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**Self-assembly of Polystyrene-*b*-poly(2-vinylpyridine)-*b*-poly(ethylene oxide)
Triblock Terpolymers**

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Abstract

Polystyrene-*b*-poly(2-vinylpyridine)-*b*-poly(ethylene oxide) (PS-*b*-P2VP-*b*-PEO) terpolymer is a versatile polymer to form isoporous films and membranes, due to the possibility of self-assembly control and the properties of the different blocks, such as the P2VP ability of complexation, and H-bond formation, and the PEO biocompatibility. Copolymers with different block ratios and sizes were synthesized. The correlation between their equilibrium bulk morphology, the self-assembly in dilute and semi-dilute solutions and the non-equilibrium porous structures of membranes, obtained by non-solvent induced phase separation, was investigated and discussed in detail. The characterization was performed by small-angle X-ray scattering (SAXS), scanning (SEM) and transmission electron microscopy (TEM). Hexagonal, cubic and lamellar arrangements were observed. The preparation conditions were optimized and a regular, isoporous morphology, suitable for membrane application, was successfully obtained with PS_{80.5k}-*b*-P2VP_{64.4k}-*b*-PEO_{16.1k}.

Keywords: block-copolymers, saxs, rheology, self-assembly, electron microscopy

1. Introduction

The self-assembly of block copolymers has attracted considerable attention for many decades. It leads to ordered structures [1], useful for the preparation of nanostructured template [2] and structured materials for selective separation [3], drug delivery [4, 5], catalysis [6], electronics [7], photovoltaic cells [8], energy storage [9] or fuel cells [10].

When dissolved in selective solvents block copolymers can aggregate into different shape micelles with a core formed by the insoluble block and a corona formed by the solvent-swollen soluble block [11-14]. Depending on the solvent concentration, block-block, block-solvent interactions and the asymmetry of block copolymers, a variety of morphologies can be obtained, such as spheres, cylinders, vesicles or lamellae and even more complex continuous network structures or hierarchical assemblies [11, 15].

A large number of block copolymer membranes and films for many applications have been based mainly on polystyrene-*b*-poly(4-vinyl pyridine) (PS-*b*-P4VP) [15-17], and polystyrene-*b*-poly(ethylene oxide) (PS-*b*-PEO) [18][19] diblock copolymers. The incorporation of a third block, e.g. polystyrene-*b*-polyisoprene-*b*-poly(4-vinyl pyridine) (PS-*b*-PI-*b*-P4VP) [20], can provide additional tuning of the morphology and of the terpolymer properties. The composition of polystyrene-*b*-poly(2-vinylpyridine)-*b*-poly(ethylene oxide), PS-*b*-P2VP-*b*-PEO, makes this polymer a good candidate for different applications that require self-assembly systems. The rigid PS has been long used as the hydrophobic segment for self-assembling systems, providing the needed structural integrity. The hydrophilic PEO block is biocompatible, has low protein adsorption and low cell adhesion, making it a good candidate for membranes or medical applications [21]. PEO has good complexing ability for transition metal cations, resistance to oxidation, reduction, and decomposition, making PEO-based block copolymers good candidates towards the synthesis of inorganic nanoparticles [22]. P2VP-based polymeric materials are of particular interest. They strongly interact with inorganic precursors to form mesoporous metal oxides [23], in the form of inorganic hollow nanoparticles [24, 25], nanotubes, or other shapes [27], after the polymer degradation by calcination or by plasma treatment [26]. PS-*b*-P2VP-*b*-PEO (87, 12, 1 and 78, 14, 8 kg/mol respective block molecular weight) has been tested for membrane fabrication [28], but the self-assembly of PS-*b*-P2VP-*b*-PEO in solution was only previously

investigated by other groups in aqueous media [29, 30]. The micelles obtained in aqueous solutions were successfully used as sacrificial templates to fabricate inorganic nanoparticles [30] and to synthesize bimetallic nanoparticles [31], due to the ability of PVP and PEO to coordinate with different metallic precursors. Core-shell-corona PS-*b*-P2VP-*b*-PEO micelles have been used as pore-directing agent for the synthesis of mesoporous platinum nanospheres with tunable pore size and superior electrocatalytic activity [32]. The structure and size distribution of the produced inorganic particles depend on the morphologies and regularity of the micellar shapes used as templates. For applications such as nanoporous membranes or templates, oriented cylindrical or spherical morphologies are required [5, 33]. Therefore, the ability to tune the parameters that govern the self-assembly of triblock terpolymers is of critical importance for application in templating, isoporous membrane fabrication or drug delivery.

The preparation of membranes using a new polymeric material often requires extensive optimization, starting by choosing the best solvent mixture. We recently proposed a semi-empirical method to facilitate this optimization [34]. We have demonstrated the importance of micelle assembly in the formation of isoporous membranes [3, 16] and have also early explored SAXS as a powerful tool to guide the ordered membrane formation for PS-*b*-P4VP and PS-*b*-PEO [35-37].

In this paper, we synthesized a series of PS-*b*-P2VP-*b*-PEO terpolymers with different molecular weights and different block ratios. We systematically investigated the equilibrium morphology in the bulk, in dilute and semi-dilute solutions, by using two different solvent mixtures, and correlate them with the non-equilibrium morphology induced by immersion in a non-solvent, which leads to the formation of porous membranes.

2. Materials and methods

2.1. Materials

The following solvents were supplied by Sigma-Aldrich and used as received: tetrahydrofuran (THF), 1,4-dioxane (DOX), *N,N*-Dimethyl Formamide (DMF), *N,N*-

Dimethyl Acetamide (DMAc), Tetramethylene Sulfone (Sulf). Four linear polystyrene-*b*-poly(2-vinylpyridine)-*b*-poly(ethylene oxide) (PS-*b*-P2VP-*b*-PEO) triblock terpolymers with different composition, 15.7k-*b*-10.9k-*b*-5.4k, 16k-11.4k-10.6k, 25.6k-40.2k-7.3k and 80.5k-64.4k-16.1k were synthesized as described below; the PS_{75k}-*b*-P2VP_{21k}-*b*-PEO_{16.5k} terpolymer was purchased from Polymer Source, Canada.

2.2. Linear triblock terpolymer synthesis

The linear triblock terpolymers PS-*b*-P2VP-*b*-PEO were synthesized by sequential anionic polymerization and high vacuum techniques (the pressure was around 10-5 mmHg) [38, 39]. Tetrahydrofuran (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. 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, before transferring it to the polymerization reactor. The phosphazene superbases, 1-*tert*-Butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)-phosphoranylideneamino]-2λ⁵,4λcatenadi (phosphazene) (P₄-*t*Bu) (Sigma-Aldrich, 0.8M in hexane) and the acetic acid (terminating agent) were stored under high vacuum and used as received.

A typical experiment for the synthesis of the PS-*b*-P2VP-*b*-PEO (Fig. 1) involves the anionic polymerization of styrene at -78 °C using *sec*-butyllithium as an initiator. After one hour, an aliquot was taken for SEC analysis, followed by transfer through distillation of the appropriate amount of 2-VP under vigorous stirring at -78 °C. After 1h, another aliquot was taken for SEC analysis. Finally, P₄-*t*Bu super base was added, followed by distillation of EO and the polymerization solution left under stirring at 50 °C [40-43]. After 5 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 48 h at 40 °C to give a colorless powder.

The number-average molecular weight (M_n) and polydispersity index ($\mathcal{D}$) of the intermediate and the final triblock terpolymers were determined by size exclusion chromatography (SEC), equipped with an isocratic pump (Spectra System P1000), three columns in series (PLgel 5 μ m Mixed-C, 300x7.5 mm), a refractive index (RI, Shodex RI-101) detector in THF, with a flow rate of 1 mL/min. Polystyrene standards (M_p : 4.300 to 3.000.000 g/mol) were used for the calibration of the instrument. The chemical composition of the terpolymers was determined using a Brücker AV-500 ^1H -NMR spectrometer in CDCl_3 .

2.3. Dense film preparation

For the investigation of bulk equilibrium morphology, 5 wt% polymer solutions were prepared by dissolving the terpolymers in chloroform, a common non-selective solvent for all three blocks. The solution was cast on a Teflon plate and allowed to evaporate slowly for four days and subsequently annealed in a vacuum oven for five days at 130 °C, well above the glass transition temperature of PS (~100 °C) and P2VP (~95 °C). The resulted films with thicknesses in the range of 0.3 to 0.8 mm were quenched in liquid nitrogen to freeze the equilibrium morphology, and then kept at room temperature for TEM and SAXS experiments.

2.4. Membrane preparation

For casting the membranes, 20, 25 or 28 wt% solutions of PS-*b*-P2VP-*b*-PEO terpolymers were prepared by dissolving the appropriate amount of polymer mainly in two ternary solvent mixtures: THF/DOX/DMF and THF/DMAc/Sulf, at the compositions given in Table 1. After stirring overnight, the polymer solution was cast on a glass plate, using a doctor blade with 200 μ m gap. The solvent was evaporated for 10-20 s, then the film was immersed in a deionized water bath, in which the phase inversion occurred. The resulted membranes were dried at ambient conditions.

2.5. Small Angle X-ray Scattering (SAXS)

SAXS experiments for the polymer in bulk and in solution were performed at the SAXS1 beamline of the Brazilian Synchrotron facility (LNLS), which works at a fixed energy of 8.0 keV. The bulk morphology of the terpolymer dense film was analyzed, using a film sample holder. For the solution characterization, the sample was injected with a syringe in a vacuum cell formed between two mica windows. The X-ray wavelength was 0.155 nm and the sample to detector distance was 3.057 m. The detector used was Pilatus 300k with a pixel size of $(172 \mu\text{m})^2$. The beam area on the sample was 1 mm^2 . The measurements were performed with 20 frames, each with 30 s exposure time. Plots of intensity versus scattering vector (q) were obtained, by calculating the average of the radially integrated 2D patterns, after normalization to the intensity of primary beam and subtraction of background.

2.6. Transmission Electron Microscopy (TEM)

TEM images were obtained using a FEI Tecnai 12 microscope, operating at 120 kV. For the bulk morphology, PS-*b*-P2VP-*b*-PEO dense thick films were annealed and quenched as described above and embedded in an epoxy resin, followed by cure at 60 °C for 24 h. Ultrathin sections with 60 nm thickness were cut with Leica EM UC6 ultra-microtome, using a diamond knife. The thin slices were placed on a copper grid and further exposed for two hours to iodine.

For micelle characterization, the samples were prepared, by directly dropping a 1 mg/mL solution onto a carbon-coated copper grid and the solvent was blotted by a filter paper. After drying, they were stained depositing a drop of 0.1 wt % phosphotungstic acid aqueous solution onto the grid with the sample.

2.7. Scanning Electron Microscopy (SEM)

SEM images of the membranes surfaces were obtained on a FEI Nova Nano microscope with 5 kV accelerating voltage and 3 mm working distances. The membranes were

mounted on an aluminum stub using aluminum tape and sputter-coated with iridium (3 nm thickness), before imaging.

2.8. Cryo-Field Emission Scanning Microscopy (Cryo-FESEM)

Cryo-microscopy was performed on a Nova Nano 630 FEI microscope, equipped with liquid nitrogen cryogenic system. The sample temperature was -115 °C. A voltage of 5 kV and 5 mm working distance were applied. For the sample preparation, a solution drop was placed on the sample holder, frozen in liquid nitrogen and fractured at -170 °C inside the preparation chamber. The fracture surface was sublimed at -90 °C to eliminate any condensed ice and coated with platinum inside the cryogenic chamber.

2.9. Dynamic Light Scattering (DLS)

DLS measurements were carried out using a Malvern instrument equipped with a laser operating at 680 nm. The sample solutions were loaded in glass cuvettes and the measurements were performed at 173° backscattering angle at 25 °C. Based on Stokes-Einstein equation, the hydrodynamic diameter (volume average), D_h , and the polydispersity index PDI were calculated. PDI values vary from 0 to 1, with 0 representing a monodisperse particle distribution. The reported values are the average of three measurements with 12–15 runs. The dilute (1 mg/mL) PS-*b*-P2VP-*b*-PEO solutions were prepared, by dissolving the copolymer in ternary solvent mixtures, followed by overnight stirring.

2.10. Rheology

The solution rheology was investigated on a AR 1500ex rheometer with a plate and cone fixture, with 20 mm diameter and 1° cone angle. To avoid sample drying during the experiments, filter paper soaked with solvent and a cover were placed around the measuring cell. Strain measurements were performed at 25 °C and 1 Hz frequency.

Frequency sweep measurements were performed with fixed oscillation strain of 1 %, which lies within the linear viscoelastic regime.

3. Results and discussion

3.1. Copolymer synthesis

Well-defined PS-*b*-P2VP-*b*-PEO triblock ternary copolymers were synthesized as model polymeric materials. The SEC traces and the molecular characteristics of all samples are given in Fig. 1 and in Table 1, respectively.

Fig. 1. (a) General reactions for the synthesis of the triblock terpolymers PS-*b*-P2VP-*b*-PEO; (b) SEC traces of the final triblock terpolymers; (c) ¹H-NMR spectrum of sample PS_{16k}-*b*-P2VP_{11.4k}-*b*-PEO_{10.6k}.

Table 1. Molecular characteristics of polystyrene (PS), poly(2-vinylpyridine) (P2VP) and poly(ethylene-oxide) (PEO) blocks.

Polymer code	$M_n^{PS}_{SEC}$ [g/mol] ^a	$M_n^{P2VP}_{SEC}$ [g/mol] ^a	$M_n^{PEO}_{SEC}$ [g/mol] ^a	$\bar{D}$	$f_{(PS)}^{(1H-NMR)}$ %(w/w) ^b	$f_{(P2VP)}^{(1H-NMR)}$ %(w/w) ^b
PS _{15.7k} - <i>b</i> -P2VP _{10.9k} - <i>b</i> -PEO _{5.4k}	15700	10900	5400	1.1	0.48	0.33
PS _{16k} - <i>b</i> -P2VP _{11.4k} - <i>b</i> -PEO _{10.6k}	16000	11400	10600	1.09	0.40	0.31
PS _{25.6k} - <i>b</i> -P2VP _{40.2k} - <i>b</i> -PEO _{7.3k}	25600	40200	7300	1.05	0.37	0.54
PS _{80.5k} - <i>b</i> -P2VP _{64.4k} - <i>b</i> -PEO _{16.1k}	80500	64400	16100	1.03	0.49	0.40

^a Size exclusion chromatography in THF at 45 °C using polystyrene standards.^b Mass fraction was calculated *via* ¹H-NMR spectroscopy in CDCl₃ at 25 °C.

3.2. Equilibrium (bulk) morphology

The bulk morphology of diblock copolymers primarily depends on the composition, expressed as the relative volume fractions of the two blocks, and the interaction between the blocks, expressed as the segregation strength χN , where χ is the Flory–Huggins interaction parameter and N is the degree of polymerization. In general, for $\chi N > 10$, ordered nanostructures with different morphology are observed, depending on the composition [1, 44]. For triblock terpolymers the number of relevant parameters is larger: three interaction parameters (χ_{AB} , χ_{BC} , and χ_{AC}) instead of one, total degree of polymerization (N), two independent volume fractions (Φ_A and Φ_B , with $\Phi_C = 1 - \Phi_A - \Phi_B$), two junction points instead of one, and two conformational asymmetry parameters between each pair of linked blocks [45]. Furthermore, the sequence of the blocks plays a significant role as well, since it alters the adopted morphology, due to changes in the interaction parameter sequence. More than 20 stable or metastable nanostructures have been previously reported as bulk morphology for linear ABC terpolymers, some of them similar to diblock (spheres, cylinders, gyroid, and lamellae) [46-48], mixed geometries, spheres in cylinders, cylinders in lamellae [49, 50], rings on rods [51], or more complex knitting pattern structure [52]. 30 morphologies have been theoretically predicted [45]. Flory-Huggins interaction parameters between the blocks were calculated from equation 4 [53]:

$$\chi_{AB} = \frac{V_0}{RT} (\delta_A - \delta_B)^2 \quad (4)$$

where χ_{AB} is the polymer – polymer interaction parameter and do not include the entropic contributions, V_0 is the geometric average of the molar volumes of polymer, δ is the solubility parameters for A and B blocks. Solubility parameters for each terpolymer block are $\delta_{PS}=19.26 \text{ MPa}^{1/2}$, $\delta_{P2VP}=23.27 \text{ MPa}^{1/2}$ and $\delta_{PEO}=19.92 \text{ MPa}^{1/2}$, calculated as $\delta = \sqrt{\delta_P^2 + \delta_D^2 + \delta_H^2}$, where δ_P , δ_D , δ_H are the polar, dispersive and hydrogen bond contributions [54]. By using eq. (4), which only takes into consideration the enthalpic contribution, we obtained $\chi_{PS-P2VP}=0.649$, $\chi_{P2VP-PEO}=0.272$ and $\chi_{PS-PEO}=0.011$ for $T = 20^\circ\text{C}$. In this case, when PS and PEO terminal blocks have the lowest incompatibility and PS and P2VP should avoid each other the most, it is possible that P2VP segments segregate and interfaces between PS and PEO phases are formed, reducing the overall interfacial tension of the system, as commonly met for frustrated terpolymers [55]. Due to the short length of the PEO block, a low segregation strengths χN is obtained between PS and PEO (Table S1). Literature data for polymers with similar composition and different geometry (specifically, 3 arm star terpolymers) reported the formation of two-phase separated systems, with PEO and PS chains forming a single phase, when the average molecular weight of PEO is very low (3000 g/mol) [56]. For higher volume fraction of PEO block ($\Phi_{PEO}=0.45$) they reported a three-phases structure formed by PS block surrounded by P2VP embedded in PEO matrix. The bulk morphology of the annealed samples was investigated by SAXS and TEM. TEM shows a clear segregation with dark phases most probably corresponding to P2VP stained by iodine, and bright phases rich in PS. From χN data in Table S1 and previous literature [56] observation with analogous copolymers, we could not exclude that PEO blocks would be partially included in the PS-rich phase.

Fig. 2 summarizes the SAXS results for samples with different molecular weight and block composition and the corresponding equilibrium morphology. A primary correlation peak at scattering vector $q = q^*$ is clearly observed for all the samples, indicating the formation of strong segregated systems with a periodic structure. In addition, the scattering profiles contain higher order correlation peaks, which are characteristic of long-range ordered systems. Their positions were obtained by fitting the data with a sum

of three or more Lorenz functions using Igor Pro 6.37 software [57]. The scattering profiles obtained by radial integration of the 2D scattering patterns, together with the fitting curves, are presented in Fig. S1. The scattering profile is given by the product of the structure factor, directly related to structure regularity and the form factor, which is proportional to the square of the electron density difference. The contrast is given by the contrast in electron density and therefore, even a very ordered structure could yield low scattering if the different phases have similar electron density. Furthermore, the contrast depends on the X-ray energy used [58]. In the investigated systems, the electron density of PS and PEO ($0.34 \text{ e}^* \text{Å}^{-3}$ and $0.37 \text{ e}^* \text{Å}^{-3}$, respectively) [58] and of PS and P2VP are similar, resulting in relatively low contrast in x-ray experiments [59].

In this case the complementing TEM information is important and is also shown in Fig. 2. The scattering profile for the polymer with the lowest molecular weight (PS_{15.7k}-b-P2VP_{10.9k}-b-PEO_{5.4k}) has only a primary peak and a wide shoulder located close to $\sqrt{3}q^*$ which could indicate a hexagonally ordered system or a 3-fold projection of 3D cubic assembly. The corresponding TEM image indicates the formation of spherical (bright) phases, richer in PS, which are distributed in a continuous darker phase (stained by iodine) constituted by P2VP and PEO blocks. Cylindrical morphologies were not detected by TEM for this sample. Based on these observations, we propose that hexagonal closed packed spheres (HCP) morphology predominates for PS_{15.7k}-b-P2VP_{10.9k}-b-PEO_{5.4k}. We could not clearly differentiate the phase composition from the TEM imaging alone, but the estimated segregation strengths between the three blocks (given in Table S1) indicate the possibility of a mixed PS-PEO phase.

TEM images of PS_{16k}-b-P2VP_{11.4k}-b-PEO_{10.6k} and PS_{25.6k}-b-P2VP_{40.2k}-b-PEO_{7.3k} samples both capture perpendicular and lateral view of the lying cylinders which are arranged on a hexagonal lattice (HEX), with the core formed by the PS (bright, non-stained by iodine) phase. This fully agrees with the SAXS results. The relative position of the SAXS peaks, q/q^* , are located at 1, $\sqrt{3}$, 2, $\sqrt{7}$ and $\sqrt{12}$, with the peak at $q/q^* = \sqrt{3}$ overlapped by a small peak at $q/q^* = 2$. This confirms the HEX cylindrical arrangement for both terpolymer samples. However, the definition of the higher order peaks is not enough to completely exclude a mixed cylindrical/lamellar phase. If a mixed PS and PEO phase occurs in the case of short PEO segments, this could favor cylindrical and lamellar

morphology for $\text{PS}_{16\text{k}}\text{-}b\text{-P2VP}_{11.4\text{k}}\text{-}b\text{-PEO}_{10.6\text{k}}$ and $\text{PS}_{25.6\text{k}}\text{-}b\text{-P2VP}_{40.2\text{k}}\text{-}b\text{-PEO}_{7.3\text{k}}$ terpolymer, respectively. The periodic distance representing the distance between the cylinders centers is larger for $\text{PS}_{25.6\text{k}}\text{-}b\text{-P2VP}_{40.2\text{k}}\text{-}b\text{-PEO}_{7.3\text{k}}$, due to larger PS and P2VP blocks.

$\text{PS}_{75\text{k}}\text{-}b\text{-P2VP}_{21\text{k}}\text{-}b\text{-PEO}_{16.5\text{k}}$, the only copolymer not synthesized in our lab, resulted in the formation of lamellar morphology as clearly evidenced by TEM in Fig. 2. The main SAXS peak is followed by second and third SAXS peaks located at $2q^*$ and respectively, $3q^*$, also confirming a lamellar order (LAM).

$\text{PS}_{80.5\text{k}}\text{-}b\text{-P2VP}_{64.4\text{k}}\text{-}b\text{-PEO}_{16.1\text{k}}$ has an exceptionally ordered hexagonal morphology, as seen in TEM images, with inverted structure, when compared to $\text{PS}_{16\text{k}}\text{-}b\text{-P2VP}_{11.4\text{k}}\text{-}b\text{-PEO}_{10.6\text{k}}$ and $\text{PS}_{25.6\text{k}}\text{-}b\text{-P2VP}_{40.2\text{k}}\text{-}b\text{-PEO}_{7.3\text{k}}$. As for the lowest molecular weight copolymer, the existence of PS and PEO blocks in a single phase could explain the observed morphology. In this case P2VP block would form the cylinders, and PS and PEO the matrix. Images obtained in different planes and presented in Fig. S2 (in addition to Fig. 2) show the cross-sectional and lateral view of the cylinders and demonstrate that the structure corresponds to hexagonally packed P2VP-rich cylinders (dark iodine-stained cores) in the PS matrix. SAXS peaks at q/q^* : 1, $\sqrt{3}$, 2 are characteristic of hexagonal arrangements and confirm the TEM observation. At higher scattering vector, the SAXS profile has a broad weak shoulder that can arise from the superposition of higher-order reflections expected for hexagonal morphology indicated by arrows. The distances between the centers of two scatterers, D , reported in Fig. 2, were evaluated for different morphologies, from the position of the first scattering peak, using the following equations [60]:

$$D = \sqrt{6}\pi/q^* \text{ (HCP, BCC)} \quad (1)$$

$$D = 4\pi/\sqrt{3}q^* \text{ (HEX)} \quad (2)$$

$$D = 2\pi/q^* \text{ (LAM)} \quad (3)$$

Fig. 2. SAXS patterns of thermal (130 °C) annealed PS-*b*-P2VP-*b*-PEO films. The curves were vertically shifted for better visualization. q^* represents the position of the first scattering peak. TEM of the corresponding samples stained with iodine with marked periodic distance; order identified by SAXS and the period distance between the centers of two scatterers, D .

3.3. Dilute solutions

The membrane manufacture is in most cases based on a solution process. The morphology of block copolymers in solution is much more complex than those observed in equilibrium bulk systems. It highly depends on the solvent interaction to different blocks and the polymer concentration. Investigating the self-assembly in solution is

highly relevant to guide the identification of the best solvent mixture/copolymer compositions for the ordered porous membrane formation. We investigated the self-assembly in solution in dilute and semi-diluted regimes. To induce the self-assembly in solution, solvent mixtures were chosen according to a recently reported method [33], that accounts for the dependence of the reduced segregation strength, $\bar{\chi}$, on the ratio of volume fraction of the blocks, Φ_A/Φ_B , where:

$$\bar{\chi} = (\chi_{sA}N_A - \chi_{sB}N_B)/\chi_{AB}N \quad (5)$$

where $\chi_{sA}N_A$ is the Flory-Huggins interaction parameter between the solvent mixture and less soluble block (A); $\chi_{sB}N_B$ is the Flory-Huggins interaction parameter between the solvent mixture and the most soluble block (B); N_i is the degree of polymerization of polymer block i ; N is the total polymerization degree. The less soluble block (A) is the PS block, the solubility parameter of the most soluble block (B) was calculated using the volume-weighted average of P2VP and PEO blocks and χ_{AB} was estimated using the volume-weighted average between the interaction parameters of PS-P2VP and PS-PEO, as described in ref. [34]. The volume fraction Φ_B was calculated as the sum of the volume fractions of P2VP and PEO.

The $\bar{\chi}$ vs Φ_A/Φ_B trend line shown in Fig. S3 can be thermodynamically correlated to the difference of the free energy between the ordered and random states of the copolymer system [61]. Optimum compositions of THF/DMF/DOX and THF/DMAc/Sulf solvent mixtures were estimated to better fit the trend line in Fig. S3, using parameters listed in Table S2. Overall, the solvent mixtures are better for P2VP and PEO blocks than for PS blocks, as indicated by the lower Flory-Huggins solvent-polymer interaction parameters ($\chi_{s,i}$) for P2VP and PEO compared to PS.

First the micelle formation in diluted solutions (1 mg/mL) was investigated by TEM and DLS. The DLS measured values of hydrodynamic diameter (D_h) and the micelle size polydispersity index (PDI) are summarized in Table S2. The most anticipated micelle structure for a linear ABC terpolymer in selective solvents for one of the two end-blocks and the middle block is a core/inner corona/outer corona [63]. However, micelles with one block forming the core and the other two incompatible blocks forming the corona can be also obtained, since solubilization of the two more incompatible blocks can happen in a common solvent [64]. Fig. 3 shows the TEM images (Fig. 3) of micelles formed in

dilute solutions, after the selective staining of the P2VP and PEO with phosphotungstic acid. Phosphotungstic acid preferentially stains P2VP and PEO. The staining of PEO occurs through the terminal hydroxyl groups. All micelles in Fig. 3 have a bright core, corresponding to the less soluble PS and a dark corona, richer in P2VP and PEO. Particularly in the case of $\text{PS}_{80.5\text{k}}\text{-}b\text{-P2VP}_{64.4\text{k}}\text{-}b\text{-PEO}_{16.1\text{k}}$, the corona thickness is much smaller than the core radius, forming what is frequently called crew-cut micelles. The core size increases with the size of the PS block in the terpolymer. For $\text{PS}_{16\text{k}}\text{-}b\text{-P2VP}_{11.4\text{k}}\text{-}b\text{-PEO}_{10.6\text{k}}$ and $\text{PS}_{25.6\text{k}}\text{-}b\text{-P2VP}_{40.2\text{k}}\text{-}b\text{-PEO}_{7.3\text{k}}$ the corona is more diffuse and the corona thickness relative to the core radius is larger. Figure 3 (bottom) represents the micelles diameters obtained from TEM images, as a function of the terpolymer molecular weight. The values are an average of 20 micelles. The micelle size is correlated with the total molecular weight of the polymer, with small deviations from linearity. Moreover, the core diameter correlates with the molecular weight of PS block. The values obtained for hydrodynamic diameter in solution measured by DLS are smaller than the micelles diameter estimated by TEM. Differences may arise from sample preparation for TEM. In addition, due to the solvent selectivity, P2VP-*b*-PEO corona blocks could adopt extended conformation and the light scattering in DLS experiments might be mainly due to PS blocks. For example, a strong dependence of the hydrodynamic diameter on the polymer conformation was previously reported for PS-*b*-P2VP-*b*-PEO in aqueous solution [65]. In that case, an extended conformation of P2VP segments was observed at $\text{pH} < 5$, due to the protonation of the P2VP, while at higher pH the tighter conformation induced a decrease of the hydrodynamic diameter with up to 45 % for the $\text{PS}_{14\text{k}}\text{-}b\text{-P2VP}_{12\text{k}}\text{-}b\text{-PEO}_{35\text{k}}$ micelles. Similar effect was evidenced for P2VP-*b*-PEO copolymers, but no correlation was found between the micellar and molecular characteristics of the copolymer [66].

Fig. 3. TEM images of PS-*b*-P2VP-*b*-PEO micelles obtained from dilute solutions in THF/DOX/DMF, stained by phosphotungstic acid; micelles size dependence on the total molecular weight, using THF/DOX/DMF and THF/DMAc/Sulf as solvents.

3.4. Semi-dilute solutions

The morphology and order in solution are highly dependent on the terpolymer concentration. Therefore, the micellar morphology in dilute solution, shown in Fig. 3, can substantially change as the semi-dilute polymer concentration regime is reached. SAXS was used to characterize the morphology of semi-dilute solutions of all PS-*b*-P2VP-*b*-PEO terpolymers in two solvent mixtures: THF/DOX/DMF and THF/DMAc/Sulf. Results are shown in Fig. 4 and Table 2. For the clarity of representation, scattering curves in Fig. 4 for increasing concentration have been vertically shifted (intensity with arbitrary unities). For PS_{15.7k}-*b*-P2VP_{10.9k}-*b*-PEO_{5.4k} even at concentrations as high as 35 wt% only a broad shoulder was observed, which indicates a disordered (DIS) system. For the other copolymers, by increasing the concentration in solution, the scattering profiles first have a broad correlation peak, indicating a lack of long range order, but by increasing the concentration, the solutions evolve into long range ordered systems, confirmed by the narrowing of the peak and the appearance of higher order reflections.

Table 2 shows the sequence of obtained Bragg reflections, the corresponding morphology or order and d -spacing values. d -spacing, also referred to Bragg or interplanar spacing, is estimated by $d=2\pi/q^*$, where q^* is the position of the first reflection. d corresponds to the repeat distance in the bulk of the sample, projected in a plane. For simple cubic (SC) and lamellar (LAM) orders, $d=D$, with D being the center-to-center distances between alternating phases. For hexagonally packed cylinders (HEX), $D = 4\pi/\sqrt{3}q^*$ [61].

For PS_{16k}-*b*-P2VP_{11.4k}-*b*-PEO_{10.6k} two different orders were found to correspond to the investigated solvent mixtures. For solutions in THF/DMF/DOX, the peak positions are close to the first five reflections of hexagonally packed cylinders (HEX): 1, $\sqrt{3}$, $\sqrt{4}$, $\sqrt{7}$, $\sqrt{9}$, with weak third and fifth observed peaks, while for THF/DMAc/Sulf the morphology is cubic. For this second solvent, the peak positions at 1, $\sqrt{2}$, $\sqrt{3}$ and $\sqrt{4}$ are characteristic of simple cubic (SC) structure, but we also consider the possibility of having a body-centered cubic structure (BCC), with the higher order reflections characteristic to BCC arrangement being missing, because of the reduced contrast. Compared to the THF/DOX/DMF solvent mixture, THF/DMAc/Sulf has higher values of Flory-Hugging interaction parameter (Table S2) and lower solubility for PS and PEO segments, which represent 72% of the polymer volume. This influences the self-assembly in dilute solutions, forming smaller micelles and different packing order in the semi-dilute regime (Table 2). Hexagonal 2D order was obtained for PS_{25.6k}-*b*-P2VP_{40.2k}-*b*-PEO_{7.3k} in both solvents, with q/q^* values indicating cylinder morphology. SAXS patterns for the 35 wt% PS_{75k}-*b*-P2VP_{21k}-*b*-PEO_{16.5k} solution in THF/DOX/DMF have peaks at $q/q^* = 1, 2, 3, 4, 5$, consistent with lamellar structure. For THF/DMAc/Sulf with the same concentration, multiple broad peaks were obtained, including a broad peak at lower q , which indicates a lower order or a heterogeneous system. Long range hexagonal order was obtained for 35 % wt PS_{80.5k}-*b*-P2VP_{64.4k}-*b*-PEO_{16.1k} solutions in both solvents. By increasing the PS_{80.5k}-*b*-P2VP_{64.4k}-*b*-PEO_{16.1k} concentration from 35 to 38 wt% in THF/DOX/DMF and THF/DMAc/Sulf, the morphology remained hexagonal with a slight decrease of the distance between the cylinders, from 45 to 39 nm, indicating a tighter packing.

Fig. 4. SAXS patterns for different concentrations of terpolymers solutions in THF/DOX/DMF: (a) $\text{PS}_{15.7\text{k}}\text{-}b\text{-P2VP}_{10.9\text{k}}\text{-}b\text{-PEO}_{5.4\text{k}}$, (c) $\text{PS}_{75\text{k}}\text{-}b\text{-P2VP}_{21\text{k}}\text{-}b\text{-PEO}_{16.5\text{k}}$, (d) $\text{PS}_{80.5\text{k}}\text{-}b\text{-P2VP}_{64.4\text{k}}\text{-}b\text{-PEO}_{16.1\text{k}}$, (g) $\text{PS}_{25.6\text{k}}\text{-}b\text{-P2VP}_{40.2\text{k}}\text{-}b\text{-PEO}_{7.3\text{k}}$, (h) $\text{PS}_{16\text{k}}\text{-}b\text{-P2VP}_{11.4\text{k}}\text{-}b\text{-PEO}_{10.6\text{k}}$; (b), (f) rheological characterization of 32 wt% $\text{PS}_x\text{-}b\text{-P2VP}_y\text{-}b\text{-PEO}_z$ solutions in THF/DOX/DMF: (full symbols) storage (G') and (open symbols) loss (G'') moduli as a function of applied strain; (e) cryo SEM of a 32 wt% $\text{PS}_{80.5\text{k}}\text{-}b\text{-P2VP}_{64.4\text{k}}\text{-}b\text{-PEO}_{16.1\text{k}}$ solution in THF/DOX/DMF.

Table 2. SAXS results for PS-*b*-P2VP-*b*-PEO terpolymer solutions.

Polymer	Solvent	Conc. (wt%)	d (nm)	q/q*	Order	D (nm)
PS _{15.7k} - <i>b</i> -P2VP _{10.9k} - <i>b</i> -PEO _{5.4k}	THF/DOX/DMF				disordered	
PS _{16k} - <i>b</i> -P2VP _{11.4k} - <i>b</i> -PEO _{10.6k}	THF/DOX/DMF	38	50	1:1.7:2:2.7:3	HEX	43
	THF/DMAc/Sulf	30	44	1:1.4:1.7:2.1	SC/BCC*	44
PS _{25.6k} - <i>b</i> -P2VP _{40.2k} - <i>b</i> -PEO _{7.3k}	THF/DOX/DMF	35	51	1:1.6:2.6		
	THF/DOX/DMF	38	51	1:1.7:2.7	HEX	45
	THF/DMAc/Sulf	32	49	1:1.7:2.1:2.7:3	HEX	42
	THF/DMAc/Sulf	35	50	1:1.7:2:2.6:3:3.5	HEX	43
PS _{75k} - <i>b</i> -P2VP _{21k} - <i>b</i> -PEO _{16.5k}	THF/DOX/DMF	35	65	1:2:3:4:5	LAM	65
	THF/DMAc/Sulf	35	82	1:1.6:1.8:2.8:4.2: 6.9	aggregates	
PS _{80.5k} - <i>b</i> -P2VP _{64.4k} - <i>b</i> -PEO _{16.1k}	THF/DOX/DMF	35	50	1:1.7:2:2.6	HEX	44
	THF/DOX/DMF	38	51	1:1.7:2:2.6:3:3.5	HEX	39
	THF/DMAc/Sulf	35	54	1:1.7:2:2.7:3:3.5	HEX	47

HEX=hexagonal; SC=simple cubic; LAM=lamellar; d = Bragg spacing (perpendicular distance between the adjacent diffraction planes); Center-to-center distances were calculated as $D=2\pi/q^*$ for SC and LAM structure and as $D = 4\pi/\sqrt{3}q^*$ for HEX order [61].

For systems in the semi-dilute regime, cryo-SEM is the best imaging method to complement the SAXS data. Fig. 4 shows the cryo-SEM image of a 32 wt% PS_{80.5k}-*b*-P2VP_{64.4k}-*b*-PEO_{16.1k} solution in THF/DOX/DMF. Cylindrical structures are clearly seen, confirming the SAXS measurement. Similar to what has been previously observed for PS-*b*-P4VP solutions [36], the cryo-SEM indicates that the cylinders might be formed as spherical micelles partially merged in an array.

3.5. Rheology of semi-dilute solutions

The self-assembly with different morphologies is reflected in the solution rheological behavior, which is shown in Fig. 4 and Fig. 5, in the form of storage and loss moduli response as a function of increasing applied strain. Fig. 6 shows the moduli dependence on the angular frequency for 1 % applied stress. Structural change and ordering under shear have been previously reported for other systems [67].

Table 3 summarizes the rheological parameters selected from strain amplitude (Fig. 4) and frequency sweep measurements (Fig. 6) for 32 wt% copolymer solutions in THF/DOX/DMF. At 1 Hz frequency, PS_{15.7k}-*b*-P2VP_{10.9k}-*b*-PEO_{5.4k} and PS_{75k}-*b*-P2VP_{21k}-*b*-PEO_{16.5k} solutions, which were classified respectively as disordered and lamellar by SAXS, had a predominant viscous response for the entire range of strain (Fig. 4). The behaviors of PS_{16k}-*b*-P2VP_{11.4k}-*b*-PEO_{10.6k}, PS_{25.6k}-*b*-P2VP_{40.2k}-*b*-PEO_{7.3k}, and PS_{80.5k}-*b*-P2VP_{64.4k}-*b*-PEO_{16.1k} solutions are characteristic of elastic systems at low strain, followed by a predominant viscous character at the higher strain. These systems were characterized as having hexagonal order by SAXS analysis and are also very similar in regard to their values of storage and loss modulus as well as the crossover frequency.

Those systems with cylindrical hexagonal order have a clear transition from elastic to viscous behavior at 14-16% strain. At low strain, the coronas of different cylinders have a strong interaction with each other, leading to a stable long-range ordered self-assembled network. As strain increases, the cylinders align with the applied shearing and at 14-16 % strain, the interaction is overcome by the tendency of flowing in a liquid-like behavior. This behavior obviously depends on the solvent quality and copolymer concentration, since the degree of entanglement changes. Above the critical entanglement concentration, a higher Flory-Huggins parameter would lead to stronger corona-corona interaction, stabilizing the network. Lower χ would lead to plasticization of the corona-corona segment contacts and promote viscous flow at lower strain or frequency values. Fig. 5 shows this behavior for PS_{16k}-*b*-P2VP_{11.4k}-*b*-PEO_{10.6k} solutions with increasing concentration. At low concentrations, viscous flow is dominant in the whole investigated strain amplitude range. At low strain and concentrations 30 wt% or higher in both

investigated solvent mixtures, a solid-like viscoelastic behavior prevails, with storage modulus G' higher than loss modulus, G'' . The viscoelastic response is linear, indicating that the sample is undisturbed by the applied oscillatory stress. By the further increase of strain amplitude, the moduli decrease as a result of increased deformation. At higher strain, the system acquires a dominant viscous character, with $G'' > G'$. When concentration increases a higher strain is required to promote the flow transition into the viscous regime, as indicated by the shifting of the cross-over strain values ($G' = G''$) to higher values. These solutions present a small strain overshoot (a small increase of G'' before flowing), which has been previously observed and explained for other block copolymer solutions with close-packed micelle arrays [68, 69]. With increasing strain the complex structure resists against deformation up to a certain strain, beyond which it is broken into clusters. When the microstructure breaks there is a dissipation of energy reflected by the initial increase of loss modulus at the intermediate strain. After this, micelle clusters or agglomerates align and flow in the field direction.

THF/DMAc/Sulf is a worse solvent for PEO blocks than THF/DOX/DMF (higher χ_{sO} value in Table S2). PEO blocks are expected to constitute the external part of the corona. Stronger corona-corona interaction and polymer-polymer segment friction above the critical entanglement concentration are expected if the solvent is bad. This reduces the mobility and increases the copolymer assembly stability. The resistance to flow is larger, with the elastic-viscous transition taking place at higher strain or angular frequency. This is seen in Fig. 5. An additional difference was observed between the two solvents. Solutions in THF/DMAc/Sulf have a two-step moduli vs strain flowing curve, which may be correlated with the different ordered structures observed by SAXS. In THF/DOX/DMF, the copolymer self-assembles into hexagonally arranged cylindrical structures. The cylinders easily flow aligned to the applied force. In THF/DMAc/Sulf, the applied strain will firstly induce a rearrangement of the cubic interacting micellar structure.

Fig. 5. Storage (G' , full symbols) and loss moduli (G'' , open symbols) as a function of increasing strain for $\text{PS}_{16\text{k}}\text{-}b\text{-P2VP}_{11.4\text{k}}\text{-}b\text{-PEO}_{10.6\text{k}}$ solutions with different concentrations in (a) THF/DOX/DMF and (b) THF/DMAc/Sulf.

For ordered block copolymer systems, morphology can be correlated with the frequency dependence of modulus. Empirical scaling laws have been previously identified for block copolymer melts with different orders and then applied also for polymer solutions [70]. Thus, block copolymer storage moduli as a function of angular for different orders, scales at low frequency as:

$$\begin{array}{ll} \text{lamellar} & G' \sim G'' \sim \omega^n, \text{ with } n = 1/2 \\ (5) & \end{array}$$

$$\begin{array}{ll} \text{cylindrical} & G' \sim \omega^n, \text{ with } n = 1/6 - 1/3 \\ (6) & \end{array}$$

$$\begin{array}{ll} \text{cubic} & G' \sim \omega^n, \text{ with } n = 0 \\ (7) & \end{array}$$

and for the systems with liquid-like behavior, as $G' \sim \omega^2$, $G'' \sim \omega^1$ [71].

For the solution with 32 wt% $\text{PS}_{16\text{k}}\text{-}b\text{-P2VP}_{11.4\text{k}}\text{-}b\text{-PEO}_{10.6\text{k}}$ in THF/DOX/DMF represented in Fig. 6, we obtained at low frequency $G' \sim \omega^n$, with $n = 0.16$ and $G'' \sim \omega^n$, with $n = 0.28$ and for 30wt% $\text{PS}_{16\text{k}}\text{-}b\text{-P2VP}_{11.4\text{k}}\text{-}b\text{-PEO}_{10.6\text{k}}$ in THF/DMAc/Sulf, $G' \sim \omega^n$,

with $n = 0.05$. The n values given in Table 3, estimated from the slope of G' and G'' as a function of angular frequency at low frequency, are similar to the expected values for the corresponding morphology detected by SAXS and shown in Fig. 4. Thus, a value close to 1 was obtained for PS_{15.7k}-*b*-P2VP_{10.9k}-*b*-PEO_{5.4k}, $0.17 < n < 0.33$ for PS_{16k}-*b*-P2VP_{11.4k}-*b*-PEO_{10.6k}, PS_{25.6k}-*b*-P2VP_{40.2k}-*b*-PEO_{7.3k} and PS_{80.5k}-*b*-P2VP_{64.4k}-*b*-PEO_{16.1k} and finally close to $n = 0.5$ for PS_{75k}-*b*-P2VP_{21k}-*b*-PEO_{16.5k} solutions in THF/DOX/DMF. Solutions with similar compositions were respectively identified as disordered, hexagonal and lamellar by SAXS in Fig. 4 and Table 2.

Table 3. Rheology parameters for 32 wt% PS-*b*-P2VP-*b*-PEO solutions in THF/DOX/DMF.

Copolymer	G' (Pa) at 1% strain ^a	G'' (Pa) at 1% strain ^a	Strain (%) at G'=G'' ^a	Slope of log G vs log ω (Pa s) ^b	
				for G'	for G''
PS _{15.7k} - <i>b</i> -P2VP _{10.9k} - <i>b</i> -PEO _{5.4k}	0.8	15		0.75±0.10	0.98±0.03
PS _{16k} - <i>b</i> -P2VP _{11.4k} - <i>b</i> -PEO _{10.6k}	382	112	14	0.16±0.05	0.28±0.02
PS _{25.6k} - <i>b</i> -P2VP _{40.2k} - <i>b</i> -PEO _{7.3k}	470	129	15	0.13±0.01	0.09±0.02
PS _{75k} - <i>b</i> -P2VP _{21k} - <i>b</i> -PEO _{16.5k}	27	33		0.33±0.02	0.65±0.07
PS _{80.5k} - <i>b</i> -P2VP _{64.4k} - <i>b</i> -PEO _{16.1k}	475	230	16	0.15±0.02	0.14±0.05

^a Values determined from strain measurements.

^b Values obtained from frequency sweep measurements.

Fig. 6. Frequency sweep for 32 wt% PS-*b*-P2VP-*b*-PEO copolymer solutions in THF/DOX/DMF. Storage modulus G' is represented with filled symbols and loss modulus G'' with open symbols.

3.6. Non-equilibrium morphology

In this section, we compare the morphology of porous asymmetric films prepared from the different PS-*b*-P2VP-*b*-PEO terpolymers investigated in this work. 20 to 28 wt% solutions in THF/DOX/DMF and THF/DMAc/Sulf were cast on a glass plate and immersed in water, after short evaporation (10-20 sec). As discussed for other polymer systems, a kinetically trapped structure is then obtained, which highly depends on the order previously achieved in solution. The surfaces of these films prepared from different terpolymers are shown in Fig. 7. Clearly, only the PS_{80.5k}-*b*-P2VP_{64.4k}-*b*-PEO_{16.1k} terpolymer led to an isoporous surface morphology, potentially suitable for membrane application. Regular pores could be obtained for this terpolymer composition in THF/DMAc/Sulf and THF/DOX/DMF, whose semi-dilute solutions were characterized by SAXS as having a hexagonal arrangement. They have a high storage modulus at low strain, which promotes high assembly stability. This stability guarantees an undisturbed order during immersion in water. A fast solvent-non-solvent exchange causes an abrupt increase of the polymer-polymer segments friction, trapping the morphology into a solid

structure. The polymer-lean regions give rise to the pores. PS_{75k}-*b*-P2VP_{21k}-*b*-PEO_{16.5k} solutions were characterized as having lamellar structure by SAXS leading also to a lamellar surface structure in Fig. 7. PS_{15.7k}-*b*-P2VP_{10.9k}-*b*-PEO_{5.4k} systems characterized as disordered led to a surface without a particular order. PS_{16k}-*b*-P2VP_{11.4k}-*b*-PEO_{10.6k} and PS_{25.6k}-*b*-P2VP_{40.2k}-*b*-PEO_{7.3k}, although with hexagonal arrangements in solution, detected by SAXS, do not form regularly porous films. Probably the highly hydrophilic P2VP and PEO blocks, which are in large ratios in these copolymers, favor deformation and micelle merging when immersed in water. As can be seen in Fig. 3, the P2VP-PEO coronas are more diffuse, swollen and probably more deformable than in the case of good membrane-forming PS_{80.5k}-*b*-P2VP_{64.4k}-*b*-PEO_{16.1k}. The latter micelles have well-defined contours.

Fig. 7. SEM images of porous membrane surfaces prepared by casting 20-28 wt% solutions in THF/DMAc/Sulf or THF/DOX/DMF, followed by short evaporation (10-20 sec) and immersion in water.

4. Conclusions

PS-*b*-P2VP-*b*-PEO terpolymers with five different molecular weight and composition were synthesized by high vacuum techniques and investigated. The equilibrium morphology of annealed samples varied from spherical, hexagonal cylinders to lamellae, as confirmed by TEM. The correlation between copolymer block sizes and ratios, their

morphology in bulk and solution and the morphology of membranes prepared therefrom were investigated. Two solvent mixtures were investigated: THF/DMF/DOX and THF/DMAc/Sulf. Micelles were observed in dilute solutions by TEM with the diameter increasing with PS block length. The order in semi-dilute solutions was characterized by SAXS, indicating that hexagonal arrangement was present in solutions of three different terpolymers. Additionally, lamellar, cubic and disordered arrangements were detected for the other copolymer compositions. The solution rheology could be well correlated with the order observed by SAXS, the block-solvent thermodynamic interactions, copolymer concentration, flow resistance and assembly stability. From the evaluated copolymers only $\text{PS}_{80.5\text{k}}\text{-}b\text{-P2VP}_{64.4\text{k}}\text{-}b\text{-PEO}_{16.1\text{k}}$ led to the preparation of regular isoporous morphology suitable for membrane application.

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Self-assembly of Polystyrene-*b*-poly(2-vinylpyridine)-*b*-poly(ethylene oxide)**Triblock Terpolymers**

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Highlights:

- Synthesis of PS-*b*-P2VP-*b*-PEO triblock copolymers
- SAXS and TEM characterization of equilibrium morphology
- TEM and DLS characterization of diluted solutions
- SAXS, Cryo-SEM and rheological investigation of semi-dilute solution.
- Correlation between order in solution and formation of isoporous films morphology

Graphical abstract