INTRODUCTION The utilization of amphiphilic block copolymers in membrane technology has attracted great interest in the last decades. Due to the incompatibility between the two polymeric blocks, controlled nanostructures and a wide variety of different morphologies are available. The self-assembly of these polymers can be a powerful tool to improve filtration performances and adjust membrane properties. This can help to expand the scope of application of ultrafiltration in biotechnology and other areas. The respective block copolymers can either be used as an additive or a bulk material. The former is interesting to tune membrane properties such as hydrophobicity but gives no precise control of the pore morphology. The use as a bulk material is more effective to exploit self-assembling properties in membrane formation.

In this context, fabrication of ultrafiltration membranes by the one-step combination of self-assembly and nonsolvent induced phase separation, called the SNIPS process, gained particular attention. In this case, combination of micro- and macrophase separation leads to well defined and isoporous membrane barrier structures. Its special attractiveness is that already industrially established equipment for the NIPS process can be used. For the SNIPS process usually solutions of a block copolymer (BCP) with at least two different solvents are employed. One of these solvents is highly volatile and the other is polar introducing a selectivity for the hydrophilic part of the BCP. The polymer solution is then cast on a substrate followed by a defined period of solvent evaporation. This leads to an increasing polymer concentration at the film surface, what in turn induces the formation of ordered nanostructures. Finally, the structure is fixed by precipitation in a nonsolvent bath. Porous structures are directly obtained by the hydrophilic block forming the pores and the hydrophobic component serving as the membrane matrix. It is now accepted that BCP micelles play a key role in the microphase separation leading to the ordered pore morphologies.
contrast to the outer membrane surface, the cross section is still shaped by macrophase separation leading to less regular or even conventional finger-like structures. In order to obtain isoporous structures by SNIPS, intense optimization of the process is needed for every newly introduced BCP type and specific polymer composition. Main parameters to adjust are the block ratio of the BCP, the polymer concentration, the solvent composition, and the evaporation time.\textsuperscript{11–13} The overall and ultimate aim of the SNIPS process is to overcome the typical trade-off relationship between membrane permeability and selectivity, which is also found for ultrafiltration membranes.\textsuperscript{14}

In principal, every block copolymer with distinct phase separation properties and enough mechanical stability should be suitable for the SNIPS process. The by far most commonly used polymerization method in this area is the anionic polymerization leading to copolymers of polystyrene (PS), polyethyleneoxide (PEO), poly(4-vinylpyridine) (P4VP), or poly(2-vinylpyridine) (P2VP), for example, PS-b-P4VP,\textsuperscript{8,11,15–17} PS-b-POE\textsuperscript{18,19} or PS-b-P2VP\textsuperscript{13,20} Hence, for upsampling of membrane manufacturing, the polymer synthesis is a critical bottleneck. Therefore, it would be desirable to establish polymers, which are easily accessible via less sensitive but controlled polymerization methods like atom transfer radical polymerization (ATRP) or reversible addition-fragmentation chain transfer (RAFT).\textsuperscript{5,21} For example, the group of Nunes employed a triblock copolymer from poly(tertiary butyl acrylate) (PtBA) and polysulfone (PSU), that is, PtBA-b-PSU-b-PtBA, synthesized via a combination of condensation and RAFT polymerizations. Nanostructured membranes with a finger-like cross section were obtained, but barrier pores were not completely isoporous.\textsuperscript{22} Another approach is to minimize the required amount of polymer, for example, by usage of spray- or dip-coating techniques to form only a thin isoporous BCP layer on top of a conventional porous membrane as support.\textsuperscript{23}

ATRP of different methacrylates toward the respective block copolymers is well known in the literature\textsuperscript{24–31} and poly(methacrylates) are a versatile option for the hydrophobic component of an amphiphilic block copolymer. In the later membrane, the polymethacrylate will form the matrix and therefore it is responsible for its mechanical stability.\textsuperscript{32} An attractive opportunity for the hydrophilic component is PEO because it introduces important antifouling properties to the membrane. In general, fouling is one of the main drawbacks in membrane technology reducing the membrane performance during application due to deposition of matter on the surface. A common method to introduce inherent antifouling properties to a membrane from a standard polymer is a surface modification with hydrophilic components like PEO.\textsuperscript{33} With the same intention, a diblock copolymer of PEO with poly(methyl methacrylate) had been synthesized via ATRP and utilized in a blend with polyvinylidene fluoride to obtain improved ultrafiltration membranes.\textsuperscript{34} Additionally, PEO is known to be blood compatible making it also attractive for pharmaceutics or biotechnology.\textsuperscript{35}

Recently, we were the first to report the controlled synthesis via ATRP of small PEO-b-PiPMA block copolymers (Fig. 1) with molar masses up to 43 kDa. Self-assembling properties in the polymer bulk were proven with the help of atomic force microscopy and differential scanning calorimetry.\textsuperscript{36}

The main aim of this study was to go one step further; based on sufficient incompatibility between the blocks for self-assembly, the respective BCP should be used in the SNIPS process. Therefore, PEO macroinitiator and BCP with higher molar masses than reported before had to be synthesized to obtain mechanically stable membranes. In general, self-assembly is a very sensitive process and influenced by a lot of parameters. Therefore, different conditions during membrane fabrication and possible disturbing factors had to be studied carefully. Disturbing factors are potentially high polydispersity indices (PDI) of the BCP or impurities like unreacted PEO macroinitiator. In the literature, it is well known that homopolymer of the core-forming block can have a strong impact on micelle size and morphology. For example, the addition of hPS to spherical micelles of polystyrene-block-poly(acrylic acid) (PS-b-PAA) leads to an increased micelle diameter and polydispersity.\textsuperscript{37} The effect strongly depends on molar mass and concentration of added homopolymer as well as micelle morphology.\textsuperscript{37–40} In this work, we will show that the newly synthesized polymers can be successfully applied as membrane material and that residuals of PEO homopolymer (hPEO) have a strong impact on membrane structure formation.

**EXPERIMENTAL**

**Materials**

1,1,4,7,10,10-Hexamethyldiethylenetramine (HMTETA, 97%), copper(I)chloride (CuCl, 99.995%), triethyamine (99.5%), PEO monomethyl ether (95%), and 2-bromoisobutyryl bromide (98%) were purchased from Sigma-Aldrich. Isopropylmethacrylate (iPMA, 98%) and anisole (99%) were purchased from TCI Chemicals. Tetrahydrofuran (THF, 99.8%) and ethanol (EtOH, 99.88%) were purchased from Thermo Fisher Scientific. Dioxane (DOX, 99%) was purchased from AppliChem, N-methyl-2-pyrrolidin (NMP, 99.6%) from Merck, dichloromethane (DCM, 99.8%) from VWR and deuterated chloroform (CDCl\textsubscript{3}, 99.8%) from Deutoer. Dextrane 100 for biochemistry (~100 kDa) was purchased from Carl Roth. Before use, PEO monomethyl ether was dried for several days in a desiccator over silica gel.

**Measurements**

NMR spectra were recorded on a Bruker DMX300 instrument at room temperature in CDCl\textsubscript{3} as a solvent. For gel permeation

![FIGURE 1 Structural formula of the block copolymer PEO-b-PiPMA (PiPMA = poly(isopropyl methacrylate)).]
chromatography (GPC) measurements a system consisting of a RI- and UV-Vis detector and four consecutive poly(styrene-co-divinylbenzene) gel columns from PSS GmbH (PSS SDV 5 μm, PSS SDV 5 μm 1000 Å, 2x PSS SDV 5 μm 100.000 Å) was used. Temperature was 40 °C and THF was used as eluent at a flow rate of 1 mL·min⁻¹ (pump PSS SECurity). The GPC system was calibrated using polystyrene standards from PSS GmbH. Scanning electron microscopy (SEM) was carried out with a Quanta 400 FEG ESEM microscope from Thermo Fischer Scientific. For dynamic light scattering (DLS) measurements, diluted polymer solutions with a concentration of 2 wt % were investigated with a Nano-flex® 180° system from Particle Metrix GmbH. For analysis, the number distributions of three single measurements were considered. Rheological characterizations were carried out with a Physica MCR301 rheometer from Anton Paar. The dynamic viscosities \( \eta \) of the casting solutions were measured in a shear rate range from 0.01 to 800 s⁻¹ at 20 °C with a cone-plate measuring system (1°, d = 50 mm). For total organic carbon (TOC) measurements, a TOC-V CPN instrument from Shimadzu was used.

Synthesis Procedure

Synthesis of Macroinitiator (PEO-Br)

In a first step, PEO macroinitiator was synthesized from commercially available PEO monomethyl ether (PEO-OMe) (Fig. 2), what had been characterized by GPC (see above). The 1 eq of PEO-OMe was dissolved in 635 eq (for \( M_n \) [PEO] = 10150 g·mol⁻¹) or 1017 eq (for \( M_n \) [PEO] = 19546 g·mol⁻¹) DCM. The solution was cooled to <0 °C and 2.5 eq triethylamine were added. After stirring for 10 min, 2.5 eq 2-bromoisobutyl bromide were dissolved in 108 eq or 209 eq, respectively, of DCM and added dropwise to the reaction mixture while keeping the temperature < 0 °C. Then the solution was slowly warmed up to room temperature and stirred for 24 h. For purification, the mixture was extracted for three times with 50 mL of deionized water. The organic phase was concentrated by solvent evaporation and transferred into a dialysis membrane was 14 kDa for the BCP with a 10 kDa PEO block. The dialysis tube was then immersed in ethanol, which was then degassed with argon. The required amount of monomer was then added to the reaction solution with an argon-flushed syringe. During reaction, samples were taken from the solution with a syringe and analyzed via \(^1\)H NMR to track the polymerization process. The ratio of iPMA polymer to iPMA monomer was used to calculate the respective conversion. The ATRP was stopped after 24 h by addition of DCM and flushing with air. For purification, the solution was filtered through a neutral alumina column. It was then concentrated by solvent evaporation and transferred into a dialysis tube. The molecular weight cut-off (MWCO) of the dialysis membrane was 14 kDa for the BCP with a 10 kDa PEO block and 25 kDa or 50 kDa for the ones with a 20 kDa PEO block. The dialysis tubes were then immersed in ethanol, which was replaced every day by fresh solvent, all at room temperature. After 3 days, ethanol was exchanged to water which was also replaced every day for three times, at room temperature. The precipitated polymer was then obtained by freeze-drying.

The degree of functionalization and purity of the product were analyzed via \(^1\)H NMR (300 MHz, CDCl₃, δ /ppm/) = 3.91–3.37 (m, 4H, –CH₂–CH₂–), 1.94 (s, 6H, C–(CH₃)₂–). Yield was 85% and degree of functionalization was 95% on average.

Synthesis of PEO-b-PiPMA

PEO-b-PiPMA BCP with different molar masses, with either a 10 or 20 kDa PEO block, have been synthesized via ATRP (Fig. 3). For this purpose, 1 eq of PEO-Br was transferred into a three-neck flask under argon atmosphere. The flask was then evacuated and vented with dry argon for three times. Afterward, the macroinitiator was dissolved in anisole; information on the respective volume used for the different BCP can be taken from the Supporting Information (Table S1). The solution was carefully degassed with argon. Then 4 eq of HMTETA and 2 eq CuCl were added. The flask was placed into a silicone bath and heated up to 60 °C. In another flask, iPMA was stirred with an inhibitor remover for at least 30 min and afterward it was degassed properly with argon. The required amount of monomer was then added to the reaction solution with an argon-flushed syringe. During reaction, samples were taken from the solution with a syringe and analyzed via \(^1\)H NMR to track the polymerization process. The ratio of PiPMA polymer to iPMA monomer was used to calculate the respective conversion. The ATRP was stopped after 24 h by addition of DCM and flushing with air. For purification, the solution was filtered through a neutral alumina column. It was then concentrated by solvent evaporation and transferred into a dialysis tube. The molecular weight cut-off (MWCO) of the dialysis membrane was 14 kDa for the BCP with a 10 kDa PEO block and 25 kDa or 50 kDa for the ones with a 20 kDa PEO block. The dialysis tubes were then immersed in ethanol, which was replaced every day by fresh solvent, all at room temperature. After 3 days, ethanol was exchanged to water which was also replaced every day for three times, at room temperature. The precipitated polymer was then obtained by freeze-drying.

Table 1 gives an overview of the composition of the synthesized polymers. The first number in the polymer name indicates the molar mass of the utilized PEO macroinitiator followed by a consecutive numbering.

The purity of the product was analyzed via \(^1\)H NMR (300 MHz, CDCl₃, δ /ppm/) = 4.86 (m, 1H, –CH–), 3.64 (s, 4H, –CH₂–CH₂–), 1.83 (m, 2H, –CH–), 1.22 (s, 6H, –(CH₃)₂), 1.05 (s, 1H, –CH₂–), 0.91 (s, 2H, –CH₃). Yield was 85% on average.
Additional Purification Procedure
Further purification of the BCP was carried out to remove residuals of hPEO or small BCP, either by another dialysis or by extraction.

For dialysis, the BCP were dissolved in ethanol ($\beta = 60$ g L$^{-1}$) at a temperature of 35 °C and transferred into a dialysis tube with a MWCO of either 25 or 50 kDa. The dialysis was carried out in an incubator at 35 °C and ethanol was exchanged daily. To track purification the solvent of the dialysate was evaporated and the polymeric residual was dissolved in CDCl$_3$ for $^1$H NMR analysis. The dialysis was conducted until the PEO peak in the spectra had an almost constant integral in relation to PiPMA peak. Afterward, ethanol was exchanged to water and the polymer was freeze-dried. The yield was 77% on average.

For extraction, the polymers were dissolved in DCM ($\beta = 70$ g L$^{-1}$) and extracted with water ($V_{\text{H2O}} = \frac{1}{3} V_{\text{DCM}}$) for three times. The organic phase was then concentrated by evaporation, the polymer was precipitated in water and freeze-dried. For this method, no detailed tracking was conducted. The yield was 80% on average.

Cloud Point Measurements
Cloud points (CP) were determined by stepwise addition of water to selected BCP solutions. The solutions were constantly stirred for 24 h after each step. CP was defined as the water concentration at which a distinct and stable turbidity can be observed by eye. To ensure that CP was reached, the solutions were heated up and cooled down slowly.

Membrane Fabrication
For membrane preparation the respective polymer was dissolved in various solvent mixtures (see Results and Discussion) and stirred for 3 days. For degassing the solutions, they were stored for another 3 days without stirring. Afterward, a polymer film was cast on a glass plate with a 200 μm doctor blade. For this purpose, an automatic casting machine (Erichsen Coatmaster) set to a speed of 25 mm s$^{-1}$ was used. The relative humidity was regulated to ≤25% at room temperature by a climate box. After a defined time of solvent evaporation, the polymer film was immersed in a coagulation bath with deionized water at ambient conditions. After 1 h, the water was replaced by fresh water und the membrane was left for another 24 h in this bath.

Membrane Characterization
For morphological characterization via SEM, the membranes were dried at ambient conditions. Furthermore, composition of the membranes was investigated via $^1$H NMR and GPC after dissolving it in CDCl$_3$ or THF, respectively.

Water flux and rejection of dextran (average M $\sim$100 kDa) were determined in dead-end mode with a stirred Amicon cell (model 8010; Merck KGaA), which was connected to a large feed reservoir and regulated pressure source. After compaction with deionized water for 45 min at a pressure of 1.3 bar the water permeability was determined by collecting the permeate for 3 × 5 min. The water was then replaced by a dextran solution ($\beta = 1$ g L$^{-1}$) and the pressure was set to 0.1 bar. The low transmembrane pressure was chosen in order to perform the ultrafiltration at low flux and thus to minimize the undesired effect of concentration polarization on observed rejection. The permeate was collected and the dextran concentrations in the feed ($C_{\text{Feed}}$) and permeate ($C_{\text{permeate}}$) were analyzed via TOC. The rejection $R$ was calculated according to eq. 1.

$$R = \left(1 - \frac{C_{\text{permeate}}}{C_{\text{Feed}}} \right) \cdot 100\%$$

RESULTS AND DISCUSSION
The investigation of the applicability of PEO-b-PiPMA as membrane material consists of three parts. In the first part, the characteristics of the synthesis via ATRP and the polymer purification are discussed. Second, studies to identify the influence of hPEO on the membrane formation process are performed. In the third part, the SNIPS process is applied to the BCP with help of a semiempirical approach from the literature for selection of suitable solvent systems. Additional information related to the membrane formation process is obtained from studying diluted BCP solutions.

Synthesis of PEO-b-PiPMA
The ATRP toward PEO-b-PiPMA was traced via $^1$H NMR spectra. The kinetics obtained for four representative polymers of this study are shown in Figure 4. Ideally, a controlled ATRP exhibits a first-order reaction regarding monomer concentration. Considering the persistent radical effect, which is typical for an ATRP, there should be a linear variation of the conversion $\beta$ with time $t^{2/3}$ in a plot with semilogarithmic scale.$^{41,42}$

The results of the synthesis tracking suggest that the ATRP is well controlled. This is also confirmed by the low values for

![FIGURE 4 Kinetics of the ATRP toward PEO-b-PiPMA according to synthesis procedures with different target molar masses at complete conversion; polymer 10_1: 100 kDa, polymers 10_2, 20_1 and 20_2: 200 kDa ($n_0$ is the amount of iPMA at $t = 0$, $n_t$ is the amount of iPMA at a certain reaction time). [Color figure can be viewed at wileyonlinelibrary.com]
TABLE 1 Overview of Synthesized BCP

| ID   | PEO block (kDa) | M_n (kDa) | PDI | PEO content (wt%) |
|------|----------------|-----------|-----|------------------|
| 10_1 | 10             | 66        | 1.20| 15               |
| 10_2 | 10             | 109       | 1.15| 9                |
| 20_1 | 20             | 93        | 1.27| 22               |
| 20_2 | 20             | 109       | 1.28| 18               |
| 20_3 | 20             | 177       | 1.26| 11               |
| 20_4 | 20             | 131       | 1.57| 15               |

the PDI (Table 1). Furthermore, we can conclude from the comparison of polymer 20_1 and 20_2 that reproducibility of the synthesis is given because reaction conditions were the same. The difference between polymer 10_1 and 10_2 can be explained by different target molar masses; that is, initiator concentration was higher for polymer 10_1 leading to a faster polymerization. Overall, controlled synthesis of the desired block copolymers was successful and desired molar masses can be adjusted by reaction conditions and ensured by tracking of conversion with NMR. The obtained PDI values are a little higher than the ones, which can be obtained in anionic polymerization but still in an adequate range with view on the use of the BCP in the SNIPS process. However, it must also be kept in mind, that there is an intrinsic inaccuracy in the GPC method due to the use of a polystyrene calibration for BPC with different chemical structure.

Purification of BCP

For commercially available PEO monomethyl ether, it is not unusual that some high molar mass diol is present as an impurity. For the 10 kDa PEO this portion was determined via GPC to be approximately 5% and for the 20 kDa PEO, it was 2% (see Supporting Information, Fig. S1). Additionally, the degree of functionalization after the first step of the synthesis toward PEO-Br is not 100%, further increasing the total fraction of nonreactive macroinitiator. Therefore, it is reasonable to assume that there might be some unreacted PEO derivative in the BCP after synthesis although purification with water should minimize the amount. Results in the following chapter will confirm this assumption. Nevertheless, with the used analytical methods due to signal overlapping, it is not possible to directly identify PEO in the BCP.

For this reason, polymers were used in their raw state after synthesis, that is, with the purification as described in the Experimental part. Furthermore, they were purified more intensively via dialysis and extraction as also described subsequently in the Experimental part. Regarding dialysis, the MWCO and temperature were higher, and another solvent was used during further purification in comparison to the procedure directly after synthesis. For a feasibility study of the extraction method the water, which was used to extract the hPEO from the BCP, was evaporated and the residual analyzed via 1H NMR (see Supporting Information, Figs. S2 and S3). Results proved that PEO was enriched in the aqueous phase but for practical reasons dialysis was more convenient.

Results for detailed tracking of the additional purification by dialysis are shown in Figure 5. The main criterion was the integral of the PEO signal relative to one of the PiPMA signals of the polymeric residual in the dialysate. Especially during the first dialysis step, the PEO peak is significantly increased in comparison to the raw polymer indicating a successful purification. Nevertheless, because the PiPMA peak can also be detected in the dialysate, it is obvious that also some block copolymer is removed. After approximately three to four dialysis steps, the relative integral of the PEO peak becomes almost constant and the mass of polymer in the respective dialysate fraction very low (cf. Supporting Information, Figs. S4 and S5), indicating that purification is finished.

Table 2 shows GPC results for the polymers in their raw state and after additional purification. Especially after dialysis an increase in molar mass is observable suggesting that hPEO and/or BCP with smaller molar mass were removed successfully. However, the overall amount of such BCP fractions with lower molar mass is relatively low so that only small changes in overall molar mass and PDI are observed.

Influence of PEO on Membrane Formation

Formation of Superstructures During Membrane Formation

During optimization of membrane fabrication from raw PEO-b-PiPMA, it appeared that under certain conditions, superstructures on the membrane surface were obtained. One example is shown in Figure 6. The diameters of the voids have a broad size distribution and are typically of about several hundred nanometers up to 1 μm. After empirical evaluation of all results (not shown here), we concluded that the formation of these structures is promoted either by comparatively fast precipitation during the NIPS process or for thermodynamically instable casting solutions.
In order to gain more detailed insights into that phenomenon, an explanation via a templating mechanism was used as hypothesis. In that scenario, one fraction of the block copolymer forms spherical particles either already in the casting solution or during casting under the influence of hPEO. These particles are then templating the outer membrane surface and can also contribute to void structure formation in the membrane cross section as observed via SEM (Fig. 7).

In general, membrane fabrication via SNIPS is done from polymer solutions with a combination of at least two solvents. One of them is polar, and the other is highly volatile. A common solvent system used in this work is NMP-THF. Considering the Hansen solubility parameters (HSP) as a measure of the interactions between solvent(s) and copolymer blocks, it is expected that crew-cut micelles with a PEO corona are formed in this environment (cf. Supporting Information, entry 6, including Table S2). Nevertheless, crew-cut micelles are rather instable and usually not formed by direct dissolution of the BCP.45 BCP with a very small hydrophilic polymer block are also known to form large compound micelles (LCM).37,45 In that case, it might also be possible that star-like micelles with a PEO core are present. Oss-Ronen et al. have also shown that PS-b-P4VP forms star-like

| ID  | $M_n$ (kDa) | PDI | $M_n$ (kDa) | PDI | $M_n$ (kDa) | PDI |
|-----|-------------|-----|-------------|-----|-------------|-----|
| 10_1| 66          | 1.20| 70          | 1.18| 64          | 1.17|
| 10_2| 109         | 1.15| 117         | 1.17| 99          | 1.18|
| 20_1| 93          | 1.27| 104         | 1.24| 90          | 1.24|
| 20_2| 109         | 1.28| 124         | 1.21| 91          | 1.46|

superstructures are promoted by a fast precipitation from thermodynamically instable systems:
- high polymer concentration
- selective solvents
- high PIPMA content (the higher, the lower the needed polymer conc.)
- water as precipitation bath

small pores from phase separation + big structures from particles

FIGURE 6 Illustration of the postulated templating mechanism leading to formation of void-like superstructures on the membrane surface combined with small pores from conventional phase separation; micellar particles are formed in casting solution or during the membrane fabrication process and can impose such structure on/in the membrane, afterward they are lost in the precipitation bath. [Color figure can be viewed at wileyonlinelibrary.com]
micelles with a P4VP core in a mixture of dimethylformamide (what has very similar HSP compared to NMP) with THF.\textsuperscript{46}

Keeping this in mind, two possibilities regarding the composition of the templating particles are considered (cf. Fig. 6). Due to the small PEO fraction in the BCP, the first one is the formation of large compound micelles. They typically show a broad size distribution and diameters of several hundred nanometers. In that case, hPEO would act as a nonsolvent, supporting particle formation. The second possibility would be the formation of inverse micelles with a PEO core exhibiting larger diameters due to the enrichment of hPEO in the core. This is also a phenomenon well known in the literature.\textsuperscript{37}

To proof this hypothesis, different experiments were conducted for which mainly the two PEO-\textit{b}-PiPMA BCP 20\textsubscript{3} and 20\textsubscript{4} (cf. Table 1) were used. A summary is given in Figures 8 and 9.

The first aspect to proof is that a fraction of the block copolymer/hPEO, which is later during membrane formation mostly lost in the precipitation bath, is responsible for the superstructure formation. For this purpose, a membrane showing superstructures was reused for fabrication of a new membrane [Fig. 8(a)]. As expected for the templating mechanism (cf. Fig. 6), the new membrane possesses a conventional surface structure because the respective polymer fraction was not present anymore to induce superstructure formation. As a step further the precipitation bath was investigated in more detail [Fig. 8(b)]. For this purpose, the water was completely evaporated, and the residual was examined via $^1$H NMR. In the respective spectra, a significant amount of PEO was detected but no BCP. This confirms that hPEO is involved in the mechanism, but we cannot exclude that a fraction of BCP is also lost. Due to practical reasons and the insolubility of the BCP in water, it might be possible that the BCP was not properly transferred from the precipitation bath to the flask used for solvent evaporation. Furthermore, the difference between the theoretical weight of the membrane (cast polymer) and the actual weight (final membrane) for the first membrane fabrication was 13 wt%. Because of this high amount, it seems reasonable that a BCP fraction is also involved in the templating mechanism.

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**FIGURE 8** Experiments conducted to proof the postulated templating mechanism during membrane fabrication: (a) reuse of a membrane with superstructures made from 25 wt% of polymer 20\textsubscript{4} in NMP-THF (60/40 w/w) for fabrication of a new membrane under the same conditions; (b) detailed investigation of the precipitation bath from membrane fabrication with 30 wt% of polymer 20\textsubscript{3} in NMP-THF (70/30 w/w), the nonsolvent was evaporated and the polymeric residual characterized via $^1$H NMR; (c) comparison of the $^1$H NMR spectra of polymer 20\textsubscript{3} used as membrane material and a respective membrane (30 wt% in NMP-THF (70/30 w/w), PEO signal integrals ($\delta = 3.65$ ppm) were determined in relation to those for PiPMA ($\delta = 4.86$ ppm). [Color figure can be viewed at wileyonlinelibrary.com]
superstructures and particle formation in water

![Diagram of BCP in THF to BCP in H2O](image)

**FIGURE 9** Additional experiments conducted to proof the postulated templating mechanism: SEM image and size analysis of particles from polymer 20_3 formed upon exchange of solvent from THF to water (β = 0.5 gL⁻¹). [Color figure can be viewed at wileyonlinelibrary.com]

Finally, the NMR spectra of the original polymer and membrane can be compared. Figure 8(c) shows that the composition of polymer and membrane significantly differ from each other. In relation to the PiPMA peak, the PEO signal integral decreases from polymer to membrane. This indicates that mainly hPEO and smaller BCP fractions are lost into the coagulation bath during membrane formation.

The second aspect to proof is that the BCP is in general able to form particles with a diameter of several hundred nanometers. In order to investigate that particles obtained from diluted solutions under conditions which are similar to the ones during NIPS were studied via SEM (Fig. 9). The BCP was transferred from THF to aqueous solution by slow addition of water and subsequent evaporation of THF. Then the solution was drop-cast on a silicon wafer. The particles observable in the SEM images have a broad size distribution and the range of diameter fits very well to the respective sizes of the void-like superstructures on the membrane surface. This clearly indicates that the formation of BCP particles upon contact with water is involved in the templating mechanism.

Because of similar molar masses and polymer compositions as well as same synthesis conditions, it is reasonable that these results are also valid for the other polymers shown in Table 1.

**Effect of Purification on Membrane Formation**

If it is true that hPEO and smaller BCP are responsible for the formation of superstructures, it should be possible to avoid them by use of further purified polymers. Therefore, membranes were fabricated using the raw, extracted and dialyzed polymers. Furthermore, the addition of hPEO to further purified polymers should induce superstructure formation again. Surfaces of membranes obtained from casting solutions of such polymers are shown in Figure 10.

The SEM images of the membrane surfaces clearly indicate that further purification of the polymers inhibits the formation of superstructures or least reduces it. At the same time, the density of the void-like structures increases again if hPEO is added to the casting solution. Therefore, it is very likely that residuals of the homopolymer are responsible for the unconventional membrane structures. This is further confirmed by the GPC traces in Figure 10, which are almost the same for re-dissolved membranes and the purified polymer. In contrast, the raw polymers contain smaller fractions with lower molar mass. However, it is still not clear from these experiments how the hPEO is involved in the particle formation.

An indication for that can be found by studying diluted organic and aqueous solutions of the raw and purified polymers (Fig. 11). The hydrodynamic diameter in NMP-THF does not differ significantly between the two polymer types. Furthermore, there is no influence of hPEO addition detectable. Particles obtained after transfer from organic to aqueous solution (analogous to experiments shown in Fig. 9) have a broad size distribution in the range of several hundred nanometers and can be found for the raw and purified polymers.

These findings indicate that the hPEO does not change the particle size or morphology significantly. Therefore, it can be claimed that during membrane fabrication, hPEO is mainly acting as a nonsolvent and thus inducing the formation of large compound micelles from BCP (cf. Fig. 6). Also, we cannot exclude that BCP with a very small molar mass have a similar effect as hPEO. Overall, we can summarize that membrane formation from BCP is very sensitive toward impurities in form of hPEO. The results might also be an indicator that a high PDI of the BCP can be problematic because only certain fractions of the BCP seem to be involved in particle formation.

**Membrane Formation via SNIPS Process**

**Semiempirical Determination of Suitable Solvent Systems**

After having evaluated the disturbing influence of hPEO, purified polymers were used in membrane fabrication with the aim to utilize the SNIPS process. To reduce the grand practical effort for the process optimization, Sutisna et al. had developed a semi-empirical approach that enables the calculation of suitable solvent systems. This is based on a segregation strength line derived from systems which have already been used successfully in the SNIPS process, that is, showed isoporous barrier layers of resulting membranes. The segregation strength line is obtained by plotting the interaction parameter χ' against the ratio of the volume fractions of block A and B, V_A/V_B (eq. 2). The resulting exponential fit (eq. 3) can be used to determine required values for χ' for not yet studied polymers and is shown in Figure 12. Using this output in
combination with eq. 2 leads to suitable solvents. The calculation was done for the dialyzed polymers 10_1 and 20_2, which possess almost the same PEO portion (cf. Table 1). Detailed descriptions of the calculation procedure and input data can be found in the Supporting Information (entry 7).

\[ \chi' = \frac{(\chi_{SA}N_A - \chi_{SB}N_B)}{\chi_{AB}N} \]  

\(\chi'\) against \(V_A/V_B\) used for calculation of suitable solvent systems for polymer 10_1 and 20_2 in the SNIPS process, red data points show required value for \(\chi'\) according to the fits of data for systems already used successfully for the SNIPS process from ref. 47. [Color figure can be viewed at wileyonlinelibrary.com]
TABLE 3 Results for Determination of Suitable Solvent Systems to be used for Polymers 10_1 and 10_2 in the SNIPS Process and Polar Component of the Hansen Solubility Parameters for the Respective Mixture Calculated by Averaging Values of the Individual Solvents According to Their Weight Fractions

| Polymer 10_1 | $\delta_p$ | Polymer 20_2 | $\delta_p$ |
|--------------|------------|--------------|------------|
| # 1 NMP-THF (90/10 v/v) | 11.7 | NMP-THF (70/30 v/v) | 10.5 |
| # 2 NMP-THF-DOX (90/5/5 v/v) | 11.5 | NMP-THF-DOX (85/5/10 v/v) | 11.0 |
| # 3 NMP-THF-EtOH (40/20/40 v/v) | 9.8 | NMP-THF-EtOH (20/60/20 v/v) | 7.7 |

$$\chi' = 0.02 \left(\frac{V_A}{V_B}\right)^3 + 0.12 \left(\frac{V_A}{V_B}\right)^2 + 0.35 \left(\frac{V_A}{V_B}\right) + 0.37 \quad (3)$$

$\chi_{SA/SB}$ is the interaction parameters of solvent and blocks A/B, $\chi_{AB}$ is the interaction parameter between blocks of BCP, and $N$ is the degree of polymerization for respective blocks.

Three different solvent systems were elaborated based on NMP and THF. NMP is used as polar component and THF is highly volatile, which is a typical solvent composition for the SNIPS process. Overall, the solvent system is selective for the PEO block according to the Hansen solubility parameters (cf. Supporting Information, Table S2). Furthermore, DOX was used to introduce a solvent which is nominally selective for the PiPMA block. Ethanol was added to introduce another solvent which is clearly selective for the PEO block but not as strong nonsolvent for PiPMA as water. Additionally, DOX evaporates faster than NMP (cf. Supporting Information, Table S2). Table 3 shows the results for the model-based solvent selection along with the value for the polar component of the HSP for the solvent mixtures. Membranes were made from respective solutions with polymer concentrations of 15, 18, and 20 wt%.

Characterization of Diluted Solutions via DLS

In preliminary experiments before membrane fabrication, diluted polymer solutions were investigated via DLS (Fig. 13). For both polymers, significant differences can be found for the different solvent systems. For both polymers, the particle diameter increases in the following order: NMP-THF < NMP-THF-EtOH < NMP-THF-DOX. Furthermore, polymer 20_2 tends to form bigger aggregates than polymer 10_1. This can be easily explained by its higher molar mass.

In NMP-THF-DOX, the particles are very large, meaning that mainly some large compound micelles or micellar aggregates are formed. As listed in Table 3, the polarity of the system does not significantly differ from the NMP-THF system. The fraction of dioxane is too small to yield overall selectivity for PiPMA. Nevertheless, the presence of DOX will induce a distinct swelling of the PiPMA block, which might destabilize primary micelles and induce aggregation or formation of other particle morphologies. Additionally, there seems to be no distinct influence on the solvent selectivity by the addition of ethanol. With or without ethanol, there might be some primary micelles as well as single polymer chains in solution. The slightly bigger diameter in the presence of ethanol can be explained by the stronger swelling of PiPMA in the EtOH-containing system, because of the significantly reduced solvent polarity (cf. Table 3). Furthermore, it cannot be concluded from these experiments whether star-like or crew-cut micelles are formed, although crew-cut micelles would be more reasonable from a theoretical point of view. Nevertheless, it was already shown in the literature that PS-b-P4VP forms star-like micelles with a P4VP core in DMF-THF. Furthermore, crew-cut micelles are usually not formed by direct dissolution of a block copolymer in a selective solvent.

Characterization of Casting Solutions via Cloud Point Determination

To characterize the casting solutions in more detail cloud point determinations were conducted. The results in Table 4 show that there is almost no difference between the two polymers although the solvent compositions vary. This is because the block ratio of the polymers is almost the same (cf. Table 1).

Obviously, the behavior in NMP-THF-EtOH differs significantly from that in the other solvents. This can be explained again by the lower polarity of the mixture making it more tolerant against the addition of water. This indicates that these solutions are more stable and at the same time less selective for the BCP.

Characterization of Membranes

The thickness of the obtained membranes was between 55 and 100 µm, depending on the BPC concentration in the casting solution and the solvent systems (cf. Supporting Information, Table S5). Membranes were characterized via SEM and ultrafiltration experiments, results of which are shown in Figures 14 and 15.

The membrane surfaces in Figure 14 as well as the ones not shown here do not exhibit any ordered pore structure. For polymer 10_1, the surfaces are rather dense; furthermore, the cross sections have finger-like structures. An exception is the membrane made from NMP-THF-EtOH solution, which has a completely dense cross section. From the cloud point measurements (cf. Table 4) and viscosity data (cf. Supporting Information, Fig. S6 and S7), it can be concluded that the structures are mainly influenced by thermodynamics. Solutions with high viscosity and low cloud-point lead to open porous membrane cross sections and the solution with the lowest viscosity and highest cloud-point to a dense structure. Regarding polymer 20_2, all cross sections are open porous

χ is the degree of polymerization for respective blocks.
and finger like. The surfaces are porous except for the membrane made from NMP-THF-EtOH. In this case, the influence of kinetics on the structure formation is apparently more prominent. This can be deduced from the cloud point and viscosity data. The EtOH system possesses a relatively low viscosity and a high cloud point leading to a finger-like cross section.

In Figure 15, rejection of a 100 kDa dextran is plotted against water permeability for every membrane. Missing data points originate from too low mechanical stability of the respective membrane, which is attributed to the brittleness of the PiPMA matrix polymer. One aim of attempts to fabricate isoporous membranes is to obtain high flux and high rejection at the same time. If polymer 10_1 is used it is partially possible to increase permeability and dextran rejection simultaneously. This is an advancement in comparison to conventional NIPS-based membranes and self-assembly of the block copolymer possibly plays a role. Nevertheless, it self-assembly is not prominent enough to obtain well-ordered pores. For polymer 20_2, we can observe a typical trade-off relationship between rejection and permeability.

The difference between the two polymers can be mainly explained by the difference in molar mass. This leads to significant differences in the mechanism of membrane formation. While the membrane structures of polymer 10_1 are mainly shaped by influences of thermodynamics of the polymer solvent–nonsolvent system, the membranes of polymer 20_2 are influenced by kinetics of phase separation to a greater extent. This also seems to influence the conservation of self-assembled structures from casting solution to the membrane, which is better for polymer 10_1 compared to polymer 20_2.

Furthermore, there seems to be a connection between membrane performance (linked to BCP membrane structure) and the DLS results of diluted BCP solutions. At first glance, both polymers behave similar in the respective solvent system regarding selectivity and self-assembly. The main difference can be found in the particle diameters which had been related to the molar masses. Polymer 20_2 has longer PiPMA and PEO chains and therefore the entanglement between different micelles is stronger than for polymer 10_1, independent of their morphology. It can be assumed, that micelles from polymer 20_2 are softer than the ones from polymer 10_1 (cf. Ref. 48). Although the more pronounced entanglement leads to a higher stability of a micelle assembly, softer spheres can more easily be deformed disturbing the order. Assuming that harder spheres are formed from polymer 10_1, their self-assembly seems to have a bigger (positive) impact on resulting membrane structure and performance compared to polymer 20_2. Ordered structures may possibly have been formed in casting solutions of polymer 20_2 as well but cannot be transferred to the membrane due to the deformability of the micelles.

Overall, there might be several reasons why no isoporous membranes were obtained. There are some ambiguities regarding the calculation of the solvent system. For example, the density of the polymer blocks is needed, but the concrete fraction of crystalline PEO is not known. Additionally, the Hansen parameters of the polymers and solvents are essential for the calculation, but they differ between different sources (cf. Supporting Information, entry 7). This influences the result very strongly, on the one hand, at the step of

**TABLE 4 Cloud Point Determination of Casting Solutions with a Polymer Concentration of 15 wt%**

| Solvent System         | Polymer 10_1 | Polymer 20_2 |
|------------------------|--------------|--------------|
| NMP-THF                | 5% H₂O       | 6% H₂O       |
| NMP-THF-DOX            | 5% H₂O       | 5% H₂O       |
| NMP-THF-EtOH           | 12% H₂O      | 10% H₂O      |
determining a suitable solvent system and on the other hand because the Flory–Huggins parameter of the respective polymer is needed. The Flory–Huggins parameter for PEO-b-PiPMA was calculated from the Hansen parameters because it was not available in the literature. Another important factor is that molar mass is needed, but for block copolymer characterization GPC always shows some systematic errors due to inhomogeneity of the polymer and—in this study also—inadequate calibration. Furthermore, the investigated range of polymer concentrations is rather small and the time of evaporation between casting and precipitation was not varied. Finally, another important factor is the stability of the micelle assembly, as already discussed above. Karunakaran et al. found for PS-b-PEO that only one specific block length in the BCP lead to ordered pores in a membrane. It is possible that the micelles formed from the

**FIGURE 14** SEM images of surfaces and cross sections of membranes made from 18 wt% of polymer 10_1 in NMP-THF (91/9 w/w), NMP-THF-DOX (91/4/5 w/w) and NMP-THF-EtOH (45/20/35 w/w) and from 18 wt% polymer 20_2 in NMP-THF (73/27 w/w), NMP-THF-DOX (86/4/10 w/w) and NMP-THF-EtOH (23/60/17 w/w), magnification cross-section 2000x
used PEO-b-PiPMA polymers are too soft in general. In that case, the order can be lost during the mechanical stress imposed during casting.

CONCLUSIONS

In the present study, we have shown that PEO-b-PiPMA BCP in a molar mass range relevant for membrane fabrication can be synthesized via ATRP. The synthesis tracking shows that the radical polymerization is well controlled and PDI lower than 1.5 are obtained, while the molar mass is adjustable. Nevertheless, there are residuals of hPEO remaining in the polymer after synthesis and conventional purification via precipitation and dialysis. This can be attributed to some diol which is already present in the macrominitiators educt and an incomplete functionalization. Furthermore, very BCP fractions with small molar mass might have an impact on PDI. They form due to a small quantity of termination reactions always occurring during ATRP.

Experiments regarding membrane fabrication and microphase separation in water lead us to the conclusion that these residuals have a strong impact on the membrane formation mechanism. We suppose that the combination of all results confirms the postulated templating mechanism (cf. Fig. 6). This means that hPEO and potentially also very small BCP can act as a nonsolvent inducing the formation of large compound micelles, which are in turn structuring the membrane surface and even its cross section. Therefore, the synthesis and purification of block copolymers are essential for the membrane formation process. Although the amount of the critical polymer fraction is obviously very small, it has a strong impact on the membrane properties. A very important finding of this work is that the complexity of the SNIPS process and the need for its extensive optimization begins already within the synthesis step. This complicates the already complex mechanism in terms of structure control and adjustment of filtration properties. Overall, ATRP should only be applied in combination with an extensive purification if defined microstructures are aimed. After further dialysis or extraction of the BCP, the formation of superstructures can be avoided successfully.

As the block copolymers possess a certain minimum molar mass, they can be successfully applied in the NIPS process to fabricate self-supported UF membranes. These will potentially offer advanced antifouling properties due to the integrated hydrophilic PEO. But it turned out, that the semiempirical determination of solvents suitable for the SNIPS process as introduced by Sutisna et al. is hindered by the limited availability of needed data like the Flory-Huggins parameter. If uncommon BCPs are newly introduced these values are usually not known and their experimental determination is very time consuming. Furthermore, the method relies on Hansen parameters which might differ between different sources especially for polymers. In the present case, it is also critical that molar mass is needed, because there are systematic errors in its determination via GPC. Nevertheless, the calculated solvent compositions might be in general suitable for PEO-b-PiPMA in the SNIPS process. Other reasons for not obtaining isoporous membranes might be that evaporation time between casting and precipitation or polymer concentrations were not chosen properly. Hence, by further refinement and optimization of fabrication parameters, it might be possible to overcome the typical trade-off relationship between selectivity and permeability.

ACKNOWLEDGMENTS

The authors want to thank Alexander Tjaberings and the working group of Prof. André H. Gröschel, at University Duisburg-Essen, for conducting the GPC measurements.

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