Fabrication of membranes of polyethersulfone and poly(N-vinyl pyrrolidone):
Influence of glycerol on processing and transport properties

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Abstract: In this study, we focus on membranes of polyethersulfone (PESU) and poly(N-vinyl pyrrolidone) (PVP) and elucidate the influence of composition on the rheological, diffusion and precipitation properties of solutions which are used for membrane preparation via a non-solvent induced phase separation process. The low molar mass component of the solution is a mixture of the solvent N-methyl-2-pyrrolidone (NMP) and the non-solvent glycerol. Cloud point measurements, viscosity and diffusion measurements as well as precipitation experiments were performed in order to achieve a comprehensive understanding of the time-dependence of the precipitation process. The addition of glycerol yields an increase of viscosity and a stronger tendency of demixing. The enhanced tendency of demixing causes a more rapid precipitation process. The average relaxation time of the solution as a function of glycerol concentration follows a similar trend as its viscosity. The increase of viscosity is associated with the increase of the monomeric friction coefficient. Two diffusive processes with clearly separated time scales appear in dynamic light scattering experiments in the presence of glycerol. This phenomenon is discussed taking into account the phase behaviour of the solution and the quality of the solvent. The addition of glycerol yields a lower pure water permeance whereas the molecular weight cut-off is not altered and in the ultrafiltration range.

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INTRODUCTION

Membranes of poly(aryl ethers) and poly(N-vinyl pyrrolidone) are frequently used for water treatment applications.\textsuperscript{1-3} Permeability, retention, molecular weight cut-off and the resistance against fouling are key properties which characterize the membrane. Essential morphological parameters which determine the membrane performance are pore size distribution and porosity. Consequently, a deep knowledge of the mechanisms which determine morphology formation in membrane fabrication is crucial for production of tailored membranes, both for porous as well as dense polymer membranes.\textsuperscript{4} However, until now a profound understanding of morphology formation during membrane preparation has been only partially achieved. An example is the pioneering work of Strathmann et al.\textsuperscript{5} where the influence of the precipitation rate on the membrane morphology was investigated. Nowadays, a large number of investigations aims to establish structure-processing-property relations for polymer membranes which are prepared by the non-solvent induced phase separation process (NIPS), see, e.g., the work of Hopp-Hirschler et al.\textsuperscript{6} For example, in the work of Bakeri et al.\textsuperscript{7} the phase separation behavior of polyetherimide solutions for different non-solvents and coagulants was investigated. An essential question is the choice of the appropriate composition of the casting or spinning solution, the bore fluid in case of hollow fiber spinning and the coagulation bath. A variety of solvents has been chosen for membrane preparation. However, glycerol has been used to a much lesser extent and only to a limited amount.\textsuperscript{8}

In previous works, various studies were performed which focused on the effect of processing conditions on the performance of polysulfone and polyethersulfone membranes.\textsuperscript{9} The study of Barth et al.\textsuperscript{9} revealed that an increasing polymer concentration in the solution leads to a smaller pore size. The general mechanism of structure formation in membrane preparation using polyethersulfone (PESU), poly(N-vinyl pyrrolidone) (PVP) and N-methyl-2-pyrrolidone (NMP) is elucidated in the work of Wienk et al.\textsuperscript{10} Generally, polyethersulfone has a higher tendency to form finger-like
structures than polysulfone because of the polarity of PESU. However, in technological applications a uniform morphological structure is preferred. Another study focused on the effect of the dope extrusion rate. A higher dope extrusion rate led to a lower water flux. Theoretical investigations were carried out by Boom et al. who analyzed the phase diagram of dope solutions. In the work of Guillen et al. it has been shown that a sponge-like morphology is created by a slow exchange of solvent and non-solvent, whereas a fast solvent/non-solvent exchange yields a finger-like morphology. Hopp-Hirschler et al. discussed in detail the role of viscous fingering in membrane formation. The role of shear fields has been addressed in the work of Gordeyev et al. Under practical conditions, shear flow at high shear rates mainly influences the molecular orientation of the polymer chains, but does not induce demixing.

Several publications are devoted to specific aspects of membrane preparation. Increasing the viscosity of the casting solution leads to a pronounced hindrance against phase separation. In the work of Han and Nam, the influence of PVP concentration was investigated and an optimum PVP concentration with respect to membrane permeability was found. The authors emphasized the role of thermodynamics (reduction of miscibility by addition of PVP) and rheology (kinetic hindrance because of high solution viscosity). An essential aspect is the mutual diffusion of the different components. A direct correlation between thickness of the membrane and the viscosity of the casting solution was found by Torrestiana-Sanchez et al. Furthermore, the addition of PVP or poly(ethylene oxide) (PEO) increased the porosity and consequently membrane permeability. A comparison between linear and hyperbranched polyethersulfone membranes was made by Yang et al. The hyperbranched polyethersulfone led to a smaller average pore diameter and a narrower pore size distribution than its linear counterpart. The influence of PVP on polyethersulfone membranes for hemofiltration has been also studied. It was shown that a PVP with a molecular weight of 360 kg/mol led to a negatively charged, hydrophilic inner surface of the hollow fiber membrane. Hollow fiber membranes were also prepared by Alsalhy et al. The authors applied a so-called steam/wet/dry process for membrane fabrication and analyzed the influence of processing parameters on the separation performance and the mechanical properties of the membrane. A strong influence of the PEO concentration in the dope solution on the membrane properties was found. Different types of additives for membrane fabrication
were tested in the work of Susanto and Ulbricht.\textsuperscript{20} The triblock copolymer Pluronic® seems to be the most efficient additive for practical applications. Consequently, it and related additives have been used in a variety of publications.\textsuperscript{3, 21-23}

In this study, we focus on the effect of the solution composition on membrane properties. The objective of this work is to analyze the role of glycerol on the fabrication of membranes of polyethersulfone and poly(N-vinyl pyrrolidone), since glycerol strongly affects the membrane structure. The change of the thermodynamic properties by addition of glycerol is studied. Rheological and dynamic light scattering experiments are carried out in order to characterize the dynamical properties of the polymer solutions. Furthermore, precipitation experiments are performed in order to compare qualitatively these experimental results with the analysis of Strathmann et al.\textsuperscript{5}

\section*{MATERIALS AND METHODS}

\textit{Materials}

The polymeric components of the solutions are commercial grades of polyethersulfone (PESU, Ultrason® E 3010, BASF SE, Ludwigshafen) and poly(N-vinyl pyrrolidone) (PVP, Luvitec® K90, BASF SE, Ludwigshafen). Ultrason® E 3010 and Luvitec® K90 were used as received. Sodium hypochlorite (14% chlorine in aqueous solution) was obtained from VWR International GmbH (Darmstadt, Germany). The weight averaged molecular weight of PESU was $M_w = 58\ 000\ \text{g/mol}$ (determined by gel permeation chromatography (GPC) in dimethylacetamide (DMAc) (calibration with a PMMA standard). The dispersity was equal to 3.3. Poly(N-vinyl pyrrolidone) has a viscosity characterized by the K-value of 90, determined according to the method of Fikentscher.\textsuperscript{24} The number averaged molecular weight of this PVP is in the order of $1.4\times10^6\ \text{g/mol}$ with a dispersity in the order of 4.3.\textsuperscript{25} The low molar fluids were N-methyl-2-pyrrolidone (NMP) (solvent) and glycerol (non-solvent) and were also used as received. N-methyl-2-pyrrolidone was supplied by BASF SE (Ludwigshafen). Glycerol (purity larger than 99.5\%) was purchased from Cremer Oleo GmbH & Co. KG (Hamburg, Germany). The chemical structure of the polymers and the solvents is shown in Figure 1.
Preparation of polymer dope solutions

In this study, two different methods (A and B) for solution preparation were used. Before mixing, the commercial polymers were dried at 130 °C for at least 24 hours under vacuum (method A). Then the polymers and the organic solvent were mixed using a magnetic stirrer at a temperature of 60 °C. After mixing, the solutions were degassed under vacuum for 2 hours.

The second method (denoted by method B) implied homogenizing the components polyethersulfone and poly(N-vinyl pyrrolidone) in the mixture of N-methyl-2-pyrrolidone and glycerol by using a SpeedMixer™ DAC 600 (Hauschild & Co. KG) with increasing mixing speeds of 800, 1100, 1500 and 2000 rpm within 60 minutes.

The composition of the solutions of method B was 19 wt% PESU, 6 wt% PVP and 75 wt% solvent. The composition of the solvent (NMP or its mixtures with glycerol with a glycerol content up to 10 wt%) was varied by changing the glycerol concentration in the complete solution from 0 to 10 wt%. A similar composition of the polymer components has been used in a related study.\textsuperscript{15} Furthermore, additional solutions for dynamic light scattering experiments were prepared using method A.

Cloud point measurements

The cloud point measurements were performed as follows: The polymer solution was put into a glass flask which was heated using a water bath of 20 °C and 60 °C, respectively. Then water or a water/NMP mixture (60/40 wt%), respectively, was added to the solution using a titration device until the solution changed from transparent to turbid (point of precipitation). After each addition of a liquid drop (water or the water/NMP mixture) the polymer solution was shaken again for at least one hour in
order to verify whether a transparent state is achieved. The mass of added water was
determined and the weight fraction of added water at each step was calculated.

**Rheological experiments**

All rheological measurements were performed at 60 °C. The viscosity of mixtures of
NMP and glycerol was measured using an Ubbelohde viscosimeter (iVisc LMV 830,
LAUDA-Scientific GmbH, Lauda-Königshofen). The kinematic viscosity is directly
measured and then converted into the dynamic viscosity using the measured value of
the solution density (Density Meter DMA™ 4100 M, Anton Paar, Graz, Austria).

The rheological experiments were performed using a rotational rheometer (MCR 502,
Anton Paar, Graz, Austria). A concentric cylinder geometry (Searle type) was chosen
for the investigations. First a defined amount (14.0 mL) of the bubble-free solution was
inserted into the gap of the Searle geometry. A waiting time of 10 min was chosen in
order to guarantee that temperature equilibration was achieved. So-called frequency
sweeps were performed. In order to determine the linear viscoelastic range of the
oscillatory shear measurements, an amplitude sweep was performed at an angular
frequency of \(\omega = 10 \text{ rad/s}\) where the shear amplitude \(\gamma_0\) was varied between 0.2 and
20%. A shear amplitude of \(\gamma_0 = 10\%\) was chosen for the frequency sweeps. The
frequency was incrementally reduced from 100 rad/s to 0.01 rad/s (5 points per
decade).

**Dynamic light scattering**

In order to study diffusion phenomena and to determine the diffusion coefficient which
is associated with these diffusion processes, dynamic light scattering (DLS)
experiments were performed with an ALV/CSG-3 Compact Goniometer-System (ALV-
Laser Vertriebsgesellschaft GmbH, Langen, Germany) which was equipped with an
ALV/LSE-5003 multiple tau digital correlator (for variation of the glycerol
concentration). The light source was a HeNe laser with a wavelength \(\lambda\) of 632.8 nm.
The experiments to vary the PVP and PESU concentration were performed with an
ALV/CSG-3 Compact Goniometer-System (ALV-Laser Vertriebsgesellschaft GmbH)
which was equipped with an ALV-7004 multiple tau correlator. The light source was a
Nd-YAG laser with a wavelength \(\lambda\) of 532.0 nm. The scattering angle \(\theta\) was varied
between 40° to 140° in increments of 5°. The magnitude \(q\) of the Bragg wave vector is
related to the wavelength \(\lambda\) and the solvent refractive index \(n\) by
\[ q = \frac{4\pi n}{\lambda} \sin(\theta/2). \] (1)

The sample vials (material glass) were placed into a measurement cell which was filled with toluene. The toluene bath was tempered by a Julabo F25 thermostat working with a mixture of water and ethylene glycol. The accuracy of the temperature was 0.01 °C. Each sample was measured at two temperatures, i.e. 20 °C and 60 °C. The time for a measurement at a constant angle was 120 s.

A fit procedure was applied in order to determine the relaxation time spectrum. A sum of two exponential functions was used as fit function for the field autocorrelation function to determine the mean relaxation rate \( \Gamma \) and the fast relaxation process. The fit was implemented as a non-linear cumulant analysis in Matlab (see ref. 26 for details). The series expansion was taken until the second order. In order to determine the relaxation time spectrum the software NLREG\textsuperscript{27} was used which is based on a regularization routine.\textsuperscript{28}

Precipitation experiments

A special precipitation experiment was carried out in order to elucidate the time-dependence of the precipitation process. The experimental set-up is similar to the technique proposed by Frommer and Lancet,\textsuperscript{29} see Figure 2. The experiment focuses on the time scale of diffusion of a water/NMP 60/40 (wt\%) mixture in the polymer solution and on the morphological features of the membrane.

![Figure 2: Scheme of the experimental set-up of the precipitation experiment which is performed using a light microscope.](image)

In our experiments, two tapes are fixed on the longer edges of a glass slide. A drop of the polymer solution is placed on the bottom glass slide. Then another glass slide is immediately put onto the droplet of the polymer solution with a distance of 30 mm to a
short edge. The two tapes guarantee that the gap between the two glass slides is constant (approx. 50 µm). A mixture of Millipore water and NMP (weight ratio of water/NMP: 60/40) is put using a syringe on the free part of the bottom glass plate. Driven by capillary forces, the water/NMP mixture flows in the gap between the bottom and the top glass plate which leads to precipitation of the solution droplet. Using an optical microscope (Leica DM LM, Wetzlar, Germany) equipped with a digital camera (Leica Type DFC320), the time-dependence of this precipitation process is monitored by an image acquisition software IMS (IMAGIC AG, Glattburg, Switzerland). By analysis of the video images, the displacement of the diffusion front of the water/NMP mixture is measured as a function of time. This experiment mimics the real precipitation process which takes place during membrane casting. These experiments were performed at room temperature similar to fabrication of the flat sheet membranes.

Casting of flat sheet membranes

The casting solutions were prepared by dissolving 19 g polyethersulfone with 6 g poly(vinyl pyrrolidone) and 0 to 10 g glycerol as additional dope additive in 75 to 65 g N-methyl-2-pyrrolidone. Under gentle stirring the mixture was heated at 60 °C until a homogeneous and clear viscous solution was obtained. To remove air bubbles the solution was subsequently degassed overnight at room temperature. Then the polymer dope solution was cast onto a glass plate by means of a knife with a thickness of 300 µm with a casting speed of 5 mm/s. Before immersion in the aqueous coagulation bath containing 40 wt% NMP at 25 °C for 10 min the polymer dope film could rest for 30 s. After the membrane had detached from the glass plate, it was carefully transferred into a water bath for 12 h. Subsequently the membrane was transferred into a bath containing 2000 ppm sodium hypochlorite at 60 °C for 1.5 h and then washed with water at 60 °C and one time with a 0.5 wt% solution of sodium bisulfite to remove active chlorine. Until characterization regarding pure water permeability (PWP) and minimum pore size the membrane was stored wet in distilled water.

Membrane characterization

The pure water permeance (PWP) of the membranes was determined with sample specimens of 60 mm diameter using a pressure cell using ultrapure water (salt-free water, filtered by a Millipore UF-system).
The molecular weight cut-off (MWCO) was measured with PEO ultrafiltration and GPC sieving curve analysis according to use a total PEO concentration of 2.5 g/L in water.\textsuperscript{30} The concentration polarization effect on the rejection was kept minimal by using the lowest possible pressure of 0.15 bar. The value of the molecular cut-off was defined as the molecular weight from which 90% rejection takes place.

The ultrafiltration membrane samples were subjected to solvent exchange with ethanol/water mixtures of increasing alcohol content and subsequently dried overnight at 40 °C in vacuum. Then the samples were characterized using mercury intrusion porosimetry with an Autopore V (Micromeritics, Norcross (GA), USA).

The membrane morphology was determined by means of scanning electron microscopy (SEM). Liquid nitrogen was used to immerse the membranes obtained before fracture. The specimens were mounted on a sample holder and sputter coated with a gold layer of 5 nm thickness to confer electrical conductivity. The cross-sectional morphology was determined using a scanning electron microscope (Phenom Pro X, Phenom-World) with a magnification of 1500x and 5000x at an acceleration voltage of 15 kV.

RESULTS AND DISCUSSION

Cloud point measurements

The results of cloud point measurements are shown in Figure 3. Pure water and a water/NMP mixture (60/40 wt/wt) were used as non-solvents in Figures 3(a) and (b), respectively. An increasing fraction of glycerol leads to a lower amount of non-solvent until demixing takes place. The data in Figure 3(a) reveal that a linear relationship holds with only minor differences between the data at 20 °C and at 60 °C. If a water/NMP (60/40 wt%) mixture is used as non-solvent (Figure 3(b)), generally higher concentrations of the non-solvent are necessary in order to cause precipitation, since NMP is a solvent for PESU and PVP. Thus a linear relation also holds in the case of the water/NMP mixture. The data in Figure 3(b) indeed are approximately equal to the data in Figure 3(a) if only the added water concentration is plotted versus $c_{\text{Glycerol}}$. In conclusion, the addition of glycerol yields a stronger tendency of phase separation. Consequently, phase separation during membrane casting should take place more rapidly with increasing fraction of glycerol if the solution viscosity remains constant.
Figure 3: Results of cloud point measurements using (a) pure water and (b) a water/NMP (60/40 wt%) mixture as non-solvent. $\phi_{\text{non-solvent}}$ is the concentration of water and the water/NMP mixture, respectively, at the cloud point and $c_{\text{Glycerol}}$ is the concentration of glycerol (both in wt%). The temperature of the solution is indicated.

**Rheology**

The viscosity of glycerol is larger than the viscosity of NMP because of the hydrogen bonding, see also the review of Ferreira et al.31 and the data in Figure 4. Consequently, the addition of glycerol leads to an overall increase of viscosity which directly influences the viscosity of the polymer solution. The increase of viscosity follows in total a strongly nonlinear trend in the whole concentration range. However in this study, the concentration range of 0 to 10 wt% for glycerol is of relevance where a linear dependence (low glycerol concentrations) of the dynamic viscosity as a function of glycerol concentration was observed at the measurement temperature of 60 °C (see the inset of Figure 4).
Figure 4: Dynamic viscosity (in mPa s) of mixtures of N-methyl-2-pyrrolidone and glycerol at a temperature of 60 °C. The inset shows the range of concentrations from 0 to 10 wt% glycerol. A linear curve was fitted to these data.

![Figure 4](image)

Figure 5: (a) Storage modulus $G'$ and loss modulus $G''$ as functions of angular frequency $\omega$ for solutions of 19 wt% PESU, 6 wt% PVP, $x$ wt% glycerol and $(75 - x)$ wt% NMP. $T = 60 ^\circ C$. (b) Magnitude of complex viscosity $\eta^*$ for these solutions as a function of $\omega$. (c) Zero shear rate viscosity $\eta_0$ and (d) average relaxation time $\tau$ versus concentration of glycerol based on the fit shown in (b).

![Figure 5](image)

Figure 5 presents the storage and loss modulus $G'$ and $G''$ of the polymer solutions as a function of the angular frequency $\omega$ at a measurement temperature of 60 °C. In this regime of a semi-dilute polymer solution, typical features of a Zimm fluid become
apparent. The addition of glycerol increases the magnitude of the complex viscosity $\eta^*$ at low angular frequencies $\omega$. This effect is caused by the relatively high value of viscosity of glycerol and the polymer-glycerol interactions. The data can be described by the Cross model

$$|\eta^*(\omega)| = \frac{\eta_0}{1 + (\tau \omega)^m}$$

with the zero shear rate viscosity $\eta_0$, the power-law exponent $m$ and the average relaxation time $\tau$. Equation (2) was fitted to the experimental data. The fit parameters are shown as a function of glycerol concentration in Figures 5(c) and (d). In the investigated range of concentrations, the increase of the magnitude of complex viscosity is linear, and the addition of glycerol is associated with a linear trend with a slope of 0.44 Pa s/1 wt%. The characteristic relaxation time $\tau$ is in the order of 20 to 30 ms depending on the concentration of glycerol. The zero shear rate viscosity and the average relaxation time follow a similar (linear) trend which indicates that the average elastic modulus remains constant within experimental scatter ($\pm$10%). Our data reveal that the viscosity increase is mainly determined by the increase of the average monomeric friction coefficient. The polymer-solvent (mixture of NMP and glycerol) interactions are described by the value of the monomeric friction coefficient. Because of its relatively high viscosity, the addition of glycerol changes the average value of the monomeric friction coefficient as detected by our rheological experiments.

**Dynamic light scattering**

Dynamic light scattering on polymer solutions can be used to analyze diffusion phenomena.\textsuperscript{32} In the semi-dilute regime which is considered here, interactions between polymer chains are of relevance and strongly influence the diffusion of the polymer chains. In a conventional DLS experiment, the time-dependent intensity auto-correlation function $g_2(q, t)$ is measured which is used for calculation of the normalized field correlation function $g_1(q, t)$ via the Siegert relation:

$$g_2(q, t) = 1 + \beta |g_1(q, t)^2|$$

with the coherence factor $\beta$ (an instrument specific constant which ranges between 0 and 1). Generally, the field auto-correlation function $g_1(q, t)$ decreases with time $t$ with a distribution $H(\tau)$ of relaxation times $\tau$.\textsuperscript{33}
\[ g_1(q, t) = \int_0^\infty H(\tau) \exp(-t/\tau) d\ln\tau. \] (7)

The relaxation rate \( \Gamma \) is defined by \( \Gamma = 1/\tau \). In case of a Brownian diffusion process, this quantity is related to the translational diffusion coefficient \( D \) by

\[ \Gamma = Dq^2. \] (8)

In the following, the experimental data are discussed using the normalized auto-correlation function which is denoted by \( \tilde{g}_2(q, t) = \frac{[g_2(q, t) - 1]}{\beta} \).

Figure 6 shows the normalized auto-correlation function, the relaxation time spectrum and the relaxation rate as a function of \( q^2 \) for the reference solution with 19 wt% PESU, 6 wt% PVP and 75 wt% NMP. The normalized auto-correlation function rapidly decays on the time scale of \( 10^{-5} \) to \( 10^{-4} \) s, see Figure 6(a). The principal relaxation processes can be seen in Figure 6(b). The most rapid process is the most dominant process. The relaxation rate \( \Gamma \) is proportional to \( q^2 \) which indicates a diffusive process (Figure 6(c)). This process is associated with the total polymer concentration (cooperative diffusion).

The influence of glycerol on the DLS data is shown in Figure 7. The experimental data reveal that the addition of glycerol leads to the visual appearance of a second relaxation process, see Figure 7(a). This process is gradually more pronounced with increasing glycerol concentration and most clearly seen at a glycerol concentration of 10 wt%. The analysis of the relaxation time spectrum also indicates that the second relaxation process appears for all \( q \) values (Figure 7(b)). The relaxation rate again is proportional to \( q^2 \) and thus also indicates a diffusion process. Furthermore, the data of the relaxation rate reveal that the addition of glycerol reduces the value of the diffusion coefficient because of the viscosity increase caused by the addition of glycerol. The DLS data convincingly demonstrate that the two main diffusive processes appear on two clearly separated time scales. This result shows that a new mechanism must be responsible for the slower diffusion process. Since glycerol changes the solvent quality to a bad solvent, concentration fluctuations may lead to the formation of clusters of polymer chains because of the stronger tendency to precipitation. The diffusion of these clusters of polymer chains leads to the second, slower diffusion process. An increasing glycerol concentration causes on the average larger clusters of polymer chains which leads to a lower diffusion coefficient \( D \).
Figure 6: (a) Normalized intensity auto-correlation function $\tilde{g}_2(q, t) = [g_2(q, t) - 1]/\beta$, (b) relaxation time spectrum $H(\tau)$ for different $q$ values and (c) relaxation rate $\Gamma$ vs. $q^2$ at 60 °C for the reference solution with 19 wt% PESU, 6 wt% PVP and 75 wt% NMP.
Figure 7: (a) Normalized intensity auto-correlation function for $q = 23.2 \ \mu m^{-1}$ and different glycerol concentrations, (b) relaxation time spectrum $H(\tau)$ for different $q$ values and (c) relaxation rate $\Gamma$ vs. $q^2$ at 60 °C for the solutions with 19 wt% PESU, 6 wt% PVP and $x$ wt% glycerol and $(75 - x)$ wt% NMP.

In order to elucidate the origin of these two relaxation processes in more detail, various different dope solutions were prepared without glycerol and analyzed using dynamic light scattering. Dope solutions with a constant PESU concentration of 19 wt% and a varying PVP concentration were prepared. In addition, solutions with a constant concentration of PVP of 6 wt% and a varying PESU concentration were also prepared. The results of these measurements are presented in Figure 8 which shows the dependence of the diffusion coefficient on glycerol, PESU and PVP concentration, respectively. Figure 8(a) reveals that the diffusion coefficient decreases with glycerol concentration which can be explained by the increase of the monomeric friction coefficient caused by the addition of glycerol (higher value of zero shear rate viscosity). In the absence of glycerol the slow process is much less pronounced than the rapid process. Figures 8(b) and (c) show that in the absence of glycerol the diffusion coefficient of the rapid process is almost independent of the total polymer concentration. The diffusion coefficient of the (less pronounced) slow process increases with polymer concentration which indicates that a cooperative diffusion process takes place.
Figure 8: Concentration dependence of the diffusion coefficient $D$ as determined by dynamic light scattering experiments. The measurement temperature is indicated. (a) The concentration of PESU is 19 wt% and the concentration of PVP is 6 wt%. The concentration of glycerol is varied. (b) The concentration of PESU is 19 wt%. The concentration of PVP is varied. The glycerol concentration is 0 wt%. (c) The concentration of PVP is 6 wt%. The concentration of PESU is varied. The glycerol concentration is 0 wt%.
Figure 9: Scanning electron micrographs of the cross section of the polymer membranes which were prepared using different dope solutions. The polymer concentration in the dope solution was 19 wt% PESU and 6 wt% PVP. The concentration of glycerol (in wt%) is (a) 0, (b) 2, (c) 4, (d) 6, (e) 8 and (f) 10.

| Glycerol concentration [wt%] | Thickness [µm] |
|------------------------------|----------------|
| 0                            | 149            |
| 2                            | 166            |
| 4                            | 161            |
| 6                            | 166            |
Table 1: Membrane thickness obtained from polymer dope solutions and coagulation in a water / NMP = 60:40 (wt/wt) mixture.

Membrane morphology

Poly(N-vinyl pyrrolidone) simultaneously acts as a pore former and as a viscosity enhancer. Scanning electron micrographs of the cross-section of the membranes are shown in Figure 9. Only in the case of 0 wt% glycerol the membrane thickness attains a significantly lower value than in the case of the other membranes (Table 1). Generally, the phase inversion process leads to an asymmetric membrane structure with smaller pores (nanometer range) in the top and larger pores (micrometer range) in the bottom layers, since the water/NMP mixture diffuses into the cast polymer solution starting from the top layer. If the solvent purely consists of NMP, a large number of macrovoids can be seen. At a concentration of glycerol of up to 4 wt% such macrovoids are still visible. The macrovoids disappear in our series of experiments at a glycerol concentration of 6 wt% and higher. Consequently, already at a glycerol concentration of approximately 6 wt% the conditions for macrovoid formation are unfavourable. It seems that the addition of glycerol accelerates phase separation such that no time for the development of macrovoids is available. Furthermore, the addition of glycerol causes a deeper quench into the region of spinodal decomposition which is associated with a strong driving force to maintain this mechanism of phase separation. The surface morphology (lower and upper side of the membrane) was investigated by scanning electron micrography. The diameter of the pores on the upper side of the membrane was smaller than the experimental resolution and thus the pores on the upper side could not be detected (see Supporting Information). It seems that the morphology on the upper side of the membrane is caused by a deeper quench into the spinodal region which is associated with a smaller wavelength of spinodal decomposition. The pore area and the median of the pore diameter of the membranes of this study were determined by porometry measurements. The pore area increases with glycerol concentration which indicates a higher surface porosity with increasing concentration of glycerol, see Figure 10(a). On the other hand, the median of the pore diameter decreases with glycerol concentration (Figure 10(b)).
The scanning electron micrographs of the lower side of the membranes also show a more uniform porous structure with smaller pore sizes and almost no macrovoids for a glycerol concentration of 10 wt% in comparison to the membrane prepared by a solution without glycerol (Figure 11). The pure water permeance as a function of glycerol concentration is shown in Figure 12(a). The decrease of pure water permeance with increasing glycerol fraction reflects the fact that the number of macrovoids and the average pore diameter decrease with increasing glycerol fraction while the molecular weight cut-off values range from 41.0 to 47.3 kDa regardless the glycerol concentration (Figure 12(b)) and thus remains approximately constant. Hence the decrease of pure water permeance with concentration of glycerol is also in agreement with the results of the porometry measurements (median of pore diameter). The PWP value linearly varies with glycerol concentration. The results of our characterization experiments reveal that the addition of glycerol simultaneously increases the polymer solution viscosity and decreases the necessary amount of non-solvent for precipitation. The phase inversion process is influenced by the thermodynamic properties (phase diagram) and viscosity which both depend on the concentration of glycerol. The increase of viscosity from the dope solution with 0 wt% glycerol to the one with 10 wt% only is approximately 50% in the Newtonian regime and lower at higher shear rates. Hence we assume that the change of the phase diagram by the addition of glycerol essentially triggers the formation of a sponge-like structure. Furthermore, after phase separation each of the two phases is associated with different viscosities. The superposition of these two effects (change of thermodynamic and viscous properties) complicate a severe conclusion about the mechanism of morphology formation. The present data for these membranes based
on different glycerol concentrations show that the formation of a compact sponge-type substructure is favoured at a large glycerol concentration, although the precipitation of the polymeric components in the solution is not slowed down. This result is in contrast to the analysis of Strathmann et al.\textsuperscript{5} In summary, the formation of defects such as macrovoids is suppressed with higher glycerol concentrations. At a glycerol concentration of 10 wt\%, a well established sponge-like substructure covered by a compact filtration layer is clearly visible.

Figure 11: Scanning electron micrographs of the lower side of the flat sheet membrane which was prepared using (a) 0 wt\% glycerol and (b) 10 wt\% glycerol in the dope solution.

Figure 12: (a) Pure water permeance (PWP) and (b) molecular weight cut-off (MWCO) of the polymer membranes of this study.

**Precipitation experiments**

In order to get more insight into the precipitation process, a fundamental precipitation experiment was performed, see the experimental setup in Figure 2. This experiment elucidates the time-dependence of the precipitation process. The experiments were performed at room temperature similar to the condition for membrane casting. The
diffusion of the water/NMP mixture (i.e. the coagulation bath) into the casting solution is analyzed by measurement of the precipitation front as a function of time. The results of these measurements are presented in Figure 13 which shows the evolution of the water/NMP front with time. We note that these experiments are associated with experimental scatter which might be caused by humidity in the air. However, a clear trend can be observed for the membranes prepared using 0 and 10 wt% glycerol. The addition of glycerol into the dope solution is associated with a faster movement of the front of the precipitated region with time. Therefore, the addition of glycerol changes the demixing rate which has a strong influence on the membrane properties, see also Torrestiana-Sanchez et al.\textsuperscript{16} In addition, the membrane morphology after one minute of diffusion time is shown in Figure 14. The micrographs also reveal the formation of macrovoids in the absence of glycerol, whereas a more uniform structure is formed for the solution with 10 wt% glycerol.

![Figure 13: Evolution of the diffusion front (precipitated region) with time in the precipitation experiments. The position of the diffusion front is denoted by $x_{\text{front}}$ with the left boundary of the drop of the polymer solution at $x_{\text{front}} = 0$.](image)

(a) 0% Glycerol  
(b) 10% Glycerol  

200 μm
Figure 14: Optical micrographs of the morphology of the precipitated solution at time $t = 60 \text{ s}$. The non-solvent diffuses into the solution and causes precipitation starting from the left side of the micrograph. The different types of morphology for different glycerol concentrations can be clearly seen. The bright area on the right of each subfigure is the non-precipitated polymer solution between the two glass slides.

**CONCLUSIONS**

In this work, we focused on membrane preparation using commercial grades of polyethersulfone and poly(vinyl pyrrolidone) at a specific polymer composition. We studied in detail the influence of adding glycerol to the casting solution on the processing and membrane properties. Generally, the addition of glycerol yields an increase of solution viscosity (roughly 40% at a glycerol concentration of 10 wt%) and precipitation at a lower water content (2 wt% in case of pristine water) as revealed by cloud point measurements. Consequently, precipitation proceeds faster at a higher glycerol concentration as shown by the analysis of a precipitation experiment. The change of rheological properties is much less pronounced than the alteration of the phase diagram by the addition of glycerol. In dynamic light scattering experiments, two diffusive processes were observed. The addition of glycerol yields a change from a morphology with many macrovoids to a sponge-like morphology with a smaller pore size. This effect was explained by the change of thermodynamic and viscous properties caused by the addition of glycerol.

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Tables

| Glycerol concentration [wt%] | Thickness [µm] |
|-----------------------------|----------------|
| 0                           | 149            |
| 2                           | 166            |
| 4                           | 161            |
| 6                           | 166            |
| 8                           | 168            |
| 10                          | 166            |

Table 1: Membrane thickness, pore area and median of pore diameter obtained from polymer dope solutions and coagulation in a water / NMP = 60:40 (wt/wt) mixture.