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Phase behaviour and dynamics of Pluronic®-based additives in semidilute solutions of poly(ethersulfone) and poly(N-vinyl pyrrolidone):
Rheological and dynamic light scattering experiments

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Abstract: The phase behaviour and dynamical properties of a pristine Pluronic® F127 and a Pluronic®-based multiblock copolymer, respectively, in semidilute solutions of poly(ethersulfone) (PESU) and poly(N-vinyl pyrrolidone) (PVP) in N-methyl-2-pyrrolidone (NMP) are investigated using shear rheological and dynamic light scattering (DLS) experiments. Pluronic® F127 is used for synthesis of the PESU-based multiblock copolymer. If the concentration of this additive exceeds a critical value, the solutions are characterized by a pronounced elasticity because of the phase behaviour of the solutions, i.e. the polymer solution with three polymeric components depicts a miscibility gap which is associated with an interfacial tension in the two-phase regime. The addition of pristine Pluronic® F127 or the Pluronic®-based multiblock copolymer leads to an additional relaxation process. The zero shear rate viscosity data are qualitatively reproduced by the Palierne model. Phase separation above the critical concentration is supported by a relatively low diffusion coefficient as determined by DLS experiments.

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Keywords: Polymer solutions, Palierne model, diffusion, phase separation, multiblock copolymers
Introduction

The non-solvent induced phase separation process (NIPS) is technologically applied for preparation of polymer membranes. This method is based on spinning or casting of a polymer solution and subsequent precipitation of the polymeric components in a coagulation bath (Ulbricht et al. 2006). Generally, multi-component solutions which include at least two polymeric components or at least two low molar liquids are used for preparation of polymer membranes. Understanding the rheological properties of such complex fluids and analysis of the relation between polymer structure, processing and precipitation of the solution and transport properties of the membrane is crucial for optimizing the preparation of membranes (Ren et al. 2002; Sharpe et al. 1999; Ullsperger and Válek 2018). For example, Ismail et al. (1997) have shown that molecular orientation caused by high shear rates enhances selectivity. The work of Shilton et al. (1997) revealed that a larger shear rate in flat sheet membrane casting leads to a higher selectivity of gas separation membranes. In the work of Ullsperger and Válek (2018), different flow profiles for polymer solutions which are relevant for hollow fiber spinning are shown. Peng et al. (2009) studied in detail the rheological properties of Torlon® solutions. In spinning of hollow fiber membranes for gas separation applications, an optimum shear rate (in the order of 600 s⁻¹ in their study) exists which yields maximum selectivity of the membrane (Chung et al. 2000). Besides the viscosity function, elastic properties of polymer liquids in general have also been the subject of various rheological investigations of complex fluids and are relevant for processing of polymer melts and solutions (Münstedt 2011). For example, extrudate swell which also occurs in spinning processes is a typical elastic phenomenon.

Generally, polymer solutions which are used for hollow fiber spinning are semidilute. Their theoretical description is associated with various time and length scales (Strobl 2007). Solutions of poly(ethersulfone) (PESU) or polysulfone (PSU) and poly(N-vinyl pyrrolidone) (PVP) are frequently used for preparation of membranes for water purification or hemofiltration (Yang et al. 2009a). These membranes are characterized by a porous structure with a pore diameter in the range of nanometers. The spinning solutions used for membrane fabrication are associated with non-trivial phase diagrams. Whereas both polymers PESU and PVP are miscible in the whole concentration range (Boom et al. 1994a,b), in a recent work it was shown that solutions which consist of poly(phenylenesulfone) (PPSU) and poly(ethylene glycol) (PEG) in N-methyl-2-pyrrolidone (NMP) depict lower and upper critical solution temperatures (Plisko et al. 2018).

The mentioned examples demonstrate that poly(aryl ether) membranes are frequently used in various applications (Alsalhy et al. 2014; Torrestiana-Sanchez et al. 1999) and consequently are the subject of intensive investigations. In several studies, various
influences such as the effect of non-solvents on the properties of the dope solutions and the membranes were investigated. Rheological studies were part of several investigations. The influence of dope extrusion rate on the performance of poly(ethersulfone) membranes was investigated by Ismail et al. (2006). Yang et al. (2009b) showed that the investigated hyperbranched poly(ethersulfone) solutions are characterized by a longer average relaxation time than their linear analogue. The study of Feng et al. (2016) is devoted to rheological properties of poly(phenylenesulfone) solutions. Even only a moderate degree of sulfonation of PPSU yields a pronounced increase of viscosity and dynamic moduli. The kinetics of the phase inversion process in such membranes was also investigated (Han and Nam 2002). The effect of the addition of non-solvents to solutions of poly(ethersulfone) and N-methyl-2-pyrrolidone (NMP) was studied by Li and Jiang (2001). The addition of non-solvents did not change the Newtonian behaviour of the solution in the investigated range of concentration. Previous publications mainly focused on the viscosity function and its dependence on the concentration. However, a detailed analysis of viscous and elastic properties of such polymer solutions as well as of time-dependent effects has not been carried out yet.

In order to reduce fouling, poly(ethylene oxide)-poly(propylene oxide) (PEO-PPO) block copolymers can be added to the dope solution (Loh et al. 2011; Susanto and Ulbricht 2009; Wang et al. 2006; Zhao et al. 2008). This kind of amphiphilic block copolymers is commercialized under the tradename Pluronic®. This block copolymer is frequently used as additive in dope solutions in order to tailor membrane properties (Loh and Wang 2013). For example, the addition of such block copolymers can lead to an enrichment of PEO blocks on the membrane surface. In this work, a multiblock copolymer with poly(ethersulfone) blocks at both ends and a PEO-PPO-PEO middle block is synthesized and studied. The multiblock copolymer can be used as additive for dope solutions for spinning of hollow fiber membranes with the aim to reduce fouling of membranes.

Because of the widespread use of Pluronic® copolymers, a variety of works focused on aqueous solutions of the Pluronic® copolymer F127, see, e.g., the work of Ricardo et al. (2012). Jalaal et al. (2017) investigated the rheological properties of such solutions. In aqueous solutions, Pluronic® copolymers can form micelles (Alexandridis et al. 1995). Furthermore the thermodynamic properties were studied in detail (Alexandridis and Hatton 1994). However, the mentioned works were devoted to the rheological properties of aqueous solutions, but not to Pluronic® solutions with the solvent NMP which is more relevant for membrane production. Properties of these membranes were the subject of the work of Loh et al. (2011).
In this study, we explore for the first time the structure and dynamics of a novel type of multiblock copolymer which is composed of PESU and a Pluronic® block in a dope solution by applying rheological and dynamic light scattering methods. The data of these complex multi-component polymer solutions are compared with results based on solutions using pristine Pluronic® F127.

Experimental

Materials

Commercial grades of poly(ethersulfone) (PESU, Ultrason® E 3010, BASF SE, Ludwigshafen) and poly(N-vinyl pyrrolidone) (PVP, Luvitec® K90, BASF SE, Ludwigshafen) were chosen as majority polymeric components of the dope solutions. The chemical structures are depicted in Figures 1(a) and (b). The molecular weight of PESU was $M_w = 58,000$ g/mol with a polydispersity of 3.3 according to gel permeation chromatography (GPC) in DMAc (calibrated to a PMMA standard) and a viscosity number of 66 mL/g (ISO 307, 1157, 1628; in 0.01 g/mol phenol/1,2 orthodichlorobenzene 1:1 solution). The different batches of PVP are industrially characterized by the so-called K-value (Knappe et al. 2010). Luvitec® K90 is a poly(N-vinyl pyrrolidone) with a solution viscosity characterized by the K-value of 90, determined according to the method of Fikentscher (1932). N-methyl-2-pyrrolidone (NMP) was used as received (BASF SE, Ludwigshafen). Differential scanning calorimetry (DSC) was performed in order to determine the thermal transitions of the pristine polymers (DSC 1, Mettler-Toledo GmbH, Gießen, Germany). In the differential scanning calorimetry experiments, the heating rate was 10 K/min. The experiments were performed in a nitrogen atmosphere. A heating-cooling-heating cycle was chosen, and the second heating interval was used for evaluation of the thermal transitions.

Fig. 1 Chemical structure of (a) poly(ethersulfone), (b) poly(N-vinyl pyrrolidone) and (c) Pluronic® triblock copolymers. In case of Pluronic® F127 the values of $p$ and $q$ are $p = 36$ and $q = 28$

Synthesis

A symmetrical ethylene oxide-propylene oxide (PEO-PPO-PEO) triblock copolymer (Pluronic® F127, BASF SE, Ludwigshafen) is used for synthesis, see Figure 1(c). The weight fraction of the propylene oxide block approximately is 31.6 wt%. The number
average $M_n$ of the total molecular weight of pristine Pluronic® F127 is 10 400 g/mol. After synthesis of the PESU-PEO-PPO-PEO multiblock copolymer the molecular weight ($M_n$) of each PESU block is 8 600 g/mol (determined by $^1$H-NMR).

Fig. 2 Scheme of synthesis of the triblock copolymer chosen as additive for the dope solution

The scheme of synthesis is depicted in Figure 2 (Weber et al. 2014). In a 4 L glass reactor fitted with a thermometer, a gas inlet tube and a Dean-Stark trap, 344.60 g (1.20 mol) of 4,4’-Dichloro-diphenylsulfone (DCDPS), 281.29 g (1.124 mol) of 4,4’-Dihydroxy-diphenylsulfone, and 183.1 g (1.325 mol) of potassium carbonate with a volume average particle size of 32.6 µm were suspended in 640 mL NMP under a nitrogen atmosphere. Then the mixture was heated to 190 °C within one hour. The water formed in the reaction was continuously removed by distillation.

After 15 minutes, 1164.1 g (0.108 mol) of a PEO-PPO-PEO block copolymer was added, which reduced the temperature of the suspension to 65 °C. Within further 30 minutes the mixture was heated again to 190 °C and stirred at this temperature for 9 h. Subsequently, 1000 mL NMP were added to the reactor to stop the reaction. Afterwards the suspension was cooled to 80 °C and transferred into a pressure filter to separate the potassium chloride formed in the reaction by filtration.

Then a part of the obtained polymer solution was precipitated in water, the resulting polymer beads were separated and then extracted with hot water (85 °C) for 20 h. Afterwards, the beads were dried at 80 °C for 24 h at reduced pressure (< 100 mbar). Finally, the filtered solution was stored in the dark. Analysis of $^1$H-NMR data of the polymer beads revealed that the polymer beads contained 54.7 wt% PESU and 45.3 wt% PEO-PPO-PEO multiblock copolymer. Thus the final polymer contained approximately 54.7 wt% PESU-PEO-PPO-PEO multiblock copolymer and 45.3 wt% free Pluronic® F127. In this work, this multiblock copolymer is denoted by 8.6 kDa PESU-Pluronic® F127.

Preparation of polymer dope solutions

Two different methods for preparation of polymer solutions were applied. Method A was applied for preparation of solutions on a small scale for rheological and scattering investigations, only. The polymers and the organic solvent were mixed using a...
magnetic stirrer at a temperature of 60 °C (method A). The multiblock copolymer 8.6 kDa PESU-Pluronic® F127 was premixed in NMP at a concentration of 35.1 wt%. Before mixing, the commercial polymers (except Pluronic® F127) were dried at 130 °C for at least 24 hours under vacuum. Pluronic® F127 was dried at 35 °C for 24 hours under vacuum. After mixing, the solutions were degassed under vacuum for 2 hours.

For the preparation of the polymer solutions using a second procedure (method B) on a larger scale the components poly(ethersulfone) (PESU, Ultrason® E 3010, BASF SE, Ludwigshafen), poly(N-vinyl pyrrolidone) (PVP, Luvitec® K90, BASF SE, Ludwigshafen) and the additive (Pluronic® F127 or 8.6 kDa PESU-Pluronic® F127, respectively) (BASF SE, Ludwigshafen) were homogenized in N-methyl-2-pyrrolidone (NMP) by using a SpeedMixer™ DAC 600 (Hauschild & Co. KG) with increasing mixing speeds of 800, 1100, 1500 and 2000 rpm within 60 minutes.

Rheological experiments

A rotational rheometer (MCR 502, Anton Paar, Graz, Austria) is used for the rheological experiments. A concentric cylinder geometry (Searle type) was chosen for the investigations. The measurements were performed at 60 °C. Before the rheological experiments, 14.0 mL of the bubble-free liquid samples were inserted into the rheometer. The time for temperature equilibration was 10 min. Measurements in oscillatory shear and experiments with a constant shear rate were performed (so-called stress-growth experiments). In order to determine the linear range of the oscillatory shear measurements, first an amplitude sweep was performed at an angular frequency of \( \omega = 10 \text{ rad/s} \). The shear amplitude \( \gamma_0 \) was varied between 0.2 and 20%. In the following frequency sweep, the shear amplitude was set to \( \gamma_0 = 10\% \) which was within the linear viscoelastic range. The frequency varied between 0.01 rad/s and 100 rad/s, starting with the highest frequency.

Dynamic light scattering

Dynamic light scattering (DLS) was carried out with an ALV/CSG-3 Compact Goniometer-System (ALV-Laser Vertriebsgesellschaft GmbH, Langen, Germany) using an ALV/LSE-5003 Multiple Tau Digital Correlator. As light source, a HeNe laser emitting at 632.8 nm was used. The measuring angle was varied between 40° to 140° in 5° steps for all measurements. The magnitude \( q \) of the scattering vector is related to the wavelength \( \lambda \) and the solvent refractive index \( n \) by

\[
q = \frac{4\pi n}{\lambda} \sin(\theta/2)
\]

where the scattering angle is denoted by \( \theta \). For the solutions in the one-phase region every single measurement was conducted for 120 s and for the solution in the two-phase region every single measurement was conducted for 600 s.
The sample vials consisted of quartz glass and were placed into a measurement cell filled with toluene. The toluene bath and therefore the samples were tempered by a Julabo F25 thermostat working with a mixture of water and ethylene glycol and delivering a temperature accuracy of 0.01 °C. Each sample was measured at a temperature of 20 °C and 60 °C. The viscosity and refractive index of the solutions were automatically corrected with temperature according to tabulated values of the solvent (Langan and Salmon 1987).

![Graph](image)

**Fig. 3** (a) Storage modulus $G'$ and loss modulus $G''$ as a function of angular frequency $\omega$ for the reference solution consisting of 19 wt% PESU, 6 wt% PVP and 75 wt% NMP. The shear amplitude was 10% and the test temperature 60 °C. (b) Magnitude of complex viscosity $\eta^*$ as a function of angular frequency $\omega$ for the reference solution at 60 °C

**Results and discussion**

**Rheology**

One objective of our investigations is to analyze the influence of the addition of pristine Pluronic® F127 and the Pluronic®-based additive to a PESU/PVP/NMP reference solution and to compare the data of both types of solution. A first approach in order to understand the rheological behaviour of the solutions is the analysis of small amplitude shear oscillations (Figure 3). Generally, the solutions under investigation belong to the semidilute regime where polymer-polymer interactions are of high relevance. The reference solution which consists of 19 wt% PESU, 6 wt% PVP and 75 wt% NMP reveals the typical Zimm behaviour of a polymer solution under $\Theta$ conditions (Doi and Edwards 1986). At high frequencies, both dynamic moduli $G'$ and $G''$ are proportional to $\omega^{2/3}$. Furthermore, the Newtonian regime with the power-laws $G' \propto \omega^2$ and $G'' \propto \omega$ is visible at low frequencies. The Newtonian plateau is also apparent in the graph of the magnitude of the complex viscosity $\eta^*$ as a function of angular frequency $\omega$. The Cross model

$$|\eta^*(\omega)| = \frac{\eta_0}{1+(\tau_0\omega)^m}$$

(2)
with the zero shear rate viscosity $\eta_0$ and the power-law exponent $m$ was fitted to the experimental data. The fit parameters are $\eta_0 = 15.4$ Pa s and $m = 0.63$. The characteristic relaxation time $\tau$ is given by 33 ms which shows that the solution very rapidly achieves its steady-state behaviour. Interestingly, DLS data of the reference solution also indicate complete relaxation after this time interval. Polymer solutions for hollow fiber spinning are not necessarily associated with a non-Newtonian behaviour, see, for example, the work of Ullsperger and Válek (2018) where solutions without a fraction of high molecular weight polymers were investigated.

Figure 4 shows the visual appearance of the solutions in dependence of the concentration of the additive 8.6 kDa PESU-Pluronic® F127. Above an additive concentration of 1 wt%, an increasing concentration of the additive yields a pronounced cloudiness which indicates the formation of tiny droplets and consequently phase separation. It appears that a two-phase fluid system is formed with different compositions of the polymer components. The two different phases are associated with an interfacial tension which also contributes to the rheological response (Palierne 1990; Palierne 1991). In case of a solution with 10 wt% of 8.6 kDa PESU-Pluronic® F127 a macroscopic phase separation was clearly visible. The influence of the additive concentration of 8.6 kDa PESU-Pluronic® F127 on the rheological properties of the solutions is shown in Figure 5. The additive concentration was varied between 0 and 7 wt% for the solutions in Figure 5. The overall behaviour can be seen in the curve of the frequency-dependent magnitude of complex viscosity. At high frequencies, the addition of the additive 8.6 kDa PESU-Pluronic® F127 leads to a monotonic decrease of viscosity with increasing concentration of the additive. This decrease of viscosity can be explained by the dilution effect which is caused by the Pluronic® block. On the contrary, at low frequencies a non-monotonic behaviour exists which indicates morphological changes with varying additive concentration. In the low frequency regime, the formation of droplets influences the viscosity and can lead to a viscosity increase in comparison to the reference solution. For an additive concentration of only
1 wt% a decrease of the zero shear rate viscosity is observed. At higher additive concentrations, the zero shear rate viscosity increases (3 wt% additive concentration) and the Newtonian regime disappears (5 wt% additive concentration) in the experimentally accessible frequency range. This happens due the interfacial tension between the two phases, an effect which in the following is quantitatively discussed using the Palierne model. At a very high additive concentration of 7 wt%, very low viscosity values in the order of 8 Pa s were also measured in the low frequency regime. At such high additive concentrations, the Pluronic® block leads to a pronounced decrease of viscosity. For these concentrations, the dilution effect dominates over the effect of the interfacial tension.

Fig. 5 (a) Storage modulus $G'$, (b) loss modulus $G''$ and (c) magnitude of complex viscosity $\eta^*$ as a function of angular frequency $\omega$ of solutions with different concentrations of the additive PESU-Pluronic® F127 at a test temperature of 60 °C. The shear amplitude was 10%.

The linear viscoelastic shear oscillations allow for the separation of elastic and viscous effects. The loss modulus which attains higher values than the storage modulus follows the same trend as the magnitude of the complex viscosity. Increasing the additive concentration yields an increase of the storage modulus at low frequencies which is
clearly visible after addition of 3 wt% additive, because the interfacial tension between the two phases is a source of elasticity. The data also indicate that the regimes of low and high frequencies are differently affected. Whereas at high frequencies, both moduli decrease with additive concentration, in the low frequency regime, the effect of the interfacial tension (increase of storage modulus) is visible. The precise shape of the curve of the storage modulus is directly affected by the droplet size distribution. The values of the loss modulus in the low frequency are determined by the molecular weight of the three polymer components in solution.

Fig. 6 Comparison of addition of pristine Pluronic® F127 (open symbols) and the synthesized additive 8.6 kDa PESU-Pluronic® F127 (closed symbols), respectively, on the storage modulus $G'$ and loss modulus $G''$ as a function of angular frequency $\omega$. The composition was $(20-x)$% PESU, $x$% PVP, 5% additive and 75% NMP ($x = 0, 3$ or 6). The shear amplitude was 10% and the test temperature 60 °C: (a) Storage modulus $G'$, (b) loss modulus $G''$ and (c) magnitude of complex viscosity $\eta^*$ based on the dynamic moduli of (a) and (b). In (a) the values of $G'$ for the solution with 0% PVP are below the limit of resolution of the rheometer.
In Figure 6, the influence of the concentration of poly(N-vinyl pyrrolidone) is presented for both types of additives. The chosen poly(N-vinyl pyrrolidone) of this study is associated with a high molecular weight which generally increases the elasticity of the solution. The data of the dynamic moduli also reveal that in the presence of PVP an additional relaxation process at low frequencies is observed. The increase of storage modulus is observed for both types of additives, see Figure 6(a) which clearly shows an additional relaxation process for PVP concentrations of 3 and 6 wt%. Since the onset of the shoulder of the storage modulus $G'$ is in the order of 0.5 rad/s, the associated relaxation time $\tau$ is in the order of 2 s. Taking a viscosity $\eta$ of 10 Pa s and an assumed droplet radius $R$ of 200 nm, one can estimate the interfacial tension by $\alpha = \eta R / \tau = 0.0005$ mN/m, i.e. a very low value. The addition of PVP with a high molecular weight increases the moduli. In Figure 6, the data of the solutions with pristine Pluronic® F127 are compared with the data for 8.6 kDa PESU-Pluronic® F127. Since Pluronic® F127 has a lower molecular weight than the PESU-Pluronic® block copolymer, it leads to lower moduli than the solutions with 8.6 kDa PESU-Pluronic® F127 and consequently to a lower value of zero shear rate viscosity than the addition of 8.6 kDa PESU-Pluronic® F127 (Figure 6). If pristine poly(ethylene oxide) (Pluriol E 8000, BASF SE) with a molecular weight of 8000 g/mol is used as additive instead of 8.6 kDa PESU-Pluronic® F127, then no such additional relaxation process was observed in our measurements, see Figure 7. Consequently, it seems that the poly(propylene oxide) block is responsible for the appearance of the miscibility gap, cf. Weber et al. (2014).

![Figure 7](image)

**Fig. 7** Magnitude of complex viscosity $\eta^*$ as a function of angular frequency $\omega$ of solutions with 5 wt% Pluriol E 8000 (BASF SE, Ludwigshafen) at a test temperature of 60 °C. The shear amplitude was 10%
Fig. 8 Results of stress-growth experiments on solutions with an additive concentration of (a) 0 wt%, (b) 5 wt% Pluronic F127, (c) 5 wt% 8.6 kDa PESU-Pluronic® F127 and (d) on PESU-Pluronic® F127 with varying additive concentration. The test temperature was 60 °C. The applied shear rates $\dot{\gamma}$ are indicated.

Stress-growth experiments also depict an interesting phenomenon (Figure 8) and were associated with a stress-overshoot followed by a stress-undershoot. The transient viscosity of the solution without any additive very rapidly achieves its steady-state value because of the very low relaxation time. Furthermore, the shear-thinning behavior is clearly visible, since at higher shear rates the viscosity decreases. For the reference solution, the data are in agreement with the linear viscoelastic data. The rheological behaviour of solutions with the additive depicts a more complicated pattern. At low shear rates (corresponding to low frequencies), the addition of the additive yields a decrease of viscosity. At medium shear rates, a stress-overshoot appears which is followed by a stress undershoot. This stress-overshoot can be explained by the deformation of domains of the two-phases and their subsequent break-up. The break-up of domains yields a decrease of interfacial area and thus a viscosity reduction (stress-undershoot). There is no linear regime for the solutions which are filled with additives, since the maximum of the stress-overshoot changes with shear rate. This observation is caused by the break-up of domains. Both phases are associated with different viscosity values. First the low viscosity domains are deformed up to the point where the interfacial stress restricts further deformation of the low viscosity domains. This is demonstrated in Figure 8(d) where the transient shear viscosity at different concentrations and a fixed shear rate of 1.0 s$^{-1}$ is plotted. At high concentrations, the
relatively large domains are deformed to a large extent. These stress-growth data also demonstrate that the Pluronic® F127 copolymer is responsible for the phase behaviour, since the stress-overshoot and undershoot only appear in the presence of the Pluronic®-based additives. The increased elasticity is also evidenced by the effect of rod-climbing which appeared in solutions with PESU, PVP and the Pluronic®-based additives.

A variety of interesting dynamical phenomena can be observed in the rheological data of the spinning solutions with three polymeric components. The most prominent appearance is the obvious increase of elasticity which only appears in the presence of poly(ethersulfone) and poly(N-vinyl pyrrolidone). The molecular weight of PVP is much larger than the molecular weight of PESU. Loh and Wang (2013) state based on the results of surface tension measurements that Pluronic® F127 does not form micelles in NMP in contrast to micelle formation in water (Ricardo et al. 2012). Consequently, in the following we assume that the polymer chains attain random conformations in a semidilute polymer solution.

![Fig. 9 Application of the Palierne model for calculation of the zero shear rate viscosity $\eta_0$ of the spinning solution of this study. (a) Value of $\eta_0$ as a function of the weight fraction $\phi_{\text{additive}}$ of the additive. (b) Zero shear rate viscosity $\eta_0$ as a function of the volume concentration $\Phi$ of the disperse phase. The parameters are indicated](image)

Phase separation indicates that a miscibility gap appears in the solution with three polymeric components and a two-phase system is formed. Each phase is associated with different values of the concentration of the additive. The interfacial tension is responsible for the increased value of storage modulus. In a simple picture, the polymer solution in the two-phase region can be described by the Palierne model for emulsions. Here we assume that both phases are purely Newtonian liquids. This is a reasonable assumption for the low-frequency range. The viscosity of the disperse and the matrix phase are denoted by $\eta_d$ and $\eta_m$, respectively. In the solutions of this study, the low-viscosity phase forms the droplets and the high-viscosity phase the matrix. Then the zero shear rate viscosity is given by (Palierne 1990; Palierne 1991)
where the viscosity ratio is denoted by $p = \eta_d/\eta_m$ and the volume fraction of the dispersed phase by $\Phi$. In this study, $\varphi_d$ denotes the weight concentration of the additive in the disperse phase, $\varphi_m$ the weight concentration of the additive in the matrix phase and $\varphi_{\text{additive}}$ the total additive concentration (weight fraction) in the solution. In a simple approach, one can assume that the two phases attain viscosity values according to a linear rule of mixture such that the following conditions hold:

\begin{align}
\eta_0 &= \eta_m \left(1 + \Phi \frac{5p+2}{2p+2}\right) \quad (3)
\end{align}

with $\varphi\varphi_d + (1 - \varphi)\varphi_m = \varphi_{\text{additive}}$ and the total weight fraction $\varphi$ of the disperse phase.

The zero shear rate viscosity of the reference solution without additive (19% PESU, 6% PVP and 75% NMP) is denoted by $\eta_{\text{ref}}$. In the following we use the approximation $\varphi \approx \Phi$. The parameter $a$ denotes the viscosity decrease per weight concentration of the additive. In this work, we estimate $a$ by 2 Pa s/1%. For relatively low concentrations $\varphi_d$ and $\varphi_m$ one has $p = \eta_d/\eta_m \approx 1 - (\varphi_d - \varphi_m)a/\eta_{\text{ref}}$. In this study, the difference $\varphi_d - \varphi_m$ is in the order of several weight percent such that we approximately have $(\varphi_d - \varphi_m)a/\eta_{\text{ref}} \approx 0.1$ and consequently the two phases in the region of the miscibility gap are roughly equiviscous ($p \approx 1$). Hence equations (3) to (5) reveal that the solution viscosity is mainly determined by the viscosity reduction of the matrix caused by the additive and the volume fraction $\Phi$. The effect of phase separation is exemplarily presented in Figure 9. The influence of additive concentration at a fixed volume concentration of the disperse phase is shown in Figure 9(a). At very low addition concentrations, the viscosity exceeds the zero shear rate viscosity of the reference solution because the Palierne model assumes the existence of an interfacial tension. The zero shear rate viscosity $\eta_0$ decreases with additive concentration because of the dilution effect of the additive. Figure 9(b) shows the zero shear rate viscosity for different additive concentrations as a function of the volume fraction of the disperse phases. At the chosen additive concentrations, the zero shear rate viscosity increases linearly with the volume concentration of the disperse phase. The slope of this linear curve is strongly influenced by the matrix viscosity which depends on the additive concentration in the matrix phase. Consequently, the viscosity data of the spinning solution can be larger or lower than the data of the reference solution. The data for additive concentrations of 2, 3 and 5 wt% show these different scenarios. In summary, the theory of Palierne can explain the viscosity increase at low additive concentrations.

*Dynamic light scattering*
Dynamic light scattering is a powerful tool for analysis of diffusion phenomena (Stetefeld et al. 2016). In contrast to the rheological experiments, the polymer chains are in a relaxed state in DLS experiments. Their movement is driven by diffusion. Our analysis of the scattering experiments focuses on the number of relaxation processes and the characteristic time scales of the processes. In a standard DLS experiment, the time-dependent intensity auto-correlation function \( g_2(q, t) \) is measured and the normalized field correlation function \( g_1(q, t) \) can be determined 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 \( g_1(q, t) \) relaxes with time \( t \) with a distribution \( H(\tau) \) of relaxation times \( \tau \) (Lodge 1996)

\[
g_1(q, t) = \int_0^\infty H(\tau) \exp(-t/\tau) d\ln \tau.
\]

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

\[
\Gamma = Dq^2.
\]

In this work, we focus on the analysis of the normalized auto-correlation function \( g_2(q, t) - 1 \) which is denoted by \( \tilde{g}_2(q, t) = [g_2(q, t) - 1]/\beta \). The objective is the identification of the number of diffusion processes. First, DLS experiments using the pristine polymer components were performed. The data of the auto-correlation function reveal a single relaxation process. These processes are purely diffusion processes. At the chosen concentration, poly(ethersulfone) is associated with the smallest relaxation time. Poly(N-vinyl pyrrolidone) which has a much larger molecular weight is characterized by a larger relaxation time than poly(ethersulfone). Surprisingly, Pluronic® F127 depicts a relatively slow diffusion behaviour which can be explained by the formation of objects being similar to micelles.

![Fig. 10](image-url)

**Fig. 10** (a) Normalized intensity auto-correlation function \( \tilde{g}_2(q, t) = [g_2(q, t) - 1]/\beta \), (b) relaxation time spectrum \( H(\tau) \) and (c) relaxation rate \( \Gamma \) vs. \( q^2 \) as determined by dynamic light scattering experiments at 60 °C for the reference solution with 19 wt% PESU, 6 wt% PVP and 75 wt% NMP.
In Figure 10, the normalized intensity auto-correlation function $\hat{g}_2(q, t)$ and the fitted relaxation time spectrum for the reference solution (19 wt% PESU, 6 wt% PVP, 75 wt% NMP) are presented. Figure 10(a) displays the normalized function $\hat{g}_2(q, t)$ measured at different values of the scattering vector $q$. By fitting a relaxation time spectrum $H(\tau)$ to the experimental data (see Figure 10(b)), two relaxation processes can be identified which correspond to the Brownian motion of the single components and an additional slower process. Figure 10(c) presents the relaxation rate $\Gamma$ as a function of $q^2$ for these two processes. A clear proportionality between $\Gamma$ and $q^2$ can be seen which indicates the existence of two Brownian diffusion processes.

![Figure 10](image1)

Fig. 11 (a) Normalized intensity auto-correlation function $\hat{g}_2(q, t)$, (b) relaxation rate $\Gamma$ vs. $q^2$ and (c) diffusion coefficient $D$ at 20 °C and 60 °C as a function of concentration $c_{\text{PESU}}$ of poly(ethersulfone) as determined by dynamic light scattering experiments at 60 °C for solutions of PESU and the additive 8.6 kDa PESU-Pluronic® F127 (5 wt%).

Figure 11(a) shows the normalized intensity auto-correlation function $\hat{g}_2(q, t)$ for solutions of PESU and the additive in NMP for various PESU concentrations. These solutions did not contain any poly(N-vinyl pyrrolidone). Two relaxation processes are clearly visible which correspond to the two polymeric components. An additional third process become visible after fitting the data. The relaxation rates $\Gamma$ are proportional to $q^2$ for all three processes (Figure 11(b)). Based on a least-squares fit of the slopes the diffusion coefficients were determined. The diffusion coefficient of the two slowest modes decreases with PESU concentration which is typical for an interdiffusion phenomenon (Borsali et al. 1989; Lodge 1996).
Fig. 12 (a) Normalized intensity auto-correlation function $\hat{g}_2(q,t)$ and (b) relaxation rate $\Gamma$ as determined by dynamic light scattering experiments at 60 °C for a solution of 17 wt% PESU, 3 wt% PVP, 5 wt% 8.6 kDa PESU-Pluronic® F127 and 75 wt% NMP.

A completely different dynamical situation is presented in Figure 12 for the solution with 17 wt% PESU, 3 wt% PVP and 5 wt% 8.6 kDa Pluronic® F127. In Figure 12(a), the function $\hat{g}_2(q,t)$ is shown. The normalized intensity auto-correlation only decreases at a timescale to zero which is much larger than the timescale of the solutions without the additive, cf. Figures 10 and 11. A much longer relaxation time appears which might be due to the relaxation of the different domains of the two-phase structure. Figure 12(b) reveals that the relaxation rate $\Gamma$ does not show a clear proportionality to $q^2$. This behaviour is possibly caused by a broad size distribution of the droplets of the disperse phase. In summary, the dynamic light scattering experiments confirm our picture of the existence of a miscibility gap.

Related results which are in agreement with our discussion were obtained in previous publications. In microemulsions two diffusive relaxation modes which are interpreted by collective and self-diffusion of droplets were observed (Shukla et al. 2004). In ternary homogeneous solutions, usually two relaxation processes are observed (Borsali et al. 1989). These two processes were also attributed to a cooperative relaxation of the concentration fluctuations in the mixture and to interdiffusion relaxation.

Conclusions

Optimization of poly(ethersulfone) hollow fiber membranes for water treatment requires a profound understanding of the membrane fabrication process. An essential aspect of membrane fabrication is the viscoelastic behaviour of the spinning solution. Modification of the spinning solution using an overall hydrophilic additive (e.g., Pluronic®-based additives) is a common approach in order to create a hydrophilic membrane surface and to reduce membrane fouling. Consequently, a strong need exists to understand the influence of such additives on the rheological behaviour of the spinning solutions. In particular, knowledge of the optimum additive concentration is crucial for tailoring hollow fiber membranes. The addition of pristine Pluronic® or a Pluronic®-based additive with a concentration of 3 wt% or higher to a spinning solution of poly(ethersulfone) and poly(N-vinyl pyrrolidone) leads to a miscibility gap which is reflected by structural (e.g., formation of a two-phase system) and dynamical (increased elasticity, long diffusion times) properties. This miscibility gap only appears in solutions with three polymeric components and is associated with the poly(propylene oxide) block of the additive. In the region of phase separation, a two-phase system is observed which is associated with an interfacial tension. The interfacial tension, a
source of elasticity, contributes to the rheological properties of the spinning solution. The addition of the multiblock copolymer based on poly(ethersulfone) and Pluronic® F127 blocks leads to an increase of storage modulus in solution (and thus to an additional relaxation process) resulting in rod-climbing in experiments with a constant shear rate. The rheological data at high shear rates indicate destruction of the two-phase structure, i.e. shearing at a high shear rate leads to a mixing of the two phases which rapidly phase separate again. These results show that an upper limit of membrane hydrophilicity can be achieved based on a maximum soluble fraction of Pluronic®-based additives. The phase separation can be partially compensated by the high shear rate in the spinneret, but only at moderate additive concentrations. The rheological data are supported by the results of dynamic light scattering experiments. In the region of the miscibility gap, complete relaxation of the intensity auto-correlation function appears only at large time scales which is associated with the diffusion of tiny droplets.

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