Chapter 7

Nanoporous gyroid channels for membrane applications

Abstract

A core-shell double gyroid self-assembled state was found for a poly(tert-butoxystyrene)-b-polystyrene-b-poly(4-vinylpyridine) triblock copolymer complex with pentadecylphenol. The amphiphile could be washed out, leaving nanoporous gyroid channels. The existence of the nanochannels was proven with SAXS and SEM. The possibility for such porous structures to be used in membrane technology is discussed.
7.1. Introduction

One of the key interest areas for applications of block copolymers is the field of separation membranes. In the last decade, a lot of work has been performed on nanoporous structures. In general, a block copolymer is allowed to self-assemble into its equilibrium morphology and afterwards, one of the blocks is selectively removed by etching, hydrolysis, ozonolysis or even depolymerization. A large portion of these studies involve materials obtained from cylinder-forming block copolymer precursors. Usually, thin films ranging from hundred to a few hundreds of nanometers are coated on a substrate. However, it is not trivial to align the cylinders in such a way that they span from top (polymer-air surface) to bottom (substrate-polymer interface) of the film. Of course, for a membrane to function properly, it is necessary for the pores to stretch continuously through the polymer. This problem was overcome by Peinemann et al. by using a combination of solvent evaporation and non-solvent-induced phase separation to create a nanoporous structure from a polystyrene-b-poly(4-vinylpyridine) or PS-b-P4VP diblock copolymer. The result was an asymmetric membrane with a highly ordered top layer of about 200-300 nm on top of a thick sponge-like layer.

Another way to avoid such alignment issues is to use a self-assembled state with continuous phases. In this way, alignment is no issue, since the resulting pores will form continuous pathways through the material by definition.

The phase diagram of PS-b-P4VP diblock copolymers complexed with pentadecylphenol (PDP) through hydrogen bonding has been extensively researched in our group. A number of hierarchically ordered self-assemblies were found, including lamellae-within-cylinders, lamellae-within-spheres and lamellae-within-lamellae (Figure 7.1). While a gyroid-within-lamellae morphology was found in which the polystyrene block \( f_{St} = 0.38 \) formed the two bicontinuous gyroid networks, the inverse gyroid self-assembly has never been found for the diblock copolymer complexes. One has to realize that a gyroid morphology for diblock copolymer systems is only possible in the weak to intermediate segregation regime. It is known that the pure PS-b-P4VP diblock copolymer will usually (depending on the molecular weight) be in the strong segregation state. However, once PDP is added this is no longer the case and gyroid structures become a distinct possibility.
Figure 7.1. Phase diagram for PS-P4VP(PDP)$_x$, as a function of temperature. The fraction of the P4VP(PDP)$_x$ block is denoted as $f_{comb,1}$. Reproduced with permission from Valkama, S.; Ruotsolainen, T.; Nykänen, A.; Laiho, A.; Kosonen, H.; ten Brinke, G.; Ikkala, O.; Ruokolainen, J. Macromolecules 2006, 39, 9327.

Such a morphology would be of great interest with respect to the membranes discussed, since it was demonstrated that washing the amphiphile away from the comb block results in the formation of nanoporous phases.\textsuperscript{18} For triblock copolymers, a number of network morphologies has already been found, including alternating gyroid,\textsuperscript{19,20} core-shell gyroid\textsuperscript{21} and orthorhombic networks.\textsuperscript{22}

Apparently, triblock copolymers offer a lot of possibilities to create network morphologies. Therefore, we turned our attention to triblock copolymers comprising P4VP as one of the blocks. If a network assembly could be found where P4VP(PDP) forms a continuous network, the amphiphile may be washed out and a promising membrane material would be obtained.
7.2. Experimental section

7.2.1. Materials

The triblock copolymer was synthesized by a three-step sequential anionic polymerization and characterized as mentioned in Chapter 5. The low molecular weight amphiphile, 3-Pentadecylphenol (PDP, 98 %, Aldrich) was recrystallized twice from petroleum ether. Ethanol and chloroform (p.a., LAB-SCAN) were used as received.

7.2.2. Characterization

Small-angle X-ray scattering (SAXS) was performed on two different setups. One is a Bruker NanoSTAR apparatus, which consisted of a Kristalloflex K760-8- 3.0 kW X-ray generator with cross-coupled Gobel mirrors for Cu Kα radiation (λ = 1.54 Å), resulting in a parallel beam of about 0.05 mm² at sample position. A Siemens multiwire type area detector was used. The sample-detector distance was 105 cm.

The second setup was at the Dutch-Belgian Beamline (DUBBLE) at ESRF in Grenoble, France. The sample-detector distance was about 7.3 m, while the X-ray wavelength was 1.24 Å (E = 10 keV). The SAXS intensity patterns were measured at different temperatures. The scattering vector $q$ is defined as $q = 4\pi/\lambda \sin \theta$ with $2\theta$ being the scattering angle.

Bright-field transmission electron microscopy (TEM) was performed on a JEOL-1200EX transmission electron microscope operating at an accelerating voltage of 100 kV. A piece of film was embedded in an epoxy resin (Epofix, Electron Microscopy Sciences) and cured overnight at 40 °C. The sample was subsequently microtomed to a thickness of about 70 nm using a Leica Ultracut UCT-ultramicrotome and a Diatome diamond knife at room temperature. The microtomed sections were floated on water and subsequently placed on copper grids. To obtain contrast during TEM, the samples were stained with iodine (3 h) or RuO₄ (100 min).

Scanning electron microscopy experiments (SEM) were performed on a JEOL 6320 Field Emission Scanning Electron Microscope working at an acceleration voltage of 3 kV and a work distance of 5 mm. Specimens were coated with a few nanometer thick layer of platina.
7.2.3. Triblock copolymer complex with PDP

The triblock copolymer ($M_n = 76.0$ kg/mol; $PDI = 1.04$; $f_{tBOS} = f_{St} = 0.46$, $f_{4VP} = 0.08$) in the amount of 386 mg (0.294 mmol 4VP units) was dissolved in chloroform together with 44.8 mg (0.147 mmol) of PDP. This corresponds to one PDP molecule per two 4VP repeat units. After stirring at room temperature overnight, the solution was poured into a glass petri dish, which was subsequently placed into a chloroform atmosphere. After two weeks of solvent annealing, the dish was heated shortly (10 min) in an oven of 130 °C. In this way, a complex was obtained, which has the following block weight fractions: $f_{tBOS} = f_{St} = 0.41$, $f_{4VP(PDP)} = 0.18$. Bulk triblock copolymer films were made by dissolving the polymer in chloroform and applying the same solvent annealing procedure; temperature annealing was performed at 180 °C for 10 minutes.

7.2.4. Removal of PDP

The low molecular weight amphiphile was removed by placing a piece of film into a beaker with 300 mL ethanol and stirring for three days at room temperature.

7.2.5. Large Amplitude Oscillatory Shear

To macroscopically align the sample, Large Amplitude Oscillatory Shear or LAOS was performed on a home-made tooth rheometer. The teeth had a surface of 5 mm x 3 mm and the gap width was 0.7 mm. The strain was below 0.5 and shearing was performed for one hour at a temperature of 175 °C.
7.3. Results

7.3.1. Bulk morphology

The complex that was formed between the polymer and 0.5 PDP molecules per 4VP unit was investigated. The SAXS intensity curves as well as some TEM images are shown in Figure 7.2.

![Figure 7.2](image)

**Figure 7.2.** Bright-field TEM image of the complex of entry 1 in Table 5.1 with 0.5 PDP molecules per 4VP moiety, stained with iodine (a) the inverse-color FFT of the same image and (b) ruthenium tetroxide-stained TEM image (c) and the corresponding SAXS intensity profile of the unsheared film at room temperature (d), the vertical lines indicate the positions of possible gyroid reflections.
The TEM micrographs clearly indicate the existence of a core-shell gyroid phase; Figure 7.2a clearly represents a section indicating the (211) plane. This plane has been well-established by a number of publications.\textsuperscript{3,12,24,25} The Fourier transform of the same image shows a substantial degree of order, reflected by the large number of scattering peaks (Figure 7.2b).

However, from the SAXS patterns we cannot conclude the same morphology. In order to strongly support a gyroid self-assembly, the first two peaks to be observed should be in the ratio $\sqrt{6} : \sqrt{8}$.\textsuperscript{26} The first peak observed is positioned at $q = 0.105$ nm\textsuperscript{-1}. The corresponding $\sqrt{8}$ peak should then be observed at $q = 0.121$ nm\textsuperscript{-1} (assuming there are no hidden peaks under the beam stop). In our case we can only assume this peak to be present in the shoulder of the first peak (second vertical line). Other possible reflections in the ratio of $\sqrt{6}$: $\sqrt{8}$: $\sqrt{14}$: $\sqrt{20}$: $\sqrt{22}$: $\sqrt{24}$: $\sqrt{26}$: $\sqrt{30}$: $\sqrt{32}$: $\sqrt{38}$: $\sqrt{40}$: $\sqrt{42}$: $\sqrt{50}$, indicating the G phase with cubic Ia\bar{3}d symmetry group (core-shell gyroid),\textsuperscript{27} were not observed, although the broad peak at around 0.2 nm\textsuperscript{-1} might comprise the $\sqrt{20}$, $\sqrt{22}$ and $\sqrt{24}$ peaks. Analogously, an alternating gyroid structure, with $I4_132$ symmetry can also not be proven or disproven.

For a particular poly(isoprene)-b-polystyrene-b-poly(dimethylsiloxane) linear triblock copolymer (ISD) Shefelbine \textit{et al.}\textsuperscript{21} also obtained a rather poor SAXS profile, while TEM evidence clearly showed a very well-ordered core-shell gyroid morphology. Two rather broad peaks, at seemingly lamellar spacings were observed, quite similar to the SAXS profile we observed (Figure 7.2d). Therefore, they shear-aligned the sample, making use of the cylindrical morphology the sample adopts at higher temperatures. After slow cooling to room temperature, the SAXS diffraction patterns showed a large number of well-defined spots, including patterns strongly resembling the FFT in Figure 7.2b, which they could assign to the proposed core-shell double gyroid morphology. There are a number of striking resemblances between that sample and the sample under investigation here (Table 7.1).

\begin{table}[h]
\centering
\caption{A comparison between the ISD triblock copolymer of Shefelbine \textit{et al.} and the sample under investigation.}
\begin{tabular}{lcc}
\hline
 & Shefelbine \textit{et al.}\textsuperscript{21} & GG145 \\
\hline
$f_a$ & 0.40 & 0.41 \\
$f_b$ & 0.41 & 0.41 \\
$f_c$ & 0.19 & 0.18 \\
$\chi_{AB}$ & 0.03 & 0.03 \\
$\chi_{BC}$ & 0.12 & <0.3 \\
$\chi_{AC}$ & 0.09 & <0.4 \\
\hline
\end{tabular}
\end{table}
7.3.2. Amphiphile removal

The amphiphile was removed by washing with ethanol, which should result in the loss of about 13 w% material. After removal of PDP, the sample showed an enormous increase of scattering as indicated in Figure 7.3. This is a clear indication of the porosity which is created by the removal of PDP.

![Figure 7.3. SAXS intensity profiles a) before and b) after washing away the amphiphile.](image)

Besides the orders of magnitude of increase of scattering, one can see a broad correlation hole peak around 0.17 Å⁻¹, which corresponds to the P4VP(PDP) complex formation. This peak is not present in the profile after washing. Both of these conclusions support the fact that not only PDP is removed, but also a nanoporous phase is obtained. To further check the resulting porous structure, SEM micrographs were taken.
This porous structure is clearly the top view of the plane observed in the TEM sections. Again, the gyroid structure is observed, which has not collapsed upon amphiphile removal. Wave-like patterns, combined with hole patterns are typical for gyroid morphologies. Moreover, at specific spots, one can recognize the typical trifunctional nodes, at which three struts come together at angles of about 180° (indicated by arrows in Figure 4a). Last but not least, the layers of the wave patterns are about 180 nm ± 2 nm thick, somewhat thicker than the layer thickness derived from the TEM images, about 156 nm ± 4 nm.

When the TEM and SEM images are scaled to the same length scale and the contrast in the TEM picture is somewhat enhanced, one clearly sees the close resemblance between the two techniques (Figure 7.5).
Now it is easy to relate which length scales correspond for both microscopy techniques, and it is clear that both give the same distance between layers of about 180 nm.

The polymer-glass interface (from the film casting process) was also examined with SEM (Figure 7.6). Although at this interface, the gyroid nature is not as easily recognized as in the previous pictures, it is a more direct resemblance to the TEM pictures. In any case, this interface is porous, as well. Therefore, this sample may very well be used to construct a nanoporous membrane by coating it on a porous support.

Figure 7.6. SEM micrograph of the porous gyroid film at the polymer-glass interface.

Besides this membrane application, the sample may also be used to make so-called metal foams, hybrid solar cells and actuators. The porous gyroid networks can be filled with inorganic material (replicating), after which the block copolymer is removed and a free-standing, inorganic gyroid replicate of the gyroid morphology is obtained.

### 7.3.3. Shear alignment

To obtain a more obvious SAXS profile, an attempt was made to shear align the sample. Some evidence was found that cylinders might be formed at temperatures around 175 °C and accordingly, LAOS was performed for one hour at 175 °C. The 2D SAXS patterns revealed some alignment, as shown in Figure 7.7.
One can see that the primary ring in the 2D SAXS pattern is not isotropic. Disappointingly, this SAXS pattern is inconclusive with respect to showing a gyroid nature. After washing away the amphiphile, the sample was investigated with SEM to judge the porous morphology that resulted.

The sample shows some cylindrical shapes rather than the gyroid morphology that was observed before applying shear (Figure 7.8). There are two possible explanations for this phenomenon. Firstly, it could mean that the observed gyroid self-assembly is not the equilibrium structure and that by shearing the sample at 175 °C, the more stable cylindrical morphology is formed and survives the cooling process until the material passes its glass transitions.

Figure 7.7. Alignment is observed with SAXS after applying LAOS (a), but again, no typical patterns are found after integration (b); the vertical line indicates the primary peak.

Figure 7.8. After shearing at 175 °C, the sample showed a cylindrical nature after removal of the amphiphile. Shown are SEM micrographs at magnifications of 15k (a) and 40k (b).
The second option is that shear induces an order-order transition into a cylindrical morphology. Such behavior has been observed in our group for a polyisoprene-\textit{b}-poly(4-vinylpyridine) block copolymer, hydrogen bonded with octyl gallate. For that particular complex, a transition from a lamellar into a cylindrical morphology was observed when LAOS was applied.\textsuperscript{28} This was ascribed to the facilitated breaking of hydrogen bonds due to shear. At present, it is not clear which of the two conclusions is correct.
7.4. Concluding Remarks

A triblock copolymer complexed with 0.5 PDP molecules per 4VP repeat showed a gyroid morphology as could be shown with TEM. The gyroid symmetry has not yet been fully elucidated, since from the SAXS pattern one cannot determine the precise nature of the morphology. To this end, additional synchotron SAXS measurements in combination with long-term annealing experiments should be performed.

Aligning the sample at 175 °C did not result in a macroscopically aligned gyroid morphology, but rather some sort of cylindrical morphology, as was shown with SEM after washing away PDP.

Additional SAXS measurements to corroborate the TEM data as well as a proper macroscopic alignment procedure of the gyroid self-assembly have to be found.
7.5. References