickness is an extremely interesting from a production point of view and intriguing with respect to the fundamental understanding of the process. Vapor phase induced phase inversion has so far hardly been applied, but surely deserves still to be investigated in more detail. Nowadays, a lot of research is focused on further improvement of the performance and chemical resistance of prepared membranes via different postsynthesis treatments, especially chemical or photo-cross-linking, but also via annealing, solvent treatment and conditioning with different agents, often accompanied by spectacular and surprising effects. Finally, extra characterization methods are still required to shed light on missing characteristics of casting solutions and resulting membranes, by preference with characterization down to the dimensions of free volume elements.

ABBREVIATIONS

AA	Acetic acid
AAACN	Acetonitrile
AC	Acetone
BSA	Bovine serum albumin
BUT	Butanol
CA	Cellulose acetate
CHB	Chlorobenzene
CTA	Cellulose triacetate
DCM	Dichloromethane
DGDE	Diethylene glycol diethyl ether
DGDE	Diethylene glycol dimethyl ether
DIO	1,4-Dioxane
DMAC	N,N-Dimethylacetamide
DMF	N,N-Dimethylformamide
DMPH	Dimethyl phthalate
DMSO	Dimethyl sulfoxide
EtAc	Ethyl acetate
EtOH	Ethanol
F	Flux
GBL	γ -Butyrolactone
GLY	Glycerol
GNPs	Gold nanoparticles
HEP	Heptane
HEX	Hexane
HSP	Hansen solubility parameters
IP	Interfacial polymerization
IPA	Isopropanol
MEK	Methylethylketone
MeOH	Methanol
MF	Microfiltration
MIBK	Methylisobutylketone
MMMs	Mixed matrix membranes
MW	Molecular weight

MWCO	Molecular weight cut-off
NF	Nanofiltration
NMP	N-methyl-2-pyrrolidone
NPs	Nanoparticles
ONF	Organophilic nanofiltration
OSN	Organic solvent nanofiltration
P	Permeance
PA	Polyamide
PAH	Poly(amide-hydrazine)
PAN	Polyacrylonitrile
PDI	Polidispersity index
PDMS	Polydimethylsiloxane
PEC	Polyelectrolyte complexes
PEEK	Poly(ether ether ketone)
PEI	Polyetherimide
PEG	Polyethylene glycol
PEGDME250	Poly(ethylene glycol) dimethyl ether 250
PES	Polyethersulfone
PI	Polyimide
PICS	Pulsed induced critical scattering
PRO	Propanol
PS	Polystyrene
PSf	Polysulfone
PVDF	Poly(vinylidene fluoride)
PVP	Polyvinylpyrrolidone
R	Rejection
R0	Radius of Hansen solubility sphere
Ra	Solubility parameter distance
RB	Rose bengal
RED	Relative energy difference
RH	Relative humidity
RO	Reverse osmosis
SEM	Scanning electron microscopy
SPEEK	Sulfonated poly(ether ether ketone)
SRNF	Solvent resistant nanofiltration
TFC	Thin-film composite
THF	Tetrahydrofuran
TOL	Toluene
UF	Ultrafiltration
UV	Ultraviolet
VIPS	Vapor phase induced phase separation

LIST OF SYMBOLS

δ	Total solubility parameter
δ_D	Dispersion solubility parameter
δ_H	Hydrogen solubility parameter
δ_P	Polar solubility parameter
$\Delta\delta_{S-NP}$	Solubility parameter difference

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REFERENCES

- Vandezande, P.; Gevers, L. E. M.; Vankelecom, I. F. J. *Chem. Soc. Rev.* **2008**, *37*, 365.

- Gould, R. M.; White, L. S.; Wildemuth, C. R. *Environ. Prog.* **2001**, *20*, 12.
- Whu, J. A.; Baltzis, B. C.; Sirkar, K. K. *J. Membr. Sci.* **2000**, *170*, 159.
- Raman, L. P.; Cheryan, M.; Rajagopalan, N. *JAOCS* **1996**, *73*, 219.
- Cuperus, F. P.; Ebert, K. In *Nanofiltration: Principles and Applications*; Schäfer, A. I., Fane, A. G., Waite, T. D., Eds.; Elsevier: Oxford, UK, **2005**; Chapter 21, pp 521–536.
- Nair, D.; Luthra, S.; Scarpello, J.; White, L.; Freitas dos Santos, L.; Livingston, A. G. *Desalination* **2002**, *147*, 301.
- Aerts, S.; Weyten, H.; Buekenhoudt, A.; Gevers, L.; Vankelecom, I. F. J.; Jacobs, P. *Chem. Commun.* **2004**, *6*, 710.
- Darvishmanesh, S.; Tasselli, F.; Jansen, J. C.; Tocci, E.; Bazzarelli, F.; Bernado, P.; Luis, P.; Degève, J.; Drioli, E.; Van der Bruggen, B. *J. Membr. Sci.* **2011**, *384*, 89.
- Rundquist, E. M.; Pink, C. J.; Livingston, A. G. *Green Chem.* **2012**, *14*, 2197.
- Vankelecom, I. F. J.; De Smet, K.; Gevers, L. E. M.; Jacobs, P. A. In *Nanofiltration: Principles and Applications*; Schäfer, A. I., Fane, A. G., Waite, T. D., Eds.; Elsevier: Oxford, UK, **2005**; Chapter 3, pp 33–65.
- Soroko, I.; Lopes, M. P.; Livingston, A. *J. Membr. Sci.* **2011**, *381*, 152.
- Soroko, I.; Makowski, M.; Spill, F.; Livingston, A. *J. Membr. Sci.* **2011**, *381*, 163.
- Soroko, I.; Sairam, M.; Livingston, A. *J. Membr. Sci.* **2011**, *381*, 172.
- Vandezande, P.; Li, X.; Gevers, L. E. M.; Vankelecom, I. F. J. *J. Membr. Sci.* **2009**, *330*, 307.
- Vandezande, P.; Gevers, L. E. M.; Paul, J. S.; Vankelecom, I. F. J.; Jacobs, P. A. *J. Membr. Sci.* **2005**, *250*, 305.
- Vandezande, P.; Gevers, L. E. M.; Jacobs, P. A.; Vankelecom, I. F. J. *J. Membr. Sci.* **2009**, *66*, 104.
- Vanherck, K.; Vandezande, P.; Aldea, S. O.; Vankelecom, I. F. J. *J. Membr. Sci.* **2008**, *320*, 468.
- Vanherck, K.; Cano-Odena, A.; Koeckelberghs, G.; Vankelecom, I. F. J. *J. Membr. Sci.* **2010**, *353*, 135.
- Stawikowska, J.; Jimenez-Solomon, M. F.; Bhole, Y.; Livingston, A. G. *J. Membr. Sci.* **2013**, *42*, 107.
- Solomono, M. F. J.; Bhole, Y.; Livingston, A. G. *J. Membr. Sci.* **2012**, *423*, 371.
- Wang, J.; Yue, Z.; Ince, J. S.; Economy, J. *J. Membr. Sci.* **2006**, *286*, 333.
- Chen, J.; Li, J.; Wang, Z.-P. Z. D.; Chen, C.-X. *Surf. Coat. Technol.* **2007**, *201*, 6789.
- Darvishmanesh, S.; Buekenhoudt, A.; Degève, J.; Van der Bruggen, B. *J. Membr. Sci.* **2009**, *334*, 43.
- Aerts, S.; Vanhulsel, A.; Buekenhoudt, A.; Weyten, H.; Kuypers, S.; Chen, H.; Bryjak, M.; Gevers, L. E. M.; Vankelecom, I. F. J.; Jacobs, P. A. *J. Membr. Sci.* **2006**, *275*, 212.

25. Gevers, L. E. M.; Vankelecom, I. F. J.; Jacobs, P. A. J. *Membr. Sci.* **2006**, *278*, 199.
26. Darvishmanesh, S.; Jansen, J. C.; Tasselli, F.; Tocci, E.; Luis, P.; Degrève, J.; Drioli, E.; Van der Bruggen, B. *J. Membr. Sci.* **2011**, *379*, 60.
27. Holda, A. K.; Aernouts, B.; Saeys, W.; Vankelecom, I. F. J. *J. Membr. Sci.* **2013**, *442*, 196.
28. Holda, A. K.; De Roeck, M.; Hendrix, K.; Vankelecom, I. F. J. *J. Membr. Sci.* **2013**, *446*, 113.
29. Holda, A. K.; Vankelecom, I. F. J. *J. Membr. Sci.* **2014**, *450*, 512.
30. Holda, A. K.; Vankelecom, I. F. J. *J. Membr. Sci.* **2014**, *450*, 499.
31. Ahmadiannamini, P.; Li, X.; Goyens, W.; Joseph, N.; Meesschaert, B.; Vankelecom, I. F. J. *J. Membr. Sci.* **2012**, *394*, 98.
32. Li, X.; Goyens, W.; Ahmadiannamini, P.; Vanderlinden, W.; De Feyter, S.; Vankelecom, I. F. J. *J. Membr. Sci.* **2010**, *358*, 150.
33. Ahmadiannamini, P.; Li, X.; Goyens, W.; Meesschaert, B.; Vanderlinden, W.; De Feyter, S.; Vankelecom, I. F. J. *J. Membr. Sci.* **2012**, *403*, 216.
34. Siddique, H.; Rundquist, E.; Bhole, Y.; Peeva, L. G.; Livingston, A. G. *J. Membr. Sci.* **2014**, *452*, 354.
35. Moermans, B.; Beuckelaer, W. D.; Vankelecom, I. F. J.; Ravishankar, R.; Martens, J. A.; Jacobs, P. A. *Chem. Commun.* **2000**, 2467.
36. Li, L. X.; Dong, J. H.; Nenoff, T. M.; Lee, R. *J. Membr. Sci.* **2004**, *243*, 401.
37. Hoek, E. M. V.; Jeong, B. H.; Yan, Y. U. S. *Application 11/364,885*. **2005**, Priority: US 60/660, 428.
38. Jeong, B. H.; Hoek, E. M. V.; Yan, Y.; Subramani, A.; Huang, X.; Hurwitz, G.; Ghosh, A. K.; Jawor, A. *J. Membr. Sci.* **2007**, *294*, 1.
39. Vandezande, P.; Gevers, L. E. M.; Jacobs, P. A.; Vankelecom, I. F. J. *Sep. Purif. Technol.* **2009**, *66*, 104.
40. Basu, S.; Maes, M.; Cano-Odena, A.; Alaerts, L.; De Vos, D. E.; Vankelecom, I. F. J. *J. Membr. Sci.* **2009**, *344*, 190.
41. Haruhiko, O.; Kudryavtsev, V. V.; Semenova, S. I. *Polyimide Membranes Application, Fabrication and Properties*; CRC Press: Kodansha, **1997**.
42. <http://duramem.evonik.com/product/duramem-puramem/en/Pages/default.aspx>. Accessed on January, 2015.
43. <http://www.solsep.com/>. Accessed on January, 2015.
44. <http://mt.borsig.de/>. Accessed on January, 2015.
45. <http://www.inopor.com/en/index.html>. Accessed on January, 2015.
46. Dalwani, M. Thin film composite nanofiltration membranes for extreme conditions, Ph.d Dissertation, University of Twente, 2011.
47. Loeb, S.; Sourirajan, S. *Adv. Chem. Ser.* **1962**, *38*, 117.
48. Mulder, M. *Basic Principles of Membrane Technology*, 2nd ed.; Kluwer Academic: Dordrecht, **2003**; Chapter 3, pp 71–156.
49. Zhou, B. Ph.D. Dissertation, Massachusetts Institute of Technology, **2006**.
50. Reuvers, A. J.; Smolders, C. A. *J. Membr. Sci.* **1987**, *34*, 67.
51. Yoo, S. H.; Kim, J. H.; Jho, J. Y.; Won, J.; Kang, Y. S. *J. Membr. Sci.* **2004**, *236*, 203.
52. Jansen, J. C.; Macchione, M.; Drioli, E. *J. Membr. Sci.* **2005**, *255*, 167.
53. Koningsveld, R.; Stockmayer, W. H.; Nies, E. *Polymer Phase Diagrams: A Textbook*; Oxford University Press: New York, **2001**.
54. Baidakov, V. G.; Skripov, V. P. *Zh. Eksp. Teor. Fiz.* **1978**, *75*, 1007.
55. Wells, P. A.; de Loos, T. W.; Kleintjens, L. A. *Fluid Phase Equilibria* **1993**, *83*, 383.
56. Kimmerie, K.; Strathmann, H. *Desalination* **1990**, *79*, 283.
57. Guillen, G. R.; Pan, Y.; Li, M.; Hoek, E. M. V. *Ind. Eng. Chem. Res.* **2011**, *50*, 3798.
58. Strathmann, H.; Kock, K.; Amar, P.; Baker, R. W. *Desalination* **1975**, *16*, 179.
59. Reuvers, A. J.; Smolders, C. A. *J. Membr. Sci.* **1987**, *34*, 67.
60. Kim, J.-H.; Lee, K.-H. *J. Membr. Sci.* **1998**, *138*, 153.
61. Lang, W.-Z.; Xu, Z.-L.; Yang, H.; Tong, W. *J. Membr. Sci.* **2007**, *288*, 123.
62. Li, J.-F.; Xu, Z.-L.; Yang, H. *Polym. Adv. Technol.* **2008**, *19*, 251.
63. Frommer, M. A.; Messalem, R. M. *Ind. Eng. Chem. Prod. Res. Dev.* **1973**, *12*, 328.
64. Berg, J. C.; Morig, C. R. *Chem. Eng. Sci.* **1969**, *24*, 937.
65. Ruckenstein, E.; Berbente, C. *Chem. Eng. Sci.* **1964**, *19*, 329.
66. Olander, D. R.; Reddy, L. B. *Chem. Eng. Sci.* **1964**, *19*, 67.
67. Sternling, C. V.; Scriven, L. E. *AIChE J.* **1959**, *5*, 514.
68. Pearson, J. R. A. *J. Fluid Mech.* **1958**, *4*, 489.
69. Sherwood, T. K.; Wei, J. C. *Ind. Eng. Chem.* **1957**, *49*, 1030.
70. Guillen, G. R.; Ramon, G. Z.; PirouzKavehpour, H.; Kaner, R. B.; Hoek, E. M. V. *J. Membr. Sci.* **2013**, *431*, 212.
71. De Roeck, M. Ph.D. Dissertation, KU Leuven, **2011**.
72. Gupta, K. *J. Appl. Polym. Sci.* **1997**, *66*, 643.
73. Mohamed, N. *Polymer* **1997**, *38*, 4705.
74. Hansen, C. H. *Hansen Solubility Parameters: A User's Handbook*; CRC Press: Boca Raton, FL, **1999**, 2007; p 269.
75. Hoy, K. L. *J. Paint. Technol.* **1970**, *42*, 76.
76. Small, P. A. *J. Appl. Chem.* **1953**, *3*, 71.
77. van Krevelen, D. W. *Properties of Polymers*; Elsevier: Amsterdam, **1990**.
78. Fried, J. *Polymer Science and Technology*; Prentice Hall: Upper Saddle River, NJ, **2003**.
79. Burke, J. <http://cool.conservation-us.org/coolaic/sg/bpg/annual/v03/bp03-04.html>. Accessed on February, 2015.
80. Chakrabarty, B.; Ghoshal, A. K.; Purkait, M. K. *J. Membr. Sci.* **2008**, *309*, 209.
81. Ma, Y.; Shi, F.; Ma, J.; Wu, M.; Zhang, J.; Gao, C. *Desalination* **2011**, *272*, 51.

82. Boom, R. Ph.D. Dissertation, Universiteit Twente, **1992**.
83. Xu, Z.-L.; Chung, T.-S.; Loh, K.-C.; Lee, B. C. *J. Membr. Sci.* **1999**, *158*, 41.
84. Kim, I. C.; Lee, K. H. *J. Membr. Sci.* **2004**, *230*, 183.
85. Shieh, J. J.; Chung, T. S.; Wang, R.; Srinivasan, M. P.; Paul, D. R. *J. Membr. Sci.* **2001**, *182*, 111.
86. Kim, J. H.; Lee, K. H. *J. Membr. Sci.* **1998**, *138*, 153.
87. Boom, R. M.; Wienk, I. M.; Van der Boomgaard, T.; Smolders, C. A. *J. Membr. Sci.* **1992**, *73*, 277.
88. Mosqueda-Jimenez, D. B.; Narbaitz, R. M.; Matsuura, T.; Chowdhury, G.; Pleizier, G.; Santerre, J. P. *J. Membr. Sci.* **2004**, *231*, 209.
89. Jung, B.; Yoon, J. K.; Kim, B.; Rhee, H. W. *J. Membr. Sci.* **2004**, *243*, 45.
90. Saljoughi, E.; Amirilargani, M.; Mohammadi, T. *Desalination* **2010**, *262*, 72.
91. Idris, A.; Zain, N. M.; Noordin, M. Y. *Desalination* **2007**, *207*, 324.
92. Arthanareeswaran, G.; Mohan, D.; Raajenthiren, M. *J. Membr. Sci.* **2010**, *350*, 130.
93. Yeo, H. T.; Lee, S. T.; Han, M. J. *J. Chem. Eng. Japan* **2000**, *33*, 180.
94. Gregory, J. *Filtr. Separat.* **1998**, *35*, 63.
95. Aerts, P.; Van Hoof, E.; Leysen, R.; Vankelecom, I. F. J.; Jacobs, P. A. *J. Membr. Sci.* **2000**, *176*, 63.
96. Kesting, R. E. *J. Appl. Polym. Sci.* **1965**, *9*, 663.
97. Curcio, E.; Fontananova, E.; Di Profio, G.; Drioli, E. *J. Phys. Chem. B* **2006**, *110*, 12438.
98. Kong, J.; Li, K. *J. Appl. Polym. Sci.* **2001**, *81*, 1643.
99. Fontananova, E.; Jansena, J. C.; Cristianoa, A.; Curcioa, E.; Drioli, E. *Desalination* **2006**, *192*, 190.
100. Tomaszewska, M. *Desalination* **1996**, *104*, 1.
101. Park, J.-S.; Kim, S.-K.; Lee, K.-H. *J. Ind. Eng. Chem.* **2000**, *6*, 93.
102. Kim, S. R.; Lee, K. H.; Jhon, M. S. *J. Membr. Sci.* **1996**, *119*, 59.
103. Mierzwa, J. C.; Veciyis, C. D.; Carvalho, J.; Arieta, V.; Verlage, M. *J. Membr. Sci.* **2012**, *421*, 91.
104. Soroko, I.; Livingston, A. *J. Membr. Sci.* **2009**, *343*, 189.
105. Li, J. B.; Zhu, J. W.; Zheng, M. S. *J. Appl. Polym. Sci.* **2006**, *103*, 3623.
106. Yang, Y. N.; Zhang, H. X.; Wang, P.; Zheng, Q. Z.; Li, J. *J. Membr. Sci.* **2007**, *288*, 231.
107. Li, Y.; Verbiest, T.; Vankelecom, I. F. J. *J. Membr. Sci.* **2013**, *428*, 63.
108. Vanherck, K.; Hermans, S.; Verbiest, T.; Vankelecom, I. F. J. *J. Mater. Chem.* **2011**, *21*, 6079.
109. Mansourizadeh, A.; Ismail, A. F. *J. Membr. Sci.* **2010**, *348*, 260.
110. Beerlage, M. Ph.D. Dissertation, Universiteit Twente, **1994**.
111. Smolders, C. A.; Reuvers, A. J.; Boom, R. M.; Wienk, I. M. *J. Membr. Sci.* **1992**, *73*, 259.
112. Kim, I.-C.; Lee, K.-H.; Tak, T.-M. *J. Membr. Sci.* **2001**, *183*, 235.
113. Hachisuka, H.; Ohara, T.; Ikeda, K. *J. Membr. Sci.* **1996**, *116*, 265.
114. Kim, I.-C.; Lee, K.-H. *J. Appl. Polym. Sci.* **2003**, *89*, 2562.
115. Tai-Ping, H.; Sheng-Hua, D.; Ling-Ying, Z. *Desalination* **1991**, *83*, 343.
116. Mohamed, N. A. *Polymer* **1997**, *38*, 4705.
117. Boussu, K.; Vandecasteele, C.; Van der Bruggen, B. *Polymer* **2006**, *47*, 3464.
118. Tasselli, F.; Jansen, J. C.; Sidari, F.; Drioli, E. *J. Membr. Sci.* **2005**, *255*, 13.
119. Azari, S.; Karimi, M.; Kish, M. H. *Ind. Eng. Chem. Res.* **2010**, *49*, 2442.
120. Hendrix, K.; Koeckelberghs, G.; Vankelecom, I. F. J. *J. Membr. Sci.* **2014**, *452*, 241.
121. Struzynska-Piron, I.; Loccufier, J.; Vanmaele, L.; Vankelecom, I. Solvent Resistant Polymeric Membrane, EP12161017.4.
122. Buonomenna, M. G.; Figoli, A.; Jansen, J. C.; Drioli, E. *J. Appl. Polym. Sci.* **2004**, *92*, 576.
123. Tasselli, F.; Jansen, J. C.; Drioli, E. *J. Appl. Polym. Sci.* **2004**, *91*, 841.
124. Kools, W. Ph.D. Dissertation, University Twente, **1998**.
125. Brunetti, A.; Simone, S.; Scura, F.; Barbieri, G.; Figoli, A.; Drioli, E. *Sep. Pur. Technol.* **2009**, *69*, 195.
126. Scharnagl, N.; Buschatz, H. *Desalination* **2001**, *139*, 191.
127. Ohya, H.; Okazaki, I.; Aihara, M.; Tanisho, S.; Negishi, Y. *J. Membr. Sci.* **1997**, *123*, 143.
128. Aerts, P.; Genne, I.; Leysen, R.; Jacobs, P. A.; Vankelecom, I. F. J. *J. Membr. Sci.* **2006**, *283*, 320.
129. Tian, X.; Wang, Z.; Zhao, S.; Li, S.; Wang, J.; Wang, S. *J. Membr. Sci.* **2014**, *464*, 8.
130. Abdel-Hady, E. E.; El-Toony, M. M.; Abdel-Hamed, M. O. *J. Membr. Sci. Technol.* **2012**, *2*, 2.
131. Finken, H. *Desalination* **1983**, *48*, 207.
132. <http://www.nonwovens-industry.com/>.
133. Su, Y. S.; Kuo, C. Y.; Wang, D. M.; Lai, J. Y.; Deratani, A.; Pochat, C.; Bouyer, D. *J. Membr. Sci.* **2009**, *338*, 17.
134. Han, M.-J.; Nam, S.-T. *J. Membr. Sci.* **2002**, *202*, 55.
135. Baker, R. W. *Membrane Technology and Applications*; Wiley: Chichester, **2004**; Chapter 3, pp 89–160.
136. Daniels, C. A. *Polymers: Structure and Properties*; Technomic Publishing Company: Lancaster, **1989**; Chapter 1, pp 1–21.
137. Petermann, J.; Miles, M.; Gleiter, H. *J. Macromol. Sci. Part B: Phys.* **1976**, *12*, 393.
138. Su, J.; Zhang, S.; Chen, H.; Chen, H.; Jean, Y. C.; Chung, T.-S. *J. Membr. Sci.* **2010**, *364*, 344.
139. Duarte, A. P.; Bordado, J. C.; Cidade, M. T. *J. Appl. Polym. Sci.* **2007**, *103*, 134.

140. Jung, B.; Yoon, J. K.; Kimm, B.; Rhee, H.-W. *J. Membr. Sci.* **2005**, *246*, 67.
141. See-Toh, Y. H.; Ferreira, F. C.; Livingston, A. G. *J. Membr. Sci.* **2007**, *299*, 236.
142. White, L. U.S. Pat. 6,180,008 (**2001**).
143. Louie, J. S.; Pinnau, I.; Reinhard, M. *J. Membr. Sci.* **2011**, *367*, 249.
144. Mukherjee, D.; Kulkarni, A.; Gill, W. N. *Desalination* **1996**, *104*, 239.
145. Zhao, T.; Yuan, Q. *J. Membr. Sci.* **2006**, *280*, 195.
146. Vankelecom, I.; Smet, K. D.; Gevers, L. M.; Livingston, A. G.; Nair, D.; Aerts, S.; Kuypers, S.; Jacobs, P. *J. Membr. Sci.* **2004**, *231*, 99.
147. Buyn, H.; Burford, R. *J. Appl. Polym. Sci.* **1994**, *52*, 813.
148. Struzynska-Piron, I.; Loccufier, J.; Vanmaeleband, L.; Vankelecom, I. F. J. *Chem. Comm.* **2013**, *49*, 11494.
149. Staudt-Bickel, C.; Koros, W. J. *J. Membr. Sci.* **1999**, *155*, 145.
150. Hendrix, K.; Van Eynde, M.; Koeckelberghs, G.; Vankelecom, I. F. J. *J. Membr. Sci.* **2013**, *447*, 212.
151. See Toh, Y. H.; Lim, F. W.; Livingston, A. G. *J. Membr. Sci.* **2007**, *301*, 3.
152. Vanherck, K.; Cano-Odena, A.; Koeckelberghs, G.; Dedroog, T.; Vankelecom, I. F. J. *J. Membr. Sci.* **2010**, *353*, 135.
153. Hendrix, K.; Vanherck, K.; Vankelecom, I. F. J. *J. Membr. Sci.* **2012**, *421*, 15.