



# Processing Guide for Polymer Membranes

Over the last thirty years, the use of porous polymer membranes has achieved a significant position as a cost-effective means of non-destructively separating components from fluid mixtures. Membrane technology possesses a number of attractive features in that it can be carried out continuously under mild operating conditions and requires little space. It is also environmentally friendly in that energy consumption is generally very low and few, if any, additives are required. It is both a cleaning and clean technology.

Solvay offers the industry's broadest selection of high-performance polymers for membranes, including:

- Solef® PVDF (polyvinylidene fluoride)
- Halar® ECTFE (ethylene chlorotrifluoroethylene)
- Udel® PSU (polysulfone)
- Veradel® PESU (polyethersulfone)
- Radel® PPSU (polyphenylsulfone)
- Algoflon® PTFE (Polytetrafluoroethylene)
- Fluorolink® PFPE (perfluoropolyether)

These materials are used extensively to manufacture isotropic and anisotropic porous hollow fiber and flat sheet membranes for the entire range of the filtration spectrum from microfiltration (MF) to reverse osmosis (RO). Dense-film gas purification membranes are also readily prepared with these materials.

Excellent chemical resistance over a large pH range, hydrolytic stability, high strength and broad agency certifications make these polymers well-suited for membranes used in demanding end-use environments. Typical application areas include water purification, wastewater treatment, pharmaceutical production, and blood purification along with a variety of industrial process separations, such as food and beverage processing, electropaint recovery and gas separation.

Many of the processes used to make separation membranes require dissolving the polymer in a solvent. Because Solef® PVDF, Udel® PSU, Veradel® PESU and Radel® PPSU are soluble in conventional solvents, they can be solvent cast by the Diffusion Induced Phase Separation (DIPS) process. This process is also referred to as a Non-solvent Induced Phase Separation (NIPS).

The DIPS process is highly sensitive to spinning process variables and dope solution variability, making it essential to closely control both the membrane casting and dope preparation processes. This can only be accomplished by using high-quality polymers with minimal lot-to-lot variability.

Thermally Induced Phase Separation (TIPS) technology is also becoming an attractive manufacturing method for porous membranes. Temperature processing allows the preparation of a defect-free membrane with excellent mechanical performance. Semi-crystalline polymers, such as Solef® PVDF and Halar® ECTFE, can be processed by TIPS due to their solubility in a range of solvents at high temperature.

This document provides useful information about polymer properties as well as guidelines for preparing dope solutions in order to improve the stability and efficiency of your membrane preparation process.

## Solef® PVDF Fluoropolymers

PVDF is a semi-crystalline fluoropolymer obtained by the polymerization of vinylidene fluoride. Solvay Specialty Polymers offers a wide range of PVDF polymers that are marketed under the Solef® tradename.

Solef® PVDF homopolymers are used for making durable, long-lasting membranes. Their toughness, chemical resistance and oxidative stability allow membranes to tolerate a wide variety of feed streams and cleaning methods. The high purity of these materials is widely recognized in other specialty market segments, such as the semiconductor industry, where released contaminants are not tolerated.

In addition to PVDF homopolymers, which are recognized worldwide for their excellent performance in membrane applications, Solvay has developed a wide range of vinylidene fluoride-hexafluoropropylene (VF2-HFP) copolymers and vinylidene fluoride-chlorotrifluoroethylene (VF2-CTFE) copolymers to respond to specific needs of various market segments. Because copolymers are characterized by lower crystallinity than homopolymers,

they have higher flexibility than homopolymers and are soluble in a wider range of solvents, such as ketones and tetrahydrofuran.

Solef® PVDF polymers are readily soluble in typical solvents that are used to manufacture membranes, and they offer a wide range of desirable properties. In particular, Solef® PVDF suspension homopolymers are widely used in membrane filtration applications due to a number of desirable features:

- Excellent toughness and durability
- Outstanding chlorine and UV resistance
- Stability at pH levels from 1 to 11
- High-purity grades
- Global agency approvals
- Easy to form MF and UF membranes

Solef® PVDF homopolymers encompass a broad range of molecular weights; select grades are shown in Table 1. Each grade has a narrow molecular weight distribution, which makes it possible to control viscosities and easier to fine-tune dope solutions as well as maximize process stability.

### Solubility

Solef® PVDF polymers are soluble in aprotic polar solvents, such as dimethylformamide (DMF), dimethylacetamide (DMAC), N-methyl-2-pyrrolidone (NMP), triethyl phosphate (TEP) and dimethyl sulfoxide (DMSO). Solvent polarity, temperature and polymer molecular weight affect the solubility of PVDF. Examples of binary phase diagrams of Solef® PVDF in NMP, TEP and DMSO obtained according to ASTM D6038 are reported in Figures 1 to 3. Additional data showing solubility in other solvents are available upon request.

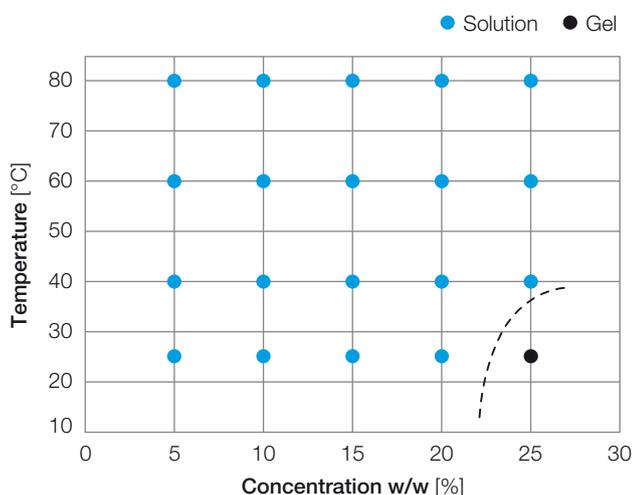
**Table 1:** Typical properties of Solef® PVDF homopolymers

Powder Grades	Melting Point [°C]	Delta H [J/g]	Molecular Weight [Mw, Da] <sup>(1)</sup>	Mw/Mn <sup>(1)</sup>	MFI
Solef® 6010 <sup>(2)</sup>	170–175	58–66	300,000–320,000	2.1–2.6	4.0–8.0 (5.0 kg)
Solef® 6012 <sup>(2)</sup>	170–175	55–65	380,000–400,000	2.1–2.6	4.0–6.0 (10.0 kg)
Solef® 1015	170–175	57–66	570,000–600,000	2.1–2.6	2.8–4.6 (21.6 kg)
Solef® 6015	170–175	55–65	570,000–600,000	2.1–2.6	2.8–4.6 (21.6 kg)
Solef® 6020	170–175	55–65	670,000–700,000	2.1–2.6	≤2.0 (21.6 kg)

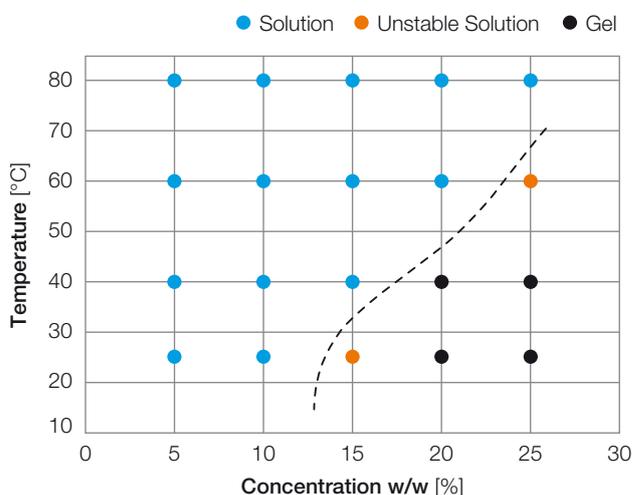
<sup>(1)</sup> Data obtained by gel permeation chromatography in dimethylacetamide (DMAC) and calibrated using a polystyrene standard. Results should be used for a relative comparison among samples only.

<sup>(2)</sup> Available in pellet form

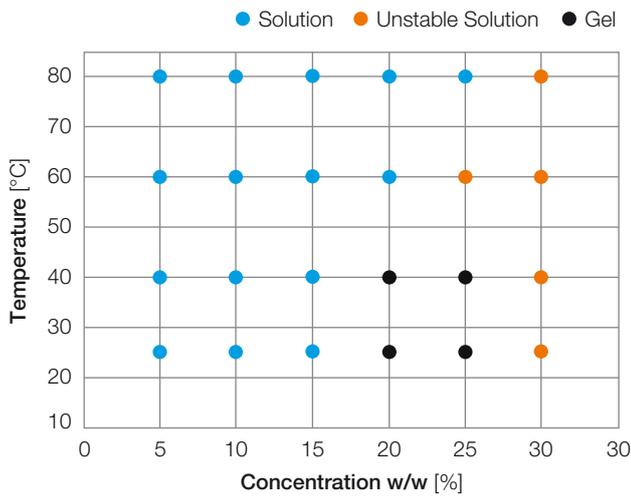
**Figure 1:** Phase diagram of Solef® 1015 in NMP



**Figure 2:** Phase diagram of Solef® 1015 in TEP



**Figure 3:** Phase diagram of Solef® 1015 in DMSO

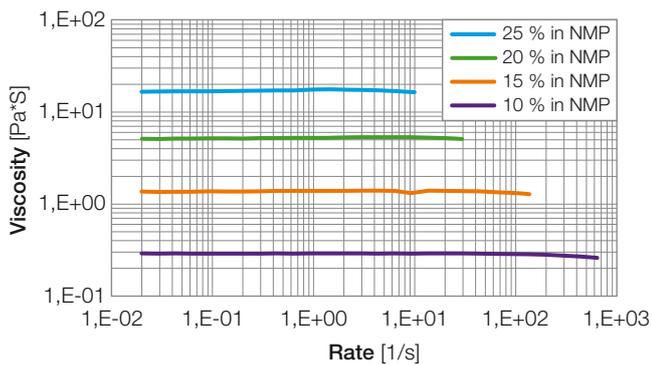


### Solution Viscosity

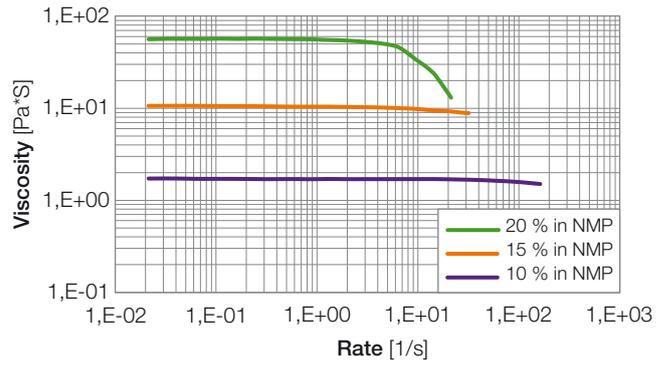
Solution viscosity depends on several parameters, including temperature, polymer concentration, polymer molecular weight and the nature of the solvent. Figures 4 through 10 show curves of Solef® PVDF solutions measured with Rheometer Rheometric Scientific RSFill in steady rate sweep mode using concentric cylinders geometry. Concentrations are expressed as the weight of the polymer over the total weight of the solution.

PVDF solutions generally show newtonian behavior in a wide range of shear rates. Very high viscosity solutions tend to deviate from standard behavior at high shear rates (shear thinning effect). Besides, the chemical nature and quantity of additives has a strong influence on the rheological behavior of the dope solutions.

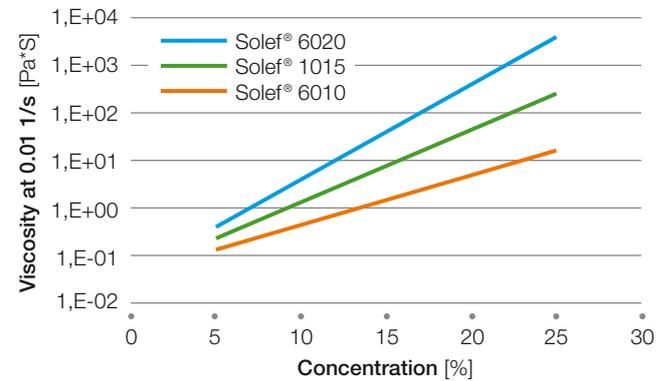
**Figure 4:** Effect of concentration on solution viscosity – Solef® 6010 in NMP at 25 °C



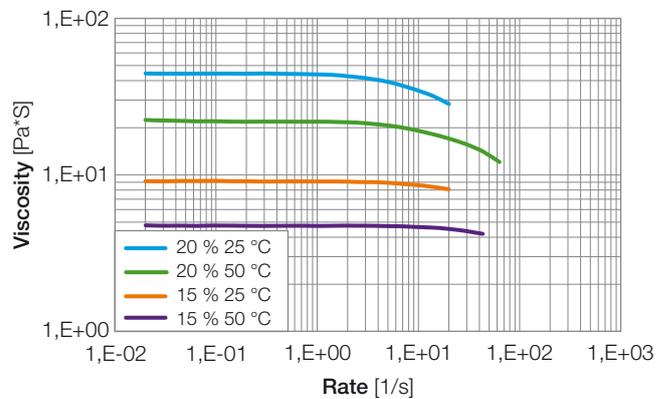
**Figure 5:** Effect of concentration on solution viscosity – Solef® 1015 in NMP at 25 °C



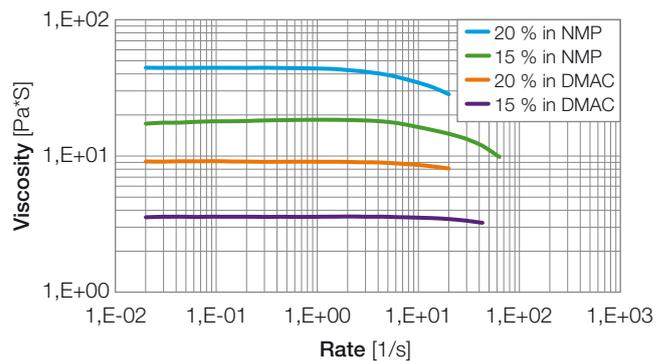
**Figure 6:** Effect of molecular weight on solution viscosity – Solef® PVDF in NMP at 25 °C



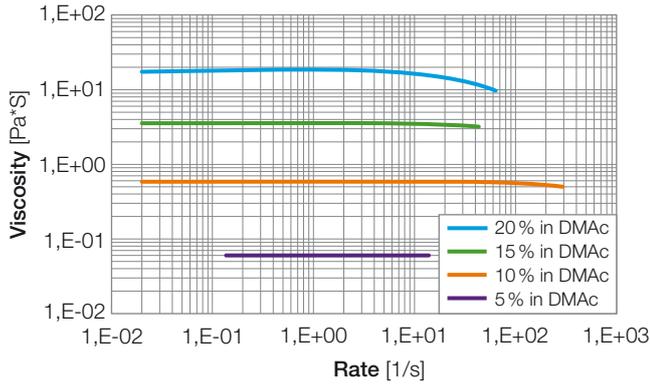
**Figure 7:** Effect of temperature and concentration on solution viscosity – Solef® 1015 in NMP at 25 °C



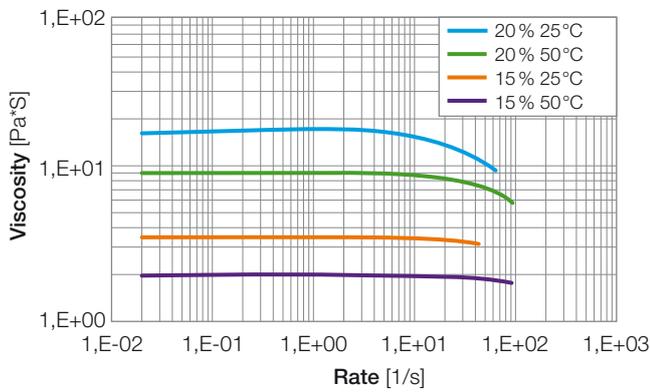
**Figure 8:** Effect of solvent on solution viscosity – Solef® 1015 at 25 °C



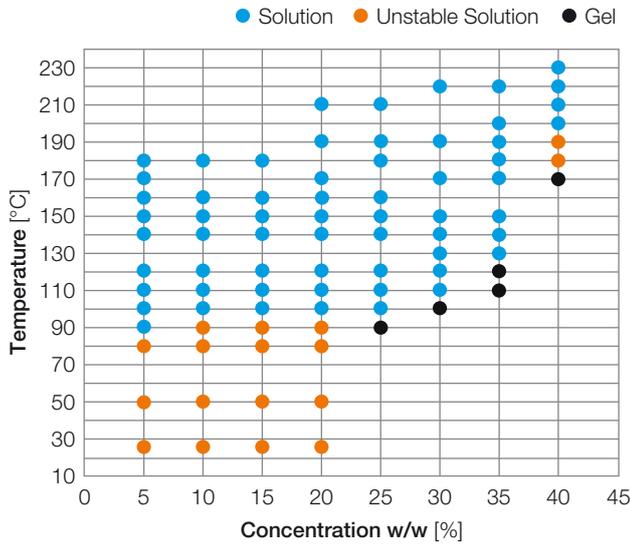
**Figure 9:** Effect of concentration on solution viscosity – Solef® 1015 in DMAc at 25 °C



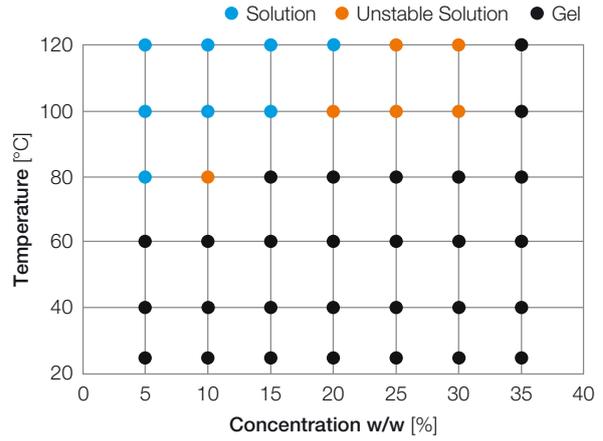
**Figure 10:** Effect of temperature and concentration on solution viscosity – Solef® 1015 in DMAc at 25 °C



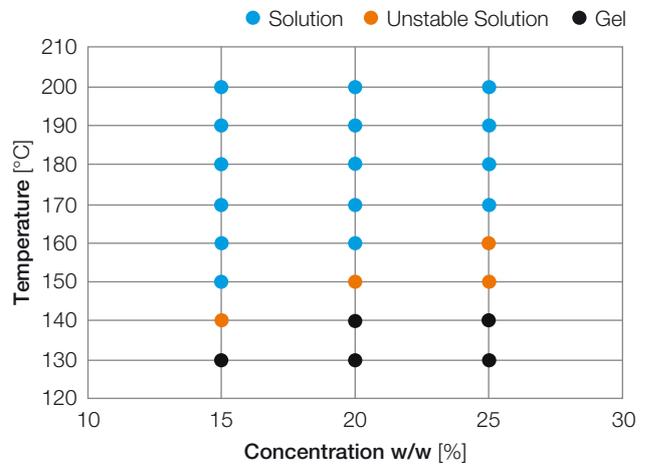
**Figure 11:** Solef® 1015 in TGDA (Triethylene Glycol Diacetate)



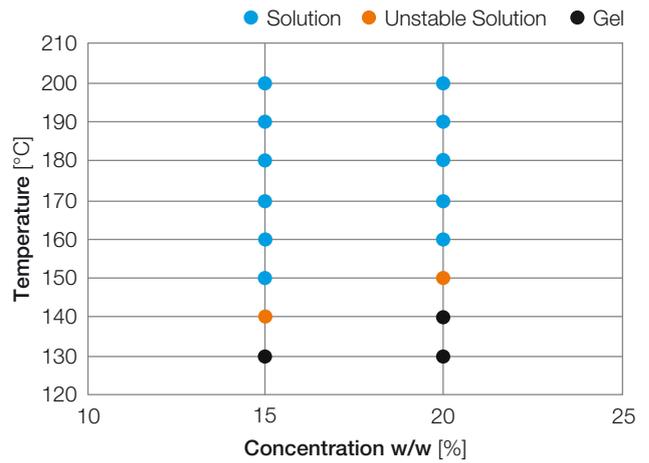
**Figure 12:** Solef® 1015 in PC (Propylene Carbonate)



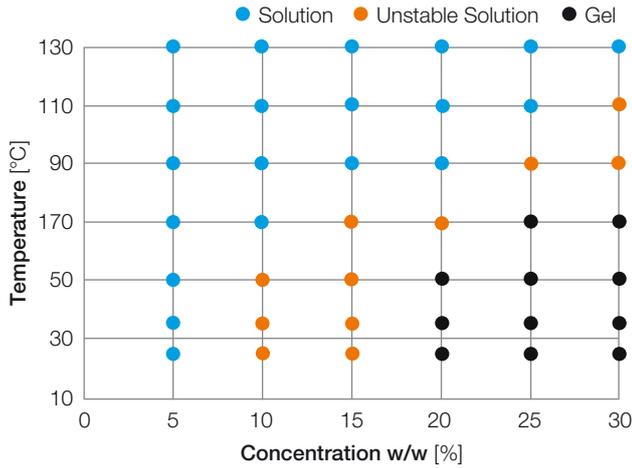
**Figure 13:** Solef® 1015 in Cytoflex A4



**Figure 14:** Solef® 1015 in Cytoflex A2



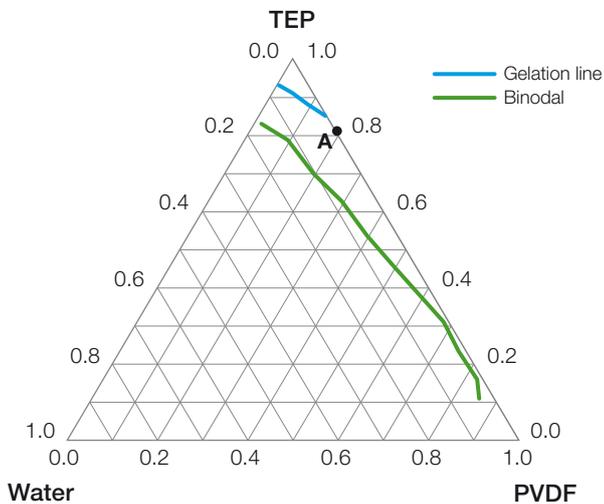
**Figure 15:** Solef® 1015 in Polar Clean



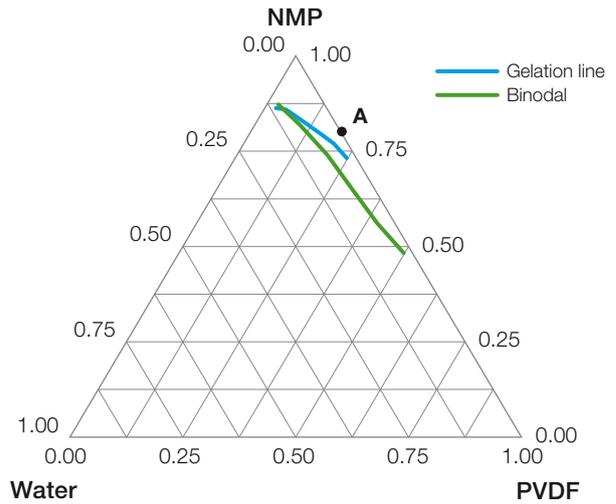
**Solef® PVDF Ternary Phase Diagrams**

Water is most commonly used as the non-solvent to cause the precipitation of PVDF polymers during membrane formation. A small concentration of a non-solvent in the dope solution is also used to modify the phase separation process (rate of polymer precipitation) and the final membrane morphology and porosity. Figures 16 and 17 show a three-component phase diagram for a system of PVDF and water in TEP and NMP solvents at room temperature. Figure 18 shows the effect of temperature on a ternary system with PVDF, DMF and water.

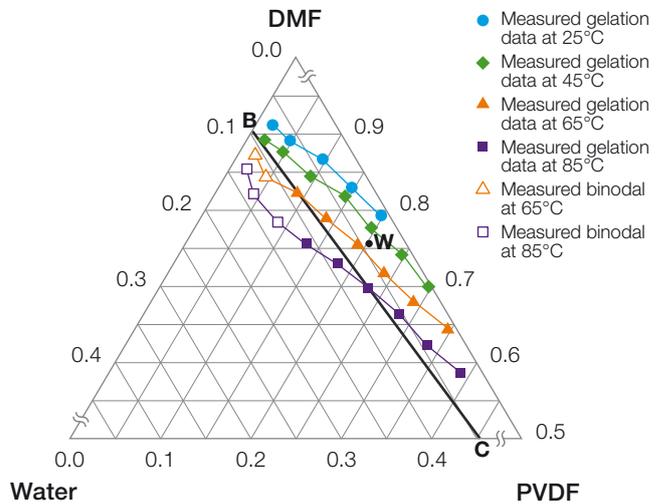
**Figure 16:** Phase diagram – PVDF in TEP



**Figure 17:** Phase diagram – PVDF in NMP



**Figure 18:** Influence of temperature on phase equilibria

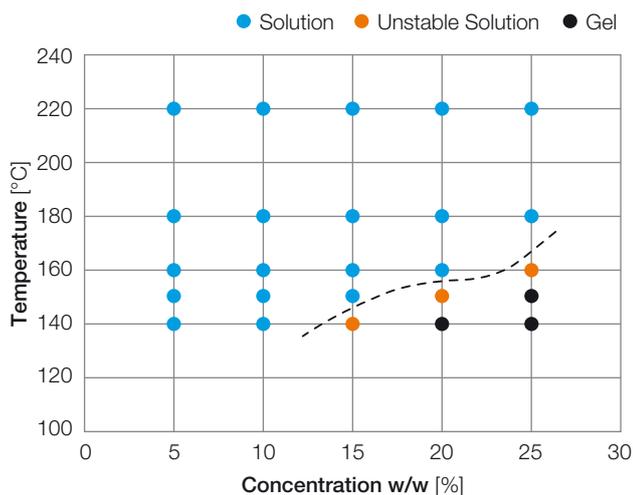


**TIPS Processing**

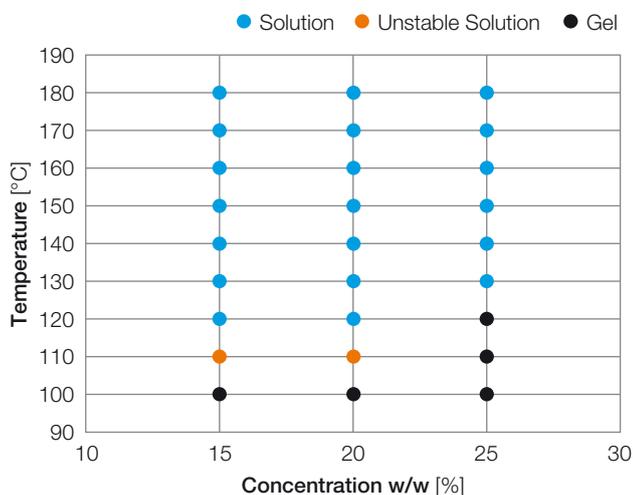
TIPS processing has become an attractive technology for manufacturing PVDF membranes. The main drivers for choosing this manufacturing technology are the durability and excellent mechanical properties that can be achieved due to the absence of macrovoids. Fewer additives and smaller amounts of additives can be utilized, as the main parameters involved in the process are polymer concentration, temperature and cooling rate.

Figures 19 and 20 show examples of the solubility of Solef® PVDF 1015 in acetyl tributyl citrate and glycerol triacetate (GTA), which are suitable non-toxic solvents used for TIPS processing. Other solvents commonly used for TIPS processing are dibutyl phthalate (DBP) and dioctyl phthalate (DOP).

**Figure 19:** Phase diagram of Solef® 1015 in acetyl tributyl citrate

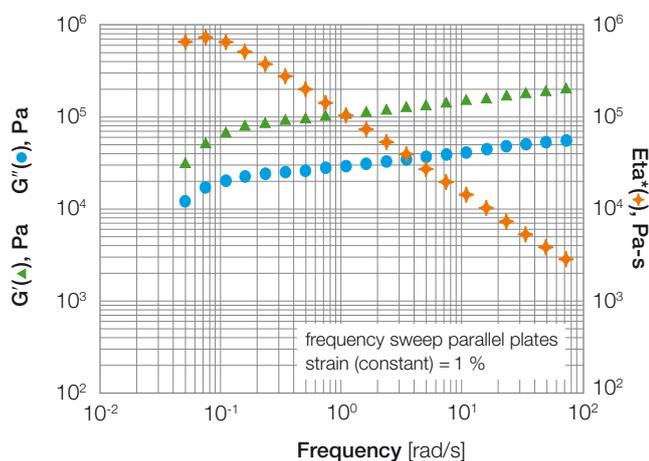


**Figure 20:** Phase diagram of Solef® 1015 in GTA



The viscosity of PVDF/solvent-plasticizer blends and the operating temperature for TIPS are higher than those for DIPS processing; equipment should be properly designed for these characteristics. An example viscosity of a melt blend suitable for TIPS is reported in Figure 21, where a mixture of Solef® PVDF 1015 at 40 % in NMP and 150 °C

**Figure 21:** Solution viscosity of Solef® 1015 in NMP at 40 % w/w and 150 °C



has been tested with Rheometer Rheometric Scientific RSIII in parallel plates configuration. Viscosity, storage modulus and elastic modulus are reported, and all curves show the typical behavior of melt polymers rather than polymeric solutions.

## Halar® ECTFE Fluoropolymers

Halar® ECTFE is a semi-crystalline fluoropolymer based on ethylene and chlorotrifluoroethylene. It is currently used in several market segments where high purity and outstanding resistance to harsh environments are needed, such as meltblown filters for pharmaceutical applications, solvent filtration and semiconductor applications where high ozone resistance is needed. Halar® ECTFE is used in a variety of demanding industries for filtration and anti-corrosion applications, including chemical processing (chemical resistance and low permeation), semiconductors (high purity), wire & cable, and the pharmaceutical industry.

The following features make Halar® ECTFE a suitable material for specialty membranes:

- Stability at pH levels ranging from 1 – 14
- Outstanding resistance to organic solvents, ozone and chlorine
- Very good tensile properties
- Temperature stability up to 150 °C
- Low level of extractibles
- FDA compliance for selected grades

Halar® ECTFE offers outstanding chemical resistance over a broad temperature range. Halar® ECTFE is a hydrophobic material due to its chemical composition. It is possible to modify surface properties with post-treatments that are typically performed at industrial levels for obtaining desired hydrophilic performances on finished membranes.

The general physical properties of the Halar® ECTFE grades available for membrane application are shown in Table 2.

**Table 2: Typical properties of Halar® ECTFE**

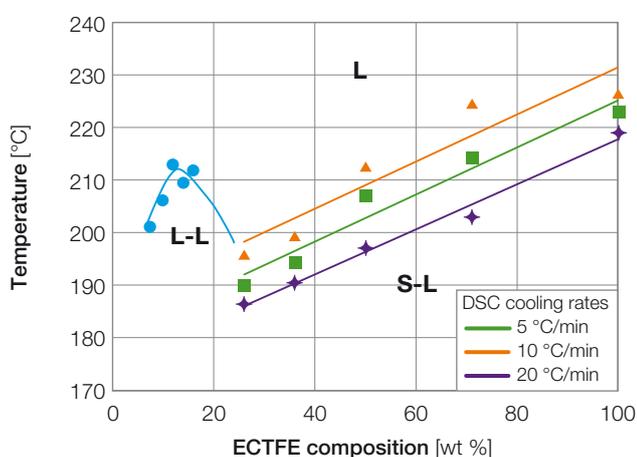
Properties	Units	Halar® 901	Halar® 902	Halar® 9501
Type		Pellet	Pellet	Powder
Melting point	°C	242	242	242
Melt flow index at 275 °C	g/10min 1 at 2.16 kg	1 at 5.0 kg	1 at 5.0 kg	1 at 5.0 kg
Tensile modulus	MPa	1,600–1,800	1,600–1,800	1,600–1,800
Contact angle		90–95°	90–95°	90–95°

Because of its exceptional chemical resistance, Halar® ECTFE cannot be processed using solution phase inversion. It must be processed at temperatures close to its melting point (200 °C to 240 °C) using a TIPS process for manufacturing hollow fiber and flat sheet membranes. Typical solvents used to process this material are acetyl tributyl citrate, glycerol triacetate (GTA), dibutyl phthalate (DBP), and dioctyl phthalate (DOP).

An example of the solubility of ECTFE in dibutyl phthalate (DBP) is reported in Figure 16. When using this solvent, it is possible to obtain a liquid-liquid demixing for concentrations below 25 % and solid-liquid demixing with polymer crystallization for polymer content above 25 %.

It is possible to extend the liquid-liquid demixing region of the phase diagram by changing the polarity of solvent, for instance by adding a non-solvent in the polymer mixture.

**Figure 22:** Phase diagram of Halar® ECTFE in DBP



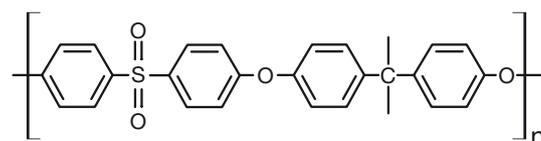
S. Ramaswamy, et al., *Journal of Membranes Science* 210 (2002), 175-180

## Sulfone Polymers

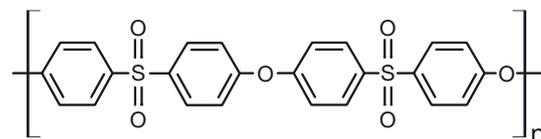
Sulfone polymers are amorphous thermoplastics comprised of aromatic units (phenylenes) bridged with sulfone, isopropylidene or ether moieties. The chemical structures of Udel® PSU, Veradel® PESU and Radel® PPSU are shown in Figure 17. PESU has the highest concentration of sulfone moieties in the polymer repeating unit. This structure gives PESU the highest water absorption of all commercial sulfone polymers, making it the most hydrophilic sulfone polymer (Figure 24).

**Figure 23:** Chemical structures of sulfone polymers

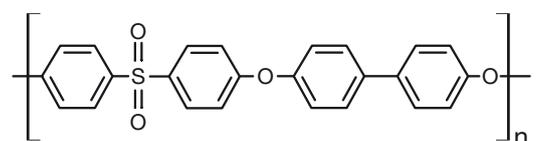
Polysulfone  $T_g = 190\text{ °C}$



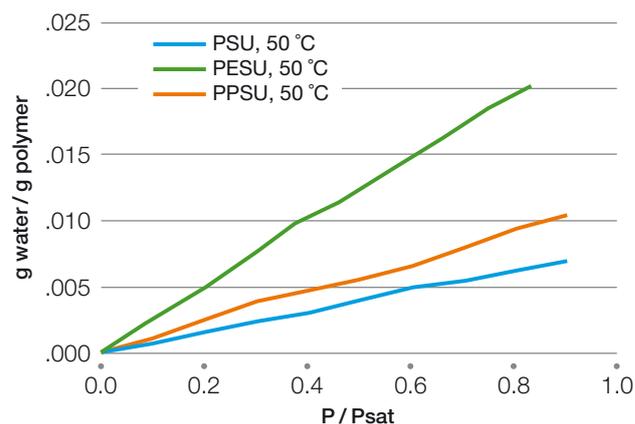
Polyethersulfone  $T_g = 220\text{ °C}$



Polyphenylsulfone  $T_g = 220\text{ °C}$



**Figure 24:** Water absorption data of sulfone polymers



E. Gaudichet-Maurin, F. Thominet and J. Verdu, *Journal of Applied Polymer Science*, 109, 5 (2008), 3279-3285

Sulfone polymers offer a unique combination of features for membrane filtration applications. They can withstand a variety of sterilization techniques, including steam, gamma, e-beam, and ethylene oxide. They can be readily formed into MF and UF hollow fiber and flat sheet membranes with highly controllable pore size distribution. In addition, they exhibit:

- Very high mechanical strength and creep resistance
- Stable at pH levels from 2–13
- Outstanding hydrolytic stability and caustic resistance
- Good resistance to moderate concentrations of chlorine
- Low levels of extractable and insoluble materials
- Outstanding biocompatibility
- Global agency approvals

## Molecular Weight and Solution Viscosity

As with the PVDF polymers, Solvay's sulfone polymers are offered in a broad range of molecular weights. Each grade has a narrow molecular weight distribution, which makes it possible to control viscosities and easier to fine-tune dope solutions and maximize process stability.

Tables 3 and 4 respectively show typical solution viscosities and molecular weight data for select sulfone polymers used in membrane production. Molecular weight data were obtained by gel permeation chromatography according to ASTM method D5296-05. Figure 25 shows the solution viscosity of sulfone polymers as a function of concentration.

**Table 3:** Solution viscosity of selected sulfone polymers\*

Polymer	Grade	Solution Viscosity Range [cP]
PSU	Udel® P-1700 LCD	1,400–1,900
	Udel® P-3500 NT LCD	1,900–2,200
	Udel® P-3500 LCD MB3	2,200–2,800
	Udel® P-3500 LCD MB7	2,200–2,700
	Udel® P-3500 LCD MB8	2,400–3,000
PESU	Veradel® 3000MP	1,600–2,000
	Veradel® 3000P	1,225–1,650
	Veradel® 3100P	700–900

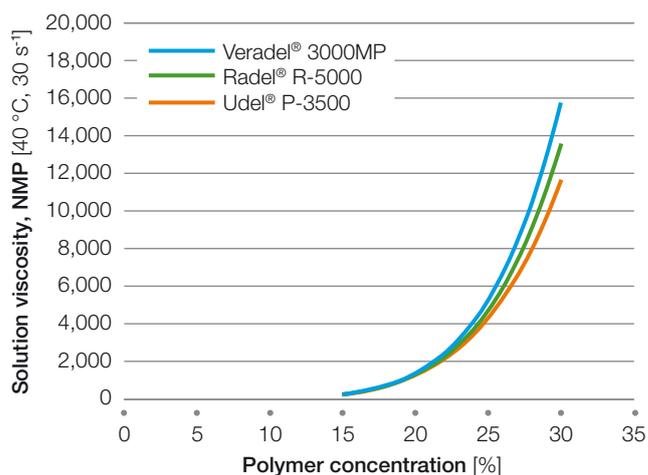
\* 25% solids in DMAC at 40 °C

**Table 4:** Typical molecular weights of selected sulfone resins

Polymer	Grade	Mn*	Mw*
PSU	Udel® P-1700 LCD	21	67–72
	Udel® P-3500 LCD	22	75–81
	Udel® P-3500 LCD MB3	22	78–84
	Udel® P-3500 LCD MB7	22	77–83
	Udel® P-3500 LCD MB8	23	80–86
PESU	Veradel® 3000MP PESU	21	64–68
	Veradel® 3000P PESU	19	62–64
	Veradel® 3100P PESU	17	52–55

\* g/mol x 10<sup>3</sup>

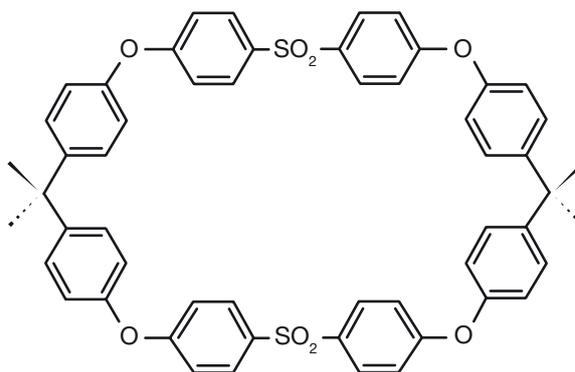
**Figure 25:** Solution viscosity of sulfone polymers as a function of concentration



## Cyclic Oligomers

During the production of PSU, small quantities of cyclic oligomers are formed; cyclic molecules have a lower solubility than molecules with a linear structure. The chemical structure of the prevalent cyclic species in Udel® PSU, the dimer, is shown in Figure 26.

**Figure 26:** Cyclic dimer structure



Solvay carefully controls its PSU manufacturing process in order to minimize the formation of cyclic oligomers. For some PSU membrane applications, particularly fine hollow fiber membrane production, it has proven beneficial to use a low cyclic dimer (LCD) grade of Udel® PSU to prolong dope solution stability and prevent filter clogging or spinneret fouling. The use of LCD grades can also help minimize fiber breakage and membrane surface defects.

The cyclic dimer content in Udel® P-3500 LCD is around 1.1%. The processes used to make PESU and PPSU are both characterized by an inherently low quantity of cyclic oligomers. Precipitation of cyclic oligomers is typically not a problem in the production of PESU and PPSU membranes.

## Solubility

Sulfone polymers are soluble in aprotic polar solvents such as dimethylformamide (DMF), dimethylacetamide (DMAC) and N-methyl-2-pyrrolidone (NMP).

Udel® PSU is soluble in a number of other solvents as well.

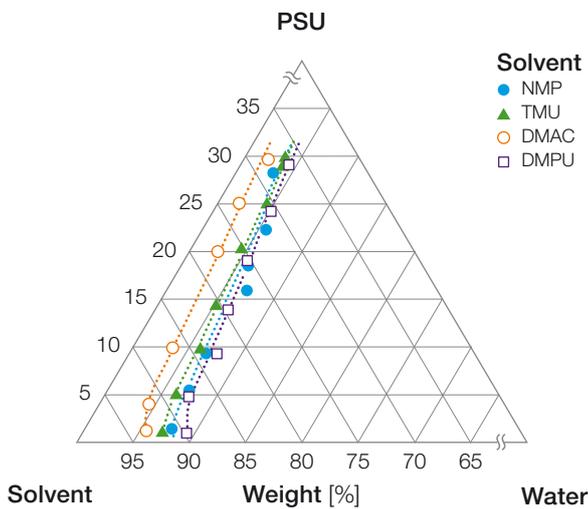
Radel® PPSU is the most difficult to put into solution, so it can take longer to dissolve. Table 5 lists some common solvents for these materials in which solubility is greater than 10 % by weight at 23 °C.

Sulfone polymer solution viscosity varies between polymers and is strongly influenced by polymer concentration as shown in Figure 25. Phase equilibria for PSU and PESU in various solvent-water systems are shown in Figures 27 and 28.

**Table 5:** Sulfone polymer solvents for membrane production

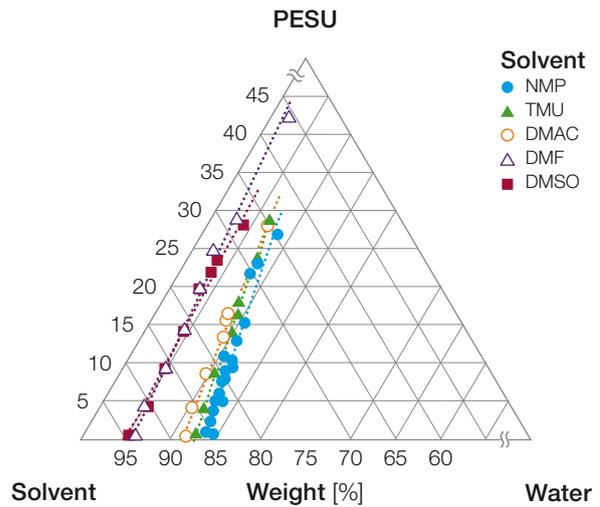
Solvent	Udel® PSU	Veradel® PESU	Radel® PPSU
N,N-dimethylformamide (DMF)	✓	✓	✓
N,N-dimethylacetamide (DMAC)	✓	✓	✓
N-methyl-2-pyrrolidone (NMP)	✓	✓	✓
Tetrahydrofuran (THF)	✓		

**Figure 27:** Polymer precipitation curves of PSU/water with various solvents at 25 °C



W.W.Y. Lau, M.D. Guiver, and T. Matsuura, *Journal of Membrane Science* 59 (1991), 219-7

**Figure 28:** Polymer precipitation curves of PESU/water with various solvents at 25 °C



W.W.Y. Lau, M.D. Guiver, and T. Matsuura, *Journal of Membrane Science* 59 (1991), 219-7

## Solution Preparation

Solvent choice is a fundamental consideration that is extremely important in dope solution preparation. For a more consistent spinning process, it is important to select a solvent with high purity and minimal water content. When using a solvent recycling system, monitor solvent purity regularly and ensure that the recycling system is working properly.

To optimize dope solution viscosity, select the most appropriate molecular weight polymer in order to tightly control the process parameters. High molecular weight polymers lead to high viscosity solutions and take longer to dissolve; however, a higher molecular weight may be required to ensure adequate strength of the nascent membrane during processing as well as the finished membrane during use.

Solef® PVDF, Udel® PSU, Veradel® PESU, and Radel® PPSU polymers are compatible with a variety of pore-forming additives, such as polyvinylpyrrolidone (PVP) and polyethylene glycol (PEG). These additives can also improve the hydrophilicity of the finished membrane.

Some precautions may be required when using high molecular weight PVP as a pore-forming additive since PVP can be sensitive to radical degradation. To maximize dope viscosity stability, select a PVP grade that contains low peroxide content and is packed in inert packaging. Low gel and other insoluble content can also minimize filter clogging and membrane defects. Non-solvent additives in membrane dopes include alcohols, water and organic acids.

When preparing membrane polymer solutions, slowly add the polymer to the solvent while agitating. Adding it too quickly can lead to the formation of aggregates that will take longer to dissolve. The geometry of the stirrer, the agitation rate, and the temperature all affect the time needed to dissolve the polymer.

Membrane dopes containing PVP and PEG should be dissolved under nitrogen to keep the dope solution viscosity as stable as possible. This is critical when high molecular weight PVP is used in the formulation. It is recommended that dope solutions are stored under nitrogen and used within 48 hours of preparation to minimize changes in solution viscosity.

For more solution preparation proposals, please contact your Solvay expert.

Summary of recommendations for preparing solutions:

- Dissolve the polymer before introducing additives
- Add polymer slowly to the solvent while stirring the solution
- Be aware that the geometry of stirrer and agitation rate will influence time to dissolve
- Heat the solution to reduce time to dissolve; the upper temperature limit will depend on the solvent
- Use dry solvents, a dry environment and consider nitrogen blanketing
- Use pure solvents and avoid contamination with salts or bases
- Check that the dope solution is stable for the necessary storage time before spinning under desired storage temperature

## Specific Material Handling Guidelines

### Solef® PVDF

Using Solef® PVDF in powder form allows faster dissolution than pellets which are more easily weighed and handled. Raising the solution temperature to 70 °C to 80 °C, depending on the solvent, will reduce the time necessary for obtaining complete dissolution of PVDF. If the solvent contains a trace of alkali components or amines, the solution may become discolored. This phenomenon does not affect the properties of PVDF or the properties of the final membrane in that solution viscosity is not affected.

### Sulfone Polymers

Udel® PSU in standard pellet form is readily dissolved in DMF, DMAc, and NMP. Subject to solvent boiling points, temperatures up to 100 °C may be used to dissolve sulfone polymers. Typically, dope solutions are extremely viscous; therefore, using baffles does not enhance solution preparation. A standard triple-bladed impeller agitator at speeds up to 500 rpm can be used to dissolve materials.

If PVP is included as part of the dope solution formulation, we recommend using a special LCD grade of Udel® PSU for improved compatibility with PVP.

## Regulatory Approvals

Solvay is committed to maintaining and updating its status with global agencies and specifications, and maintains a large range of global agency listings for food (NSF 51), water (NSF 61), and medical applications (ISO 10993, etc.). Regulatory status varies by grade. Please contact your Solvay representative for the current regulatory status of specific grades.

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