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Design of block copolymer membranes using segregation strength trend lines

Burhannudin Sutisna^a, Georgios Polymeropoulos^b, Valentina Musteata^c, Klaus-Viktor Peinemann^d, Apostolos Avgeropoulos^{b,e}, Detlef-M. Smilgies^f, Nikos Hadjichristidis^{*,b}, Suzana P. Nunes^{*,c}

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Block copolymer self-assembly and non-solvent induced phase separation are now being combined to fabricate membranes with narrow pore size distribution, and high porosity. The method has the potential to be used with a broad range of tailor made block copolymers to control functionality and selectivity for specific separations. However, the extension of this process to any new copolymer is challenging and time consuming, due to the complex interplay of influencing parameters, such as solvent composition, polymer molecular weights, casting solution concentration, and evaporation time. We propose here an effective method for designing new block copolymer membranes. The method consists of predetermining a trend line for preparation of isoporous membranes, obtained by computing solvent properties, interactions and copolymer block sizes for a set of successful systems and using it as a guide to select the preparation conditions for new membranes. We applied the method to membranes based on poly(styrene-*b*-ethylene oxide) diblocks and extended it to newly synthesized poly(styrene-*b*-2-vinyl pyridine-*b*-ethylene oxide) (PS-*b*-P2VP-*b*-PEO) terpolymers. The trend line method can be generally applied to other new systems and is expected to dramatically shorten the path of isoporous membrane manufacture. The PS-*b*-P2VP-*b*-PEO membrane formation was investigated by *in situ* Grazing Incident Small Angle X-ray Scattering (GISAXS), which revealed a hexagonal micelle order with domains spacing clearly correlated to the membrane inter-pore distances.

1. Introduction

The ability of block copolymers to self-assemble has enabled application in many fields, such as drug delivery¹⁻³, catalysis^{4,5} and electronics⁶. Guided by thermodynamic interactions and entropic constraints, a rich variety of morphologies can be obtained in the melt and in solutions of diblock and triblock copolymers.⁷⁻¹³ The equilibrium morphology in the melt, achieved after long periods of annealing, can be predicted by considering the Flory-Huggins interactions between blocks, molecular weight and block ratio following excellent theoretical work in the field and applying for instance self-

consistent field simulations¹⁴⁻¹⁶. The morphology in solution is strongly influenced by the interfacial energy between blocks, block-solvent interactions, block copolymer architectures, polymerization degree of each block and copolymer concentration. Solid work has been reported particularly in diluted systems, adapting the concept of packing factors used initially for low molecular weight surfactants in solution to predict morphology, which might be in the form of spherical micelles, wormlike rods and vesicles.^{17,18} In high concentration range, self-consistent field has been used to understand changes of morphology promoted by solvent annealing.¹⁹ The semi-diluted concentration range has been less investigated and might be even more complex. In addition to the factors influencing the geometry of single assemblies in diluted solutions, in this concentration range micelles themselves might strongly interact with each other and self-organize in a quasi-crystalline structures as hexagonal, body center cubic (bcc) or face center cubic (fcc) arrangements.²⁰⁻²² High concentration promotes inter-micelle entanglement with additional elastic considerations. The core rigidity and the friction between segments of different micelle coronas can influence the adopted morphology and promote the existence of metastable structures. Fast solvent evaporation, solvent-non-solvent exchange and *in-situ* polymerization can kinetically trap morphologies far from equilibrium.²³⁻²⁶ These strategies are being used to stabilize morphologies, which might be more convenient for specific applications than equilibrium ones. An important example is the development of membranes for selective separation. Membranes cast from block copolymer solutions have a remarkable advantage

^aKing Abdullah University of Science and Technology (KAUST), Physical Science and Engineering Division (PSE), 23955-6900 Thuwal, Saudi Arabia

^bKing Abdullah University of Science and Technology (KAUST), Catalysis Center (KCC), Physical Science and Engineering Division (PSE), 23955-6900 Thuwal, Saudi Arabia

^cKing Abdullah University of Science and Technology (KAUST), Biological and Environmental Science and Engineering Division (BESE), 23955-6900 Thuwal, Saudi Arabia

^dKing Abdullah University of Science and Technology (KAUST), Advanced Membranes and Porous Materials Center (AMPMC), Physical Science and Engineering Division (PSE), 23955-6900 Thuwal, Saudi Arabia

^eUniversity of Ioannina, University Campus-Dourouti, Department of Materials Science Engineering, 45110 Ioannina, Greece

^fCornell High Energy Synchrotron Source, Wilson Laboratory, Cornell University, Ithaca, New York 14853, USA

*Corresponding Authors: suzana.nunes@kaust.edu.sa and nikolaos.hadjichristidis@kaust.edu.sa

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compared to commercial homopolymer membranes prepared by phase inversion. By combining self-assembly and non-solvent induced phase separation membranes can be manufactured with narrow pore size distribution and exceptionally high porosity^{27–29}. The pore formation is highly sensitive to the solvent composition and reflects the self-assembly in the bulk of the casting solution. Membranes based on polystyrene-*b*-poly(4-vinyl pyridine) (PS-*b*-P4VP)^{30, 31}, poly(isoprene-*b*-styrene-*b*-4-vinyl pyridine) (PI-*b*-PS-*b*-P4VP) membranes³² and polystyrene-*b*-poly(ethylene oxide) (PS-*b*-PEO)^{33, 34} have been demonstrated and optimized to achieve long-range pore order. We have used dissipative particle dynamics to understand the effect of solvent composition, concentration and molecular weight on copolymer self-assembly in the semi-dilute regime, close to conditions used for membrane preparation.^{35, 36} The synthesis of copolymers with different molecular architectures and functionalization could extend the application of self-assembly non-solvent induced phase separation membranes with exact tuned porosity and functional properties. However, each time a new molecular weight combination or a new copolymer is explored for membrane fabrication, strenuous optimization is required. A practical method is needed to simplify the selection of the best solution composition for a membrane starting from a new copolymer. We have been investigating the correlation between the different parameters, looking for practical semi-empirical procedures to drastically shorten the path of membrane manufacture. We propose here a simple semi-empirical selection method, which identifies a trend line or master curve for block copolymer membrane manufacture. The curve calculation takes into consideration block volume ratios and the different interactions between blocks and solvent mixtures. We demonstrated the method by first comparing data published for previously reported copolymer systems. We synthesized then a new triblock copolymer and optimized the morphology, by using the proposed method. We followed the membrane formation by SAXS, time-resolved GISAXS experiments and electron microscopy, demonstrating the efficiency of the method. We believe the proposed approach will substantially facilitate new developments in the field.

2. Materials and Methods

2.1 Materials

Poly(styrene-*b*-ethylene oxide) copolymers, PS_{195k}-*b*-PEO_{45k} (PDI = 1.18), were purchased from Polymer Source, Inc, Canada. Tetrahydrofuran (THF), 1,4-dioxane (DOX), N,N-Dimethylformamide (DMF), and pyridine (Pyr) were supplied by Sigma-Aldrich and used as received. MilliQ water was used as non-solvent bath.

For the synthesis of PS_{80.5k}-*b*-P2VP_{64.4k}-*b*-PEO_{16.1k} the following chemicals were used after purification. THF (Sigma Aldrich, 99.9%) was refluxed over sodium, stirred in the presence of CaH₂ overnight and distilled over Na/K alloy. *sec*-Butyllithium (Sigma-Aldrich, 1.4M

in cyclohexane) was diluted to the appropriate concentration in purified hexane, in a specific glass apparatus under high vacuum. Styrene (Sigma Aldrich, 99%) was purified by distillation over CaH₂ and dibutyl-magnesium (Sigma-Aldrich, 1M solution in heptane) and stored in pre-calibrated ampoules. 2-Vinylpyridine (Sigma Aldrich, 97%) was distilled twice over CaH₂ and once over sodium mirror, stirred in the presence of trimethyl-aluminum (Sigma Aldrich, 97%) at 0 °C and used directly for the polymerization. Ethylene oxide (Sigma-Aldrich, 99.5%) was purified by consecutive distillations over CaH₂ and *n*-Buli at 0 °C, prior distillation to the polymerization reactor. The phosphazene superbases, 1-*tert*-Butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)-phosphoranylideneamino]-2λ⁵,4λ⁵-catenadi (phosphazene) (P₄-tBu) (Sigma-Aldrich, 0.8M in hexane) was diluted in purified hexane and stored at pre-calibrated ampoules. Acetic acid (terminating agent) was stored under high vacuum and used as received.

2.2 Triblock terpolymer synthesis and chemical characterization

The linear triblock terpolymer PS_{80.5k}-*b*-P2VP_{64.4k}-*b*-PEO_{16.1k} (PS: polystyrene; P2VP: poly(2-vinylpyridine); PEO: poly(ethylene oxide) was synthesized *via* sequential anionic polymerization high vacuum techniques.³⁷ The synthesis (Scheme 1) by sequential addition of the monomers according to their reactivity involves the anionic polymerization of styrene (5g, -78 °C, THF) with 0.062 mmol of *sec*-butyllithium as initiator. After completion of the polymerization of the first block (one hour), an aliquot was taken for size exclusion chromatography (SEC) analysis, followed by transfer through distillation of the appropriate amount of 2-VP (4g) under vigorous stirring at -78 °C. After 1h, another aliquot was taken for SEC analysis. Finally, 0.056 mmol of P₄-tBu superbases was added, followed by distillation of 1g EO and the polymerization solution left under stirring at 50 °C.^{38–41} After 7 days, the polymerization was quenched by acetic acid and the polymer precipitated in cool hexane. The final product was dried in a vacuum oven for 48h at 40 °C (colorless powder).

The number-average molecular weight (*M_n*) and polydispersity index (PDI) of the PS, the diblock copolymer PS-*b*-P2VP and the final triblock terpolymer PS-*b*-P2VP-*b*-PEO, were determined by SEC, equipped with an isocratic pump (Spectra System P1000), three columns in series (PLgel 5 μm Mixed-C, 300x7.5 mm), a refractive index (RI, Shodex RI-101) detector in THF with a flow rate of 1 mL/min at 45 °C in order to prevent crystallization of the PEO block. Polystyrene standards (*M_p*: 4.300 to 3.000.000 g/mol) were used for the calibration of the instrument. The chemical nature of the different blocks and the composition of the terpolymer was determined by a Brücker AV-500 ¹H-NMR spectrometer in CDCl₃ (Acros 99.6 %) in the presence of tetramethylsilane (TMS) as internal standard. It should be noted that the molecular weights determined by SEC calibrated with PS standards are apparent. Nevertheless, in this case since PS and P2VP, on one hand have similar hydrodynamic characteristics (key parameter in SEC) and on the other hand constitute the 895 of the terpolymer, its molecular weight is very close to the real one.

Scheme 1 Synthesis of linear PS-*b*-P2VP-*b*-PEO terpolymer

2.3 Membrane preparation

Block copolymers were dissolved in a mixture of solvents with a polymer concentration of 18–25 wt%. The solution was cast on a glass plate using a casting knife with 200 μm air gap. The solvent was then let to evaporate for 10–20 s before precipitation in water at room temperature. The resulting membrane was dried under atmospheric condition.

2.4 Field emission scanning electron microscopy (FESEM)

FESEM micrographs of the membranes were obtained by using FEI Quanta 200 or Novanano microscopes at an accelerating voltage of 5 kV and working distances of 7–5 mm. The samples were mounted on an aluminum stub using aluminum tape and sputter coated with 3 nm Pt before imaging.

2.5 Transmission electron microscopy (TEM)

TEM of the membrane cross-sections and micelle morphology of the copolymers in diluted solutions was performed using a FEI Tecnai 12 microscope operating at 120 kV. Membranes were first stained with ruthenium tetroxide (RuO₄) for a better contrast in TEM. Stained membranes were embedded in epoxy resin and cured at 60°C for 24 h. Ultrathin sections of the membranes with a thickness of 80 nm were prepared using ultramicrotome (Leica EM UC6) with a diamond knife and placed on a copper grid before imaging. For micelle characterization, block copolymers were dissolved in a mixture of solvents with a polymer concentration of 1 g/L followed by stirring overnight. The solution was dropped onto a carbon-coated copper grid, and the solvent was immediately

blotted using a filter paper followed by drying at room temperature for about 5 min.

2.6 Dynamic light scattering (DLS)

DLS measurements were performed using Malvern Zetasizer with 173° backscatter measurement angle and a glass cuvette with square aperture. The samples were prepared by dissolving copolymers in solvents with a polymer concentration of about 1 g/L followed by stirring overnight. The solutions were filtered through a 0.2 μm syringe filter before measurements.

2.7 Small Angle X-ray Scattering (SAXS)

SAXS of the copolymer solutions were measured at the SAXS1 beam line of the Brazilian Synchrotron facility (LNLS) with a fixed energy of 8.0 keV and X-ray wavelength of 1.55 Å. The solution was injected into a vacuum cell with mica windows using a syringe. The detector used was PILATUS 300k with a pixel size of $(172\ \mu\text{m})^2$ and the sample-to-detector distance was 3.057 m. For each measurement a number of 20 frames with 30 s exposure time and the beam area on the sample was $1\ \text{mm}^2$. Data were obtained as the average of azimuthal integrated scattering patterns after normalization to the incident beam intensity and subtraction of the background.

2.8 Grazing Incident Small Angle X-ray Scattering (GISAXS)

In situ GISAXS experiments of the film casting were performed at the beam line D1 of the Cornell High Energy Synchrotron Source (CHESS) as described previously.⁴² An in situ doctor blading system⁴³ installed at the beam line was used with a controlled coating gap of 200 μm and a casting speed of 1500 $\mu\text{m/s}$. The beam energy of 10.6

keV and X-ray wavelength of 1.162 Å were used with an incident angle of 0.13°. The copolymer solution was initially transferred with the use of a pipette onto a glass substrate positioned on the sample goniometer. A sample-to-detector distance of 1.82 m was used throughout the experiments. The automatic casting system allowed the blade to pass through the cast solution and form a film with 200 µm thickness. The GISAXS measurements of the film were started immediately after the blade reached its final position. The 2D scattering patterns were acquired every 3.3 s, which attributed to 0.3 s exposure time and 3 s detector read-out time. The X-ray detector used was MedOptics CCD camera of $(1024)^2$ pixels with a pixel size of $(46.9 \text{ µm})^2$. Integrations of the horizontal cuts of the 2D patterns were performed using Fit2D software. A set of scattering peaks can be attributed to a certain order after normalizing with the value of the first peak (q^*). The corresponding domain spacing (d-spacing) was calculated as $2\pi/q^*$.

3. Results and discussion

We propose a simple method to guide the solvent selection for membranes manufacture by self-assembly and non-solvent induced phase separation (SNIPS). The method is expected to substantially shorten the manufacture process of isoporous membranes when new copolymers are explored. The method is demonstrated by using PS-*b*-PEO diblock copolymers and a newly synthesized PS-*b*-P2VP-*b*-PEO triblock copolymer. The motivation for exploring the ternary block copolymers is the following. Compared to PS-*b*-PEO membranes, PS-*b*-P2VP-*b*-PEO membranes could exhibit pH-responsiveness due to the presence of pyridine block as demonstrated previously.⁴⁴ Meanwhile, compared to PS-*b*-P2VP membranes, the addition of PEO could potentially increase the membrane resistance to fouling and biocompatibility due to the hydrophilicity of PEO.^{45, 46}

3.1 PS-*b*-P2VP-*b*-PEO copolymer synthesis and characterization

Figures 1 and 2 and Table 1 show the characterization of the synthesized triblock copolymer. This includes the SEC traces (Fig. 1) and the molecular characterization (Table 1) results for different intermediary and final copolymerization products (PS, PS-*b*-P2VP and PS-*b*-P2VP-*b*-PEO) and the ¹H-NMR spectrum of the linear triblock terpolymer PS-*b*-P2VP-*b*-PEO (Fig. 2). The triblock copolymer structure is very well defined and is considered as a model polymeric material for this work.

Fig. 1. SEC chromatograms of (A) PS homopolymer, (B) PS-*b*-P2VP diblock copolymer and (C) final PS-*b*-P2VP-*b*-PEO terpolymer.

Table 1. Molecular characteristics of polystyrene (PS), PS-*b*-P2VP diblock copolymer and PS-*b*-P2VP-*b*-PEO triblock copolymer

Samples	$\bar{M}_n^a$ (g/mol)	PDI ^a	$f_{(PS)}^b$ %(w/w)	$f_{(P2VP)}^b$ %(w/w)	$f_{(PEO)}^b$ %(w/w)
PS	80,500	1.03	-	-	-
PS- <i>b</i> -P2VP	145,500	1.04	0.55	0.45	-
PS- <i>b</i> -P2VP- <i>b</i> -PEO	161,500	1.04	0.49	0.40	0.11

^a SEC in THF at 45°C, ^b ¹H-NMR at CDCl₃

Fig. 2. ¹H-NMR spectrum of the linear triblock terpolymer PS-*b*-P2VP-*b*-PEO.

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Table 2. Polymer-solvent systems leading to isoporous membranes in previous reports

ID	Copolymer	Solvent ^a	Solvent ratio (wt%)	V_A/V_B	$\chi_{sA}N_A$	$\chi_{sB}N_B$	$\chi_{AB}N^b$
P1	PS _{175k} - <i>b</i> -P4VP _{65k} ⁴⁷	THF/DOX/DMF	1/1/1	2.8	779	141	804
P2	PS _{188k} - <i>b</i> -P4VP _{64k} ⁴⁸	Ac/DOX/DMF	20/51/29	3.1	831	144	845
P3	PS _{182.4k} - <i>b</i> -P4VP _{57.6k} ⁴⁹	THF/DOX/DMF	1/1/1	3.3	812	125	805
P4	PS _{138k} - <i>b</i> -P4VP _{41k} ⁵⁰	THF/DOX/DMF	1/1/1	3.6	614	89	600
P5	PS _{162.4k} - <i>b</i> -P4VP _{28.7k} ³⁰	THF/DMF	30/70	6.0	1313	82	641
P6	PS _{138k} - <i>b</i> -PEO _{18k} ³³	THF/DMAc/Sulf	48/29/23	8.2	839	158	139

^aTHF=Tetrahydrofuran; Ac=Acetone; DOX=1,4-Dioxane; DMF=N,N-Dimethylformamide; DMAc = N,N-Dimethyl Acetamide; Sulf = Sulfolane

^bFlory-Huggins interaction parameters, χ_{AB} , of PS-P4VP and PS-PEO were 0.35 and 0.08, respectively.^{51, 52}

3.2 Trend line for isoporous membrane preparation

The proposed method for solvent selection to guide the self-assembly and lead to effective membrane manufacture is based on the values of segregation strengths estimated from Flory-Huggins interaction parameters (χ) multiplied by the degree of polymerization (N). We analyzed χ and N values for different copolymer systems, for which isoporous membranes have been previously reported. A trend line was plotted with a suitable ratio of parameters and used for further solvent selection for new systems. The method is explained in detail in this section.

Table 2 summarizes diblock copolymers and solvent mixtures, which led to ordered isoporous membranes in previous reports. Three segregation strengths were calculated for the polymer-solvent systems in Table 2:

- 1) solvent mixture and the less soluble block (A): $\chi_{sA}N_A$
- 2) solvent mixture and the most soluble block (B): $\chi_{sB}N_B$
- 3) less soluble block and the most soluble block (B): $\chi_{AB}N$

where χ_{si} is the Flory-Huggins interaction parameter between the solvent mixture and the polymer blocks i ; N_i is the degree of polymerization of polymer block i , and N is the total degree of polymerization ($N = N_A + N_B$).

The Flory-Huggins interaction parameters between the solvent mixture and the polymer blocks (χ_{si}) were calculated using Eq. 1:

$$\chi_{si} = \frac{VA_{si}}{RT} \quad (1)$$

where V is the molar volume of the solvent mixture (volume-weighted average); A_{si} is the difference between the Hansen solubility parameters (HSP) for the solvent (s) and the polymer (i); R is gas constant (8.314 J/mol.K); and T is temperature (K). The A_{si}

term was calculated using Eq. 2, in which the dispersion (δ_D), polar (δ_P), and hydrogen bond (δ_H) terms of the solvent mixtures were calculated as the volume-weighted average of the Hansen parameters of each component.

$$A_{si} = (\delta_{Ds} - \delta_{Di})^2 + 0.25(\delta_{Ps} - \delta_{Pi})^2 + 0.25(\delta_{Hs} - \delta_{Hi})^2 \quad (2)$$

Table 2 shows the calculated segregation strengths for the previously reported polymer-solvent systems. The copolymers (P1-P6) are listed in the increasing order of V_A/V_B , which are the molar volume ratio of the less soluble block (A) to the most soluble block (B). $\chi_{sA}N_A$ values are higher than $\chi_{sB}N_B$ in all of the mixtures, implying that the A blocks (i.e. PS) should form the micelle core, while the B blocks (P4VP or PEO) form the corona due to their better compatibility with the solvent mixtures.

The segregation strengths vary with the copolymer and influence the form and deformability of micelles in solution. The micelles assembly affects the final membrane morphology. Previous observations indicate that the micelle arrangement in the casting solution bulk can directly reflect the pore order on the membrane surface.²⁷ The rigidity can affect the micelle arrangement in solution.⁵³ Furthermore additives, which increase the micelle rigidity, or reduce their deformability, lead to more ordered pore morphology.⁵⁴ A motivation in this paper is to find a general parameter or set of parameters to predict which solvent combination would lead to effective segregation into spherical micelles and coronas with low deformability. A strong amphiphilic character favors aggregation into micelles. Core segments with low interaction with the solvent should have a positive effect on the ordered pore formation. But this is only a first requirement. The corona characteristics are at least as important. Favorable corona interaction with the solvent is a key requirement for the micelle formation. However the right combination of block length and corona-solvent interaction seems to be necessary to achieve ordered pore morphology. Long corona segments with too strong

interaction with the solvent mixture might lead to excessively deformable assemblies and less order.

We propose here to use the segregation strength, the dimensionless parameter $\bar{\chi}$ to choose the most convenient solvent composition. Its calculation should follow Eq. (3):

$$\bar{\chi} = \frac{(\chi_{SA}N_A - \chi_{SB}N_B)}{\chi_{AB}N} \quad (3)$$

Remarkably, the $\bar{\chi}$ values for the polymer-solvent mixtures listed in Table 2 could be fitted very well into a third-order polynomial trend line (with R-square 0.9999), when plotted against V_A/V_B (Fig. 3):

$$\bar{\chi} = 0.02 (V_A/V_B)^3 + 0.12 (V_A/V_B)^2 + 0.35 (V_A/V_B) + 0.37 \quad (4)$$

$\bar{\chi}$ values increase with V_A/V_B for the polymer-solvent systems that led to isoporous membranes.

As far as the thermodynamic meaning of $\bar{\chi}$ is concerned, it could be correlated to the difference (Δg) between the free energy per unit volume for the ordered micelle state and that of the random state, described by Noolandi and Hong⁵⁵. The contribution of interaction energies to Δg can be estimated as Δg_{int} from Eq. 5:

$$\begin{aligned} \Delta g_{int} = & -\chi_{AB}f_Af_B(\varphi_C^0)^2 + \chi_{AS}f_A\varphi_C^0\varphi_S^0F_2^S/G_2^v \\ & - \chi_{AS}f_A\varphi_C^0\varphi_S^0 + \chi_{BS}f_B\varphi_C^0\varphi_S^0F_1^S/G_1^v \\ & - \chi_{BS}f_B\varphi_C^0\varphi_S^0 \end{aligned} \quad (5)$$

where f_A and f_B are direct functions of the degree of polymerization of blocks A and B, respectively; φ_C^0 and φ_S^0 are the overall volume fractions of the copolymer and the solvent, respectively ($\varphi_S^0 = 1 - \varphi_C^0$) in the solution; F_1^S and F_2^S are fractions of solvent (by volume) in the corona and core, respectively; G_1^v and G_2^v are the ratios between the total volume occupied by the corona or core, respectively, and the total micelle volume (core + corona). In addition to Δg_{int} entropic terms related to stretching or compression of chains in the micelle and interfacial aspects contributions should be added for a complete account of Δg . Yuan et al. used self-consistent field theory to estimate the energy involved in the micellization of block copolymers.⁵⁶

The term $\bar{\chi}$, used in this work, is a simplified and semi-empirical ratio, estimated only from solubility parameters and polymerization degree. This information is easily available for the copolymers and solvents and should be used as a fast indicator of the most suitable cast solution composition.

Plotting $\bar{\chi}$ against V_A/V_B for different successful ordered systems gives a polynomial trend line as shown in Fig. 3. For final ordered membrane morphology, $\bar{\chi}$ values should be as close as possible to the line.

Fig. 3 shows $\bar{\chi}$ values for single solvents. In general, the solvents leading to $\bar{\chi}$ values above the trend line (e.g. DMF, $\bar{\chi} = 2.4$ for PS_{138k}-*b*-P4VP_{41k}, and DMAc, $\bar{\chi} = 8.2$ for PS_{138k}-*b*-PEO_{18k}) were good solvents for the most soluble blocks (P4VP or PEO), which form the corona. This favors micelle formation, but is not a sufficient condition for ordered membrane morphology. On the other hand, the solvents with $\bar{\chi}$ below the trend line (i.e. THF, $\bar{\chi} = 0.5$, and DOX, $\bar{\chi} = 0.5$ for PS_{138k}-*b*-P4VP_{41k}) were good solvents for both blocks. $\chi_{SB}N_B$ and $\chi_{SA}N_A$ values are closer for systems below the trend line (e.g. for PS_{138k}-*b*-P4VP_{41k}, THF, $\chi_{SB}N_B = 108$, $\chi_{SA}N_A = 428$) than above the trend line (e.g. for PS_{138k}-*b*-P4VP_{41k}, DMF, $\chi_{SB}N_B = 193$, $\chi_{SA}N_A = 1658$). THF is less favorable for the micelle formation in this case. A combination of solvents above and below

the trend line might lead to an optimal composition, favouring well-formed micelles with low deformability.

The effect of solvent selectivity on block copolymer self-assembly in solution has been extensively demonstrated by the group of Eisenberg⁵⁷⁻⁶⁰. They controlled the selectivity of water-DMF or water-dioxane systems for copolymer blocks, by adjusting the amount of water in the solution to form various micelle morphologies, such as spheres, rods, and vesicles. Lodge et al.⁶¹ have also investigated the effect of solvent selectivity by adjusting the ratio of various dialkyl phthalates to control the formation of micelle morphologies of an asymmetric PS-*b*-PI copolymer from spheres to cylinders to vesicles. As the solvent selectivity increased, the solvent-core block interactions decreased, and the interfacial tension increased, which resulted in various aggregate morphologies.⁶¹ In a similar way the solvents can be adjusted to fit the trend line in Fig. 3.

Fig. 3. Dimensionless parameter $\bar{\chi}$ versus V_A/V_B for various polymer-solvent systems (P1-P6, filled data points), previously confirmed as leading to isoporous membrane; Trend line fitted from the data points; unfilled data points corresponding to unordered systems.

The trend line was estimated disregarding the effect of solvent evaporation during the membrane preparation. Correction for evaporation is considered in the supporting information (Table S1).

3.3 Trend line method applied to an unexplored diblock copolymer

The trend line in Fig. 3 was used to estimate the best solvent mixtures for the preparation of isoporous membranes from an unexplored copolymer, PS_{195k}-*b*-PEO_{45k} ($V_A/V_B = 4.7$). From the third-order polynomial equation in Eq. 4, the estimated $\bar{\chi}$ for PS_{195k}-*b*-PEO_{45k} was 1.42.

$\bar{\chi}$ calculations were done for the copolymer in various mono solvents as summarized in Table 3. Almost all the water-miscible solvents, including THF, DOX, and DMF, have $\bar{\chi}$ above the value

calculated from the trend line while pyridine (Pyr) was the only water-miscible solvent that has χ lower than the trend line. We then chose a ternary mixture of THF/DOX/Pyr as the solvent mixture for the preparation of isoporous membranes from PS_{195k}-*b*-PEO_{45k}. Table 3 shows Hansen solubility parameters for copolymer blocks and components of the solvent mixture, including their dispersion, polarity, and hydrogen bond contributions.⁶² THF and DOX are better solvents for PEO compared to pyridine, mainly due

to their close dispersion and hydrogen bond terms, while pyridine is a more compatible solvent for PS.

The calculated Flory-Huggins interaction parameters between the polymer blocks and the solvents are presented in Fig. 4.

The interaction parameters for PEO/THF and PEO/DOX are lower than those for PS/THF and PS/DOX, whereas the PEO/Pyr is higher than for PS/Pyr.

Table 3. χ of various solvents for the copolymer PS_{195k}-*b*-PEO_{45k} ($\chi_{\text{trend line}} = 1.42$) and Hansen solubility parameters for selected solvents and copolymer blocks⁶²

Block or solvent	χ	δ_D (MPa ^{0.5})	δ_P (MPa ^{0.5})	δ_H (MPa ^{0.5})	$\delta = \sqrt{\delta_D^2 + \delta_P^2 + \delta_H^2}$
Polystyrene		18.5	4.5	2.9	19.3
Poly(ethylene oxide)		17.3	3.0	9.4	19.9
Acetone	2.9				
Acetonitrile	4.2				
DOX	3.3	17.5	1.8	9.0	19.8
DMAc	5.6				
DMF	6.0				
Pyridine	-0.2	19.0	8.8	5.9	21.8
Sulfolane	8.4				
THF	2.2	16.8	5.7	8.0	19.5

Fig. 4 Flory-Huggins interaction parameters between the copolymer blocks (PS-*b*-PEO) and selected solvents.

To closely fit the trend line, the weight ratio of THF/DOX/Pyr was then optimized to 42/25/33, giving a χ value of 1.32. By using this fixed solvent composition, PS_{195k}-*b*-PEO_{45k} membranes were prepared by casting and immersion in water with different polymer concentrations and evaporation times.

Ordered isoporous membranes were obtained from 19 wt% PS_{195k}-*b*-PEO_{45k} solutions in 42/25/33 THF/DOX/Pyr with evaporation time of 10 s. FESEM and AFM images of the membrane surfaces (Fig. 5 and S1) and cross sections (Fig. 6) showed that the membranes had a uniform pore diameter of about 63 nm on the

top of a macro porous substructure. In contrast, at a lower polymer concentration of 18 wt%, disordered structures were obtained (Fig. S2). Copolymers in THF/DOX binary solvent mixtures had χ values far above the trend line leading to a non-uniform porous surface. These results show that the trend line can be helpful to find an effective solvent mixture for a certain block copolymer, from which isoporous membranes can be prepared after optimizing the polymer concentration and evaporation time experimentally.

Membranes with uniform pore sizes were also obtained when binary solvent mixtures were used. THF/Pyr and DOX/Pyr were estimated to produce isoporous membranes since each single solvent leads to χ values above and below the trend line. χ values for the binary mixtures were 0.82 for 1/1 THF/Pyr and 1.25 for 1/1 DOX/Pyr. Uniform membranes could be obtained with larger copolymer concentration (20 wt% with 5 s) as shown in Fig. 5. The predictions using the trend line in Fig. 3 were reinforced by TEM investigation using diluted PS_{195k}-*b*-PEO_{45k} solutions in each solvent or solvent mixture. Images are shown in Fig. 7. Micelles prepared from solvent mixtures, which led to ordered isoporous membranes were perfectly spherical and well defined. In contrast, micelles prepared from THF/DOX led to an irregularly interconnected structure. These results show that the micelle morphology in dilute solution observed by TEM can serve as screening and indication of suitable solvent mixtures for ordered final membrane morphology. The micelle deformation and aggregation into larger structures hinder the formation of regular pores in the final membrane. One needs to be aware that this is just an indication. In the semi-dilute regime morphological might take place and affect the final structure.

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Fig. 5. FESEM images of PS_{195k} - b - PEO_{45k} membrane surfaces prepared from different solutions: (a, b) 19 wt% copolymer in (a) 42/25/33 THF/DOX/Pyr with 10s evaporation time and (b) in 1/1 THF/DOX with 10 s evaporation time; (c, d) 20 wt% copolymer in (c) 1/1 THF/Pyr, with 5s evaporation time and in (d) 58/42 DOX/Pyr, with 5s evaporation time.

Fig. 6. (a) FESEM and (b) TEM images of PS_{195k} - b - PEO_{45k} membrane cross sections (stained with RuO_4 prior to TEM imaging).

Table 4. DLS results for PS_{195k} - b - PEO_{45k} solutions in various solvent mixtures and the average pore diameter of the corresponding membranes

Solvent mixture	Z-average (nm) (DLS)	PDI (DLS)	Membrane average pore diameter ^a (nm)
42/25/33 THF/DOX/Pyr	35.0	0.22	63 ± 7
1/1 THF/Pyr	28.7	0.21	55 ± 6
58/42 DOX/Pyr	24.3	0.13	45 ± 7

^a estimated from FESEM images

Fig. 7. TEM images of PS_{195k} - b - PEO_{45k} micelles prepared from dilute solutions of the copolymers in (a) 42/25/33 THF/DOX/Pyr, (b) 1/1 THF/Pyr, (c) 58/42 DOX/Pyr, and (d) 1/1 THF/DOX. Scale bars are 200 nm.

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Table 4 shows average hydrodynamic radii (Z-average) measured by dynamic light scattering (DLS) for the dilute solutions of PS_{195k}-*b*-PEO_{45k} copolymers (0.1 wt%) in various solvent mixtures, which follow the trend line of Fig. 3. The DLS measurements showed that the copolymer formed monodispersed micelles (PDI < 0.25) with Z-average between 24–35 nm.

As can be seen in Table 4, the Z-average decreased proportionally to the decrease in the average pore sizes of the membranes produced from the corresponding solvent mixtures. This correlation supports the contribution of the micelle morphology in solution to the final membrane structure.

3.4 Trend line method applied to new triblock copolymer

The poly(styrene-*b*-2-vinyl pyridine-*b*-ethylene oxide) copolymer synthesized with a total molecular weight of 161 kg/mol (PS_{80.5k}-*b*-P2VP_{64.4k}-*b*-PEO_{16.1k}) was explored for membrane preparation.

The self-assembly in this case was expected to have a composite structure of P2VP and PEO as the corona and PS as core. Accordingly, the solvent composition was chosen to be more selective for P2VP/PEO as the more soluble blocks, while being less soluble for PS.

Analogous to the optimization of PS_{195k}-*b*-PEO_{45k} membranes, the selection of the solvents for PS_{80.5k}-*b*-P2VP_{64.4k}-*b*-PEO_{16.1k} was conducted by estimating the segregation strength which would better fit the trend line in Fig. 3. For the calculation of the Flory-Huggins interaction parameters between the polymer and the solvents, solubility parameters of the more soluble block (B) were calculated using the volume-weighted average of P2VP and PEO. Flory-Huggins interaction parameter between the most soluble block (A) and the less soluble block (B), χ_{AB} , was estimated using the volume-weighted average between the interaction parameter of PS-P2VP and PS-PEO, which were 0.18⁶³ and 0.08⁵², respectively. According to the isoporous trend line, the required $\bar{\chi}$ for PS_{80.5k}-*b*-P2VP_{64.4k}-*b*-PEO_{16.1k} ($V_A/V_B = 1.06$) was 0.63.

Fig. 8. (a) TEM image of micelles of PS_{80.5k}-*b*-P2VP_{64.4k}-*b*-PEO_{16.1k} in 51/30/19 THF/DOX/DMF and (b) FESEM image of a membrane surface prepared a 25 wt% copolymer solution in the same solvent mixture after 10 s evaporation and immersion in water.

A mixture of THF/DOX/DMF (51/30/19) was selected as the effective solvent mixture for the membrane preparation. The dimensionless parameters $\bar{\chi}$ for the single solvents were 0.22 for THF, -0.31 for DOX, 2.36 for DMF. In the solvent mixture of THF/DOX/DMF, the high value of $\bar{\chi}$ from DMF was counterbalanced by THF and DOX, which had $\bar{\chi}$ lower than the trend line. By adjusting the composition of THF/DOX/DMF to 51/30/19 weight ratio, the $\bar{\chi}$ of the mixture could be well fitted to the trend line.

Fig. 9. (a) FESEM and (b) TEM images of PS_{80.5k}-*b*-P2VP_{64.4k}-*b*-PEO_{16.1k} membrane cross-sections. For TEM the membrane was stained with RuO₄.

Fig. 8 shows TEM image of the $\text{PS}_{80.5\text{k}}\text{-}b\text{-P2VP}_{64.4\text{k}}\text{-}b\text{-PEO}_{16.1\text{k}}$ micelles formed using 51/30/19 THF/DOX/DMF. Well-defined spherical micelles were obtained, similar to the diblock copolymer in Fig. 7a. Membranes were then fabricated using the same solvent composition with different polymer concentrations and evaporation times. 25 wt% copolymer and evaporation time of 10 s led to isoporous $\text{PS}_{80.5\text{k}}\text{-}b\text{-P2VP}_{64.4\text{k}}\text{-}b\text{-PEO}_{16.1\text{k}}$ membranes. A FESEM image of the surface is seen in Fig. 8, with hexagonally ordered pores of average diameter 29 ± 2 nm. DLS measurements confirmed a narrow micelle size distribution with Z-average of about 20 nm (Pdl = 0.05). FESEM and TEM micrographs of the membrane cross-sections are shown in Fig. 9. Ordered cylindrical pores are seen in the top layer of about 200 nm.

In situ GISAXS experiments were performed to study the evolution of the film morphology as the solution was cast and the solvent evaporated. Two-dimensional GISAXS patterns and scattering curves for the films cast from 25 wt% $\text{PS}_{80.5\text{k}}\text{-}b\text{-P2VP}_{64.4\text{k}}\text{-}b\text{-PEO}_{16.1\text{k}}$ in 51/30/19 THF/DOX/DMF are presented in Fig. 10a and 10b, respectively. Order evolves as evaporation proceeds. From the scattering curve in Fig. 10b, a peak around 0.12 nm^{-1} was detected for the evaporation time of 10 s, which corresponded to d-spacing of 53 nm. The calculated d-spacing is similar to the distances between the pore centers measured from the membrane FESEM micrograph (53 ± 2 nm). The arrows in the scattering curve for 10 s evaporation attribute to the first three terms of the characteristic ratio of hexagonal structures ($1, \sqrt{3}, \text{ and } \sqrt{4}$)⁶⁴. The q values close to this ratio could be detected from the 10 s scattering curve after fitting with Gaussian functions.

3.5 Time-resolved pore formation experiments

Fig. 10. (a) GISAXS 2D-patterns for thin films cast from 25 wt% $\text{PS}_{80.5\text{k}}\text{-}b\text{-P2VP}_{64.4\text{k}}\text{-}b\text{-PEO}_{16.1\text{k}}$ in 51/30/19 THF/DOX/DMF with varying evaporation times. (b) Scattering peaks of the horizontal cuts of GISAXS patterns and (c) calculated d-spacing for thin films cast from 25 wt% $\text{PS}_{80.5\text{k}}\text{-}b\text{-P2VP}_{64.4\text{k}}\text{-}b\text{-PEO}_{16.1\text{k}}$ in 51/30/19 THF/DOX/DMF at varying evaporation times. Scattering curves at $t > 0$ s were shifted for clarity. (d) SAXS patterns of $\text{PS}_{80.5\text{k}}\text{-}b\text{-P2VP}_{64.4\text{k}}\text{-}b\text{-PEO}_{16.1\text{k}}$ in 51/30/19 THF/DOX/DMF at increasing polymer concentration.

The ring at the evaporation time of 10 s smeared out as the evaporation proceeded, but then another ring with a high

intensity was observed for higher evaporation times. This ring disappeared as the film completely dried at 600 s. From the

scattering curves of 60 s to 300 s in Fig. 10b, this high-intensity ring corresponded to the scattering peaks around 0.07 nm^{-1} , which attributed to a d-spacing of around 90 nm. Fig. 10c shows that the d-spacing increased as the evaporation proceeded until it reached a relatively constant value after 120 s. This result possibly indicated the formation of bigger aggregates as the polymer concentration increased in the film. As the most volatile solvents (THF and DOX) evaporated, the film was richer in the least volatile solvent (DMF), which was a more selective solvent for P2VP/PEO blocks. The PS blocks, therefore, tended to aggregate while trying to minimize interactions with the solvent. The scattering curves from 90 s to 300 s also showed shoulders at a characteristic ratio of $\sqrt{5}$, which is one of the characteristic ratios of body-centered cubic (BCC) structures.⁶⁴ It indicated that a completely different structure from that of 10 s evaporation time was formed. Overall, the observed GISAXS patterns exhibited a similar trend to the evolution of the membrane structures produced at increasing evaporation times. At an optimum polymer concentration and solvent mixture, regular pores were formed at a certain time after casting, and the ordered structures disappeared as the evaporation time increases.³³

Fig. 10d shows SAXS patterns of the bulk of the polymer solution with various concentrations. For polymer concentrations lower than 25 wt%, no particular ordered could be observed. A broad peak around 0.15 nm^{-1} developed for polymer concentration identical to the casting solution, and higher. The peaks at these concentrations correlated to a d-spacing of 18–19 nm, which was close to the hydrodynamic radii of the micelles of about 20 nm, as detected from the DLS measurement of the dilute solution. A sharper peak around 0.14 nm^{-1} can be clearly seen for the polymer concentration of 30 wt%. This peak corresponded to a d-spacing of around 27 nm, which was close to the average pore diameter of the $\text{PS}_{80.5\text{k}}\text{-}b\text{-P2VP}_{64.4\text{k}}\text{-}b\text{-PEO}_{16.1\text{k}}$ membranes of $29 \pm 2\text{ nm}$. At this higher concentration, the bulk state was closer to that of on the film surface as the solvent evaporated and created a more concentrated layer at the top of the film. A shoulder around the characteristic ratio of $\sqrt{3}$, which was one of the hexagonal order characteristics, also started to appear at 30 wt% polymer concentration.

The d-spacing values obtained from SAXS measurements were lower than that of observed from GISAXS. This result is consistent with our previous findings for $\text{PS-}b\text{-P4VP}$ copolymer.⁴² At semi-dilute concentrations, micellar entities are close to each other, and, therefore, the SAXS measurement reflects the inter-micellar distances in the solution bulk. The GISAXS measurement, on the other hand, characterizes more surface effects and the first bulk sub-layers.

4. Conclusions

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A simple method to select the best solvent compositions for manufacturing isoporous block copolymer was proposed. The method is based (i) on a guiding trend line calculated from the segregation strength analysis of the polymer-solvent mixtures, using Flory-Huggins interaction parameters and Hansen solubility parameter data, supported by (ii) TEM imaging micelles in dilute solutions. The proposed theoretical method was validated by effectively using it to prepare isoporous membranes from a diblock and a triblock copolymers not tested before: $\text{PS}_{195\text{k}}\text{-}b\text{-PEO}_{45\text{k}}$ and $\text{PS}_{80.5\text{k}}\text{-}b\text{-P2VP}_{64.4\text{k}}\text{-}b\text{-PEO}_{16.1\text{k}}$. Various solvent mixtures containing THF, DOX, and pyridine were identified as potentially useful for manufacture of isoporous membranes. THF/DOX/DMF was used as effective solvent to fabricate $\text{PS}_{80.5\text{k}}\text{-}b\text{-P2VP}_{64.4\text{k}}\text{-}b\text{-PEO}_{16.1\text{k}}$ isoporous membranes with a long-range order. The proposed method based on a trend line can be extended to other copolymer systems and is expected to shorten the development time when new copolymers are tested. Identifying the most suitable solvent mixture for a block copolymer is the first and most essential step in the successful manufacture of isoporous membranes. In addition to solvent composition, polymer concentration and molecular weight are relevant parameters, which influence order and pore size.

Time resolved GISAXS experiments were conducted to follow the pore formation by casting $\text{PS}_{80.5\text{k}}\text{-}b\text{-P2VP}_{64.4\text{k}}\text{-}b\text{-PEO}_{16.1\text{k}}$ solutions, which were partially evaporated before immersion in water. d-spacing values of 53 nm were measured, which is close to the interpore distance in the final membranes.

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