NANOPOROUS BLOCK COPOLYMER MEMBRANES FOR SEPARATION AND FILTRATION

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NANOPOROUS BLOCK COPOLYMER MEMBRANES FOR SEPARATION AND FILTRATION

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Thesis

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ABSTRACT

This project will focus on the Block Copolymers (BCPs) membranes that have high density and vertically oriented etched cylinder forming diblock copolymer thin film. Diblock copolymer has ability to self-assemble and gets periodic microdomain structures. It also can be applied as effective membranes for oil-water separation. It is the first time for diblock copolymer membranes as separation membranes. There are some potential advantages for Block copolymers (BCPs) as filtration membranes, such as diverse nanoscale morphology (cylinder, gyroid, spheres, etc). Directed self-assembly for orientation control and selective etchability of part of domain for nanoporous with high uniformity pore size (15-60)nm, and ultrahigh pore density up to $10^{10}$ can cover some important requirements such as high selectivity and high throughput (HS/HT) for membranes. Recently, we have developed a new process named cold zone annealing to produce etched, perpendicular well-defined cylindrical polystyrene-block-poly(methacrylate) (PS-b-PMMA). UV etches the PMMA domain to produce a hydrophilic channel that can allow water going through with high flow rate by capillary wetting flow. UV can also cause PS domain crosslinking for high mechanical strength. This is a new route for oil-water separation.
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CHAPTER I
INTRODUCTION

With the development of the nanotechnology, how to use petroleum as a general source of energy efficient has attracted more attention. According to the ability to self-organize into periodic nanostructure of block copolymers (BCPs), it can be well applied to nanotechnology fields. The area of applying block copolymer as membranes may be useful with a handful of studies of polymer filtration, but no oil-water separation. The cylindrical morphology is usually a better way for membrane applications. The field of using block copolymer films as membranes materials has a huge profit to find an efficient method to separate some components that is much more valuable from “crude oil”. The “crude oil” from the oil well is a complex mixture of oil, gas, produced water and solid particulates. The first step is transferred the mixture to primary gravity separators to produce well defined layer of gas, oil, and water. Therefore the separator outputs three major components: crude oil, process water (emulsion) and gas. In the decade years, there are lots of techniques for separation of emulsions, but most of them also show some defects. There is a best method for large-scale separation of oil
That is membrane filtration. Because of processing factors such as recyclability of throughput material in cross-flow membrane assemblies, ease of cleaning, as well as highly pure permeate make it useful. And their surface properties are a significant influence for membranes properties. Therefore, hydrophilic and hydrophobic membranes are made by diverse block copolymer. Surface segregation, surface coating and surface graft polymerization are the methods utilized for changing the surface energy to make hydrophilic membranes. Under this situation, I want to produce a well-defined vertical ordered block copolymer thin film to be as a selective layer of filtration membranes.

Figure 1- 1 Reverse osmosis, nanofiltration, ultrafiltration, microfiltration, and conventional filtration are all related processes, differing principally in the average pore diameter of the membrane.

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Currently, there are some available microporous hydrophobic membranes in capillary are made of polypropylene (PP), polyvinylidene fluoride (PVDF) and polytetrafluoroethylene (PTFE)\(^\text{12}\). From now on, hydrophobic MF membranes as a potential applicant were prepared by coating thin fluoro-containing film on stainless steel mesh which contributed stable water resisting, anti-chemical erosion and anti-hot aging properties\(^\text{13}\). Higher hydrophobicity of polymer materials has attracted more surface adsorption\(^\text{13}\)\(^\text{14}\). For example, Boussu et al\(^\text{15}\) clearly obtained trend of increasing adsorption with increasing hydrophobicity of studied organic compound and showed that a large surface charge and a high hydrophilicity are favorable in minimizing of fouling. From now on, because of this inspiration, I try to use hydrophilic cylindrical channels to separate water with some macromolecular by wetting flow of water.

![Figure 1-2 Schematic of a composite or thin film membrane. The specific polymers are for a reverse osmosis application; however the design construction can be generalized to other membrane application categories such as ultrafiltration (UF).](image-url)
Recently, there are four membrane separation processes in water and wastewater treatment, named microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). We can divide them into two types of membranes by nanostructure. For the specific requirement in this study is the multilayer composite or thin film membrane and its typical structure is illustrated in Figure 1-2 (for a reverse osmosis (RO) application in the illustrate case). It consists of a very thin top selective filtration layer with a thickness generally less than 100nm, on top of porous support and backing polymer layer or layers. On the top of this membrane, the selective layer, it has a nanoporous structure with etched hydrophilic nano-scale channels. It can allow water going through and impede polymer molecular such as alkane, the component of crude oil.

Those days, block copolymer (BCPs) have attracted advances in this field. It can be applied to membrane films.\textsuperscript{16,17,18,19} Above this, block copolymer can be used as nanoporous membrane films with highly ordered periodic domain structures in the range of 10-100nm typically. And one of the domain can be etched out to form hydrophilic channels, thin films of etched block copolymers can act as high fidelity membranes for filtration as the etched channel size between 15-60nm is ideal for separation of oil-water and filtering macromolecular structures. With above reason, it is obvious to use block copolymer as membrane films become an inevitable result. And then, Typical etch methods such as ultraviolet radiation or plasma to degrade one of the minority phase to form channel. Recently, we focus on producing well
defined ordered thin film and method of etching minority phase to form channel for separation.

The range of periodic structures for block copolymer phase separation includes cylinders, spheres, lamellae and bicontinuous gyroid phases. For all of them, the cylinder has attracted the most interest because it can act as perpendicular cylindrical nanochannels through the whole block copolymer membrane films. For key requirements of UF membranes, they have some advantages such as resistance to fouling, selectivity and mechanical integrity. For the size of nanochannels, there is an efficient method that is blending homopolymer and adjusting of their percentage in the block copolymer.\textsuperscript{20} The homopolymer to create channels within the minority domains.\textsuperscript{17} The homopolymer is typically the same polymer as the minority phase of the block copolymer such as the cylinder forming phase. The pore dimension in this case is determined by the volume fraction of the added homopolymer.
CHAPTER II
BACKGROUND

2.1. Phase separation of block copolymer

The block copolymer is consisting of two or more components with huge
difference in physical or chemical properties. Every parts of the components has
repeating monomer units. Under this situation, it can produce phase separation
when the repeating units can move. At the same time, block copolymer can display
different nanoscale morphology, such as cylinder, lamellar, gyroid, etc. In this article,
we focused on diblock copolymer with perpendicular cylindrical orientation.

For diblock copolymer, there are two immiscible repeating units A and B. They
are jointed with each other by covalent bonding. The thermodynamic is governed by
entropy and enthalpy. The enthalpy is the main factors in nanostructures and
promotes phase separation due to the incompatibility blocks when the temperature
is below the order-to-disorder transition temperature ($T_{ODT}$). If the nanostructure
changes to periodic microdomain, the interfacial energy reduced but the chain
conformation increased. When the temperature is above $T_{ODT}$, the entropic will
become the key factor to homogeneous phase. And the critical temperature $T_{ODT}$
is determined by three parameters: the volume fraction parameter $f$ of the block,
the Flory-Huggins interaction parameter $\chi$ and the degree of polymerization $N$. The
value of represents the segregation strength, which refer to both enthalpy and entropy contribution. Chains of block copolymer are intermixed and the morphology will be disordered when the value of $\chi N$ is below a certain level under a given constitution. For diblock copolymer with symmetric chain length, the critical value of $\chi N$ is 10.5. Two types of morphology will occur depending on the value of $\chi N$, which is segregation power. The strong segregation limit (SSL) ($\chi N \gg 10.5$) and week segregation limit (WSL) ($\chi N << 10.5$). Above all, we can determine the morphology by the volume fraction of blocks repeating units, while the dimension of these structures depends on the molecular weight of the block copolymer. Figure 2-1 shows the phase diagram of diblock copolymer morphology. With the increasing of volume fraction, the morphology changes from body-centered cubic spheres (bcc), passing into hexagonally packed cylinder (hex) and bicontinuous gyroid (gyr), and lamellae (lam).

![Figure 2- 1 Phase diagram of diblock copolymer predicted by SCMF theory](image)

2.2. Self-assemble block copolymer thin films

In most case, parallel orientation of microdomain form block copolymer thin films due to different surface energy of different interaction with substrate.
Producing well-defined block copolymer nano-cylinders thin film is the key step for filtration membranes and nanotechnology such as perpendicular cylindrical block copolymer as marks. Surface energy is the main factor for the morphology of block copolymer thin films.

For cylindrical block copolymer thin films, if the surface energy of substrate surface and the air/polymer surface are the neutral to both blocks, it will be perpendicular orientation. There are several methods for producing perpendicular cylindrical thin films. For example, casting a neutral layer between substrate and block copolymer films can lead to a vertical arrangement because of no preferential interaction with each block blocks. Another method is controlling solvent evaporation to balance the surface energy between two blocks. It can cause perpendicular orientation to the surface. Oven annealing is the traditional method with simply operation. And annealing block copolymer films in different solvents can be applied to product parallel to vertical cylindrical block copolymer thin films. Other methods by blending homopolymer into block copolymer can also induce perpendicular orientation. It also can be used as size-controlled methods.

From now on, there is a most common utilized method to induce block copolymer phase separation to produce ordered perpendicular orientation named thermal annealing. Zone annealing is the most useful way used in block copolymer phase separation. Under a moving temperature gradient $\nabla T$, it can induce many kinds of polymer to create ordered nanostructures. Zone annealing can be divided into hot zone annealing (HZA) and cold zone annealing (CZA) by the different maximum
temperature ($T_{\text{MAX}}$). In hot zone annealing, the maximum temperature is above the order-disorder transition temperature ($T_{\text{ODT}}$). And for cold zone annealing the maximum temperature is below the order-disorder transition temperature. Figure 2-2 demonstrated the principle of zone heating method for lamella forming block copolymer.

Figure 2-2 Schematic illustration of the principle of zone-heating method for lamella-forming block copolymer. (a) The temperature gradient from $T_1$ to $T_2$ moves from left to right keeping the specimen position fixed. As a result, temperature of the sample can be lowered below $T_{\text{ODT}}$ sequentially from the place that is near to glass surface to the place inside the specimen. The motion brings about a sequential ordering from the place that is near the glass surface (b) toward the interior of the specimen (e). The slow-moving rate and sharp temperature gradient suppress bulk nucleation from the region below $T_{\text{ODT}}$.23
The figure 2-2(a) shows that the specimen goes through under the temperature gradient $\nabla T$ with a glass plate. The temperature at the heating block ($T_1 > T_{ODT}$) and the cooling block ($T_2 < T_{ODT}$) controlled by the different zones. It has two regions: $\alpha$-region with $T < T_{ODT}$ and $\beta$-region with $T > T_{ODT}$. In this case, the block copolymer melt in the front at $\beta$-region in the disordered transition temperature while the block copolymer melt in $\alpha$-region changes the transition from disordered to ordered state. The morphology of block copolymer will change when it goes through the $\alpha$-region. Takeji Hashimoto and coworkers$^{24}$ applied the HZA method to a polystyrene-block-polyisoprene diblock copolymer with cylindrical nanostructures. The sweep rate and temperature gradient will influence the morphology when the maximum temperature below the order-disorder transition temperature. Cold zone anneal is similar to hot zone anneal, beside the maximum temperature is below the order-disorder transition temperature. Furthermore, there is a new advance in zone annealing, that is sharp thermal gradient in cold zone annealing. Sharp thermal can be used producing vertically well-ordered block copolymer nanostructures in thin films.

2.3. Fabricating perpendicular cylindrical block copolymer thin films

Previous research in self-assemble of block copolymer thin films has concentrated on the electric$^{25, 26, 27}$, chemical patterning$^{28, 29, 30}$ and confinement fields$^{31, 32, 33}$. Recently, A new approach has been applied to produce block copolymer films for membrane application that have long range vertical order of cylindrical nanoporous phase we have pioneered a simple yet forceful technique of orienting
perpendicular domains of cylindrical block copolymers using a dynamic thermal gradient technique termed sharp “Cold Zone Annealing” (CZAsharp). Here, we demonstrated that basic of CZA system (Finger 2-3). Cold Zone Annealing can provide exceptional orientation order with faster annealing than conventional oven annealing. This method is based on Lovinger et al\textsuperscript{34} in the 1980’s and revived by Hashimoto\textsuperscript{35} two decades later application to bulk block copolymer films. The system of Cold Zone Annealing (CZA) consists of two cold blocks on either side of a hot block that is a hot wire (~1 mm). A sample is pulled at a speed with a temperature gradient (~35°C /mm). At the same time, the substrate is replaced by quartz that has a low thermal conductivity. When it touches with the hot region, it melts and recrystallizes at the front. At the same time, growth occurs and it contributed to an oriented crystal with limited defect. With different temperature gradient, it has different morphology. In my experiment, the temperature gradient is 35 °C /mm. We called this method as Cold Zone Annealing with sharp temperature gradient. (CZA-S). Under this temperature gradient, the vertical orientation can be produced though the whole block copolymer thin films.
Figure 2-3 Schematic of CZA-S setup with overlapped thermal image showing real-time $\nabla T$ profile, BCP thin film is pulled with help of a linear actuator that can be programmed to move at desired translation speed. For static CZA-S experiments, linear actuator is not used and the BCP sample is stationary for desired time period, after which it is removed in a direction normal to quench morphology development.

2.4. Blending homopolymer in block copolymer

To align block copolymer with perpendicular to the surface attract more attention by its ordered nanopattern. Most of methods can make this ordered block copolymer thin film satisfied some specific aim such as controlling the size of perpendicular cylinder blocks. But they have a limit about surface energy effect. Under this situations, compared with others methods, an alternative method by blending homopolymer the same polymer as the minority or majority phase of the block copolymer has been attracted more interests. It also has some potential advantages, Such as no external electrical fields are required. In this way, we can easily to produce well-defined and long-range ordered thin films that can be
controlled size of part of blocks. Block-copolymer and homopolymer mixture have attracted considerable interest because they can easily modified by adjusting the relatively molecular weight. The relationship between morphology and the molecular weight of homopolymer is depending on the ratio \((r)\) of molecular weight of homopolymer over the molecular weight of block homologous component.\(^{36}\) Sancaktar et al. concluded the relationship when \(1<r<1.6\), can observe the perpendicular orientation. Because the molecular weight we blend into will influence the diffusion rate of the block copolymer microdomains.

Here, we demonstrate the influence of the degree of polymerization of homopolymer \(A\), \(NAH\) and that of the block component \(A\) in block copolymer, \(NAC\). When \(NAH<NAC\), the homopolymer will be selectively solubilized into an \(A\) microdomain, an \(A\) swelling occurred and it induce change of space and morphology\(^{37}\). If \(NAH=NAC\) the homopolymer is tend to localized at the center of the \(A\) domains. When \(NAH>NAC\), macrophase separation and microphase separation between block copolymer component and homopolymer occurred at the same time. From now on, we mainly concerned about the influence of entropy, even though the enthalpy and kinetic were also contributed to the morphology. But when the degree of incompatibility between the blocks can be influenced by blending homopolymer, the enthalpic contribution of blending homopolymer will be the mainly contribution to the microseparation. In my current work, I try to use CZAsharp with blending homopolymer to produce ordered thin film. Figure 2-4 shows the location of homopolymer blended in block copolymer in PS-b-PMMA blending PMMA system. We can know that the homopolymer will locate at the center of the cylindrical
domain. More than 90% homopolymer will locate at the center of the PMMA domain.

Figure 2- 4 A schematic for a homopolymer distribution within cylindrical microdomains. The y-axis is the homopolymer concentration: region I with PS block chain only, region II where the homopolymer chains are uniformly distributed, and region III containing the homopolymer only.  

2.5. Separation filtration membranes of block copolymer

For Poly (styrene-b-methylmethacrylate) (PS-b-PMMA) diblock copolymer as our selective layer of the filtration membranes occur to our mind. Form above, PS-b-PMMA is the most interesting block copolymer for our aim. Figure 2-5 show the percentage of perpendicular cylinder of PS-b-PMMA thin films after cold zone annealing with different thickness. When the thickness is more than 75nm, the percentage of vertical cylinder will up to 70%. In this article, we will use 100nm PS-b-PMMA film as the selective layer. The percentage of perpendicular cylinder will
up to 90%, which are well-ordered and periodic nanostructures. It is the basic idea for highly throughput.

Figure 2-5 Film thickness range of vertically ordered PS-PMMA block copolymer cylinders (PMMA phase) and corresponding percentages over which ordering is observed using CZA sharp process as described in detail below.

An important step is to be able to convert the cylinder block into nanochanneals by some etch method. We have used the UV based etch method with selective solvent rinse applicable to PS-b-PMMA and likely many other block copolymer. Due to different sensation between PS phase and PMMA phase. UV under vacuum can selective etch PMMA phase. Figure 2-6(b) show the PS-b-PMMA diblock copolymer of etched PMMA cylinders of CZA annealed. We can change etching time to make different nanochanneals. And than, we need transfer this film onto a supporting membranes. PES (Polyethersulfone) as our basic membrane by film flotation. It has hydrophilic pore (size from 0.03 micron to 5 micron). And the PES membranes can provide highly mechanical properties and integrity. Polyethersulfone (PES) membrane has superior resistance to harsh cleaning chemicals with no degradation of processing performance through multiple cleaning cycles. Cut out membrane
samples of appropriate dimensions will be placed in an Amicon 8010 stirred cell (Millipore Co., Cambridge, MA) and secured using a silicone O-ring. Oil-water mixture will be passed through by a controlled pressure drop applied across the membrane. For unetched membranes we will check that no flow is observed over several hours to check for nonblock copolymer related defects.

Figure 2-6 AFM image of surface morphology of PS-b-PMMA. (a) Cold zone annealed PS-b-PMMA thin film. (b) UV etched PS-b-PMMA thin film remove PMMA phase of CZA annealed.
In this paper, I focus on the block copolymer (PS-b-PMMA) system with the morphology and etched method for filtration membranes. I will investigate the influence of thickness, the percentage of homopolymer and the type of blended components to the morphology of the block copolymer system. Solution is Toluene and the flow coating film with thickness around 100nm. In order to induce morphology of BCP, Cold Zone Annealing has been applied. Blending homopolymer is for adjusting the size of PMMA domain. And then the film was treated by ultraviolet to make an multilayer membranes for ultrafiltration.

3.1. Materials

The sample of poly(styrene-block-methylmethacrylate) (PS-b-PMMA) (Mw=57k-b-25k) was used and bought from Polymer Source Inc. The ratio of polymer chain lengths (volume fraction of the PS block is ~0.7) leads to forms a cylindrical morphology. The cylinder spacing $L_0=50$nm. The material safety data from Polymer Source Inc. show that the glass transition temperature for PS block is 110°C and for PMMA block is 124°C. And homopolymer Poly-methylemethacrylate (PMMA)
of molecular weight is 25,000 and polystyrene is 58,000 that bought from Polymer Source Inc.

For supporting membrane is PES (Polyethersulfone) Membranes. We bought from STERLITECH Corporation. Sterlitech Polyethersulfone (PES) membranes are hydrophilic filters constructed from pure polyethersulfone and available in pore sizes ranging from 0.03 micron to 5.0 micron. This strong, microporous PES membrane is constructed from a high-temperature polyethersulfone polymer that is acid and base resistant. The strength and durability of PES membrane filters are especially advantageous during procedures that require aggressive handling or automated equipment. Figure 3-1 show the surface morphology of PES membrane.

![Figure 3-1 The morphology of PES membranes.](image)

3.2. Sample Preparation

Quartz substrates were bought from Chemglass, Inc. It followed by 1h of ultraviolet-ozone (UVO) treatment. And flow coated a PSS layer onto the quartz
substrates. Oven annealing under vacuum for 6h to remove the solution. BCPs and homopolymers were dissolved in toluene. Different solutions were prepared: (1) PS-b-PMMA (3 wt% in toluene), (2) PS-b-PMMA with PMMA (99 wt% of BCPs, 1 wt% of PMMA, Mw of PMMA is 25k), (3) PS-b-PMMA with PMMA (95 wt% of BCPs, 5 wt% of PMMA, Mw of PMMA is 25k), (4) PS-b-PMMA with PMMA (90 wt% of BCPs, 10 wt% of PMMA, Mw of PMMA is 25k), (5) PS-b-PMMA with PMMA (85 wt% of BCPs, 15 wt% of PMMA, Mw of PMMA is 25k), (6) PS-b-PMMA with PMMA (80 wt% of BCPs, 20 wt% of PMMA, Mw of PMMA is 25k), (7) PS-b-PMMA with PS (99 wt% of BCPs, 1 wt% of PS, the Mw of PS is 56k), (8) BCPs with PS (95 wt% of BCPs, 5 wt% of PS, the Mw of PS is 56k), (9) PS-b-PMMA with PS (90 wt% of BCPs, 10 wt% of PS, Mw of PMMA is 56k), (10) BCPs with PS (85 wt% of BCPs, 15 wt% of PS, Mw of PMMA is 56k), (11) PS-b-PMMA with PS (80 wt% of BCPs, 20 wt% of PS, Mw of PMMA is 56k). And then BCP films were flow-coated onto quartz substrates with different thickness range. Different speed of flow-coating leads to various thickness. Film thicknesses were measured by a thin film interferometer, (F-20 UV Thin Film Analyzer, Filmetrics, Inc.)

Table 1 Different content of sample element

<table>
<thead>
<tr>
<th>Sample</th>
<th>content</th>
<th>molecular weight</th>
<th>r</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>BCP</td>
<td>57K-b-25K</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>BCP +1%PMMA</td>
<td>57K-b-25K+25K</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>BCP +5%PMMA</td>
<td>57K-b-25K+25K</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>BCP+10%PMMA</td>
<td>57K-b-25K+25K</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>BCP+15%PMMA</td>
<td>57K-b-25K+25K</td>
<td>1</td>
</tr>
</tbody>
</table>
Table 1 Different content of sample element (continued)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Content</th>
<th>Molecular weight</th>
<th>r</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>BCP+20%PMMA</td>
<td>57K-b-25K+25K</td>
<td>1</td>
</tr>
<tr>
<td>7</td>
<td>BCP+1%PS</td>
<td>57K-b-25K+56K</td>
<td>1</td>
</tr>
<tr>
<td>8</td>
<td>BCP+5%PS</td>
<td>57K-b-25K+56K</td>
<td>1</td>
</tr>
<tr>
<td>9</td>
<td>BCP+10%PS</td>
<td>57K-b-25K+56K</td>
<td>1</td>
</tr>
<tr>
<td>10</td>
<td>BCP+15%PS</td>
<td>57K-b-25K+56K</td>
<td>1</td>
</tr>
<tr>
<td>11</td>
<td>BCP+20%PS</td>
<td>57K-b-25K+56K</td>
<td>1</td>
</tr>
</tbody>
</table>

*BCP refers to PS-b-PMMA; r is ratio of molecular weight of homopolymer over relatively component in block copolymer.

3.3. Cold zone annealing

The basic components of sharp cold zone annealing (CZA-S) are based on Lovinger et al. Described perviously. The hot zone is heated by a low resistance nickel-chrome wire. The cold blocks are cooled by circulation low molecular weight PDMS oil at -5°C. PS-b-PMMA thin film were swept at several sets of speed with the maximum of temperature $T_{\text{MAX}} \approx 210^\circ\text{C}$ and temperature gradient $\nabla T=45^\circ\text{C/mm}$. Figure 3-2 is a schematic of the CZA-S set-up.

![Figure 3-2 A schematic of CZA-S](image)

Figure 3-2 A schematic of CZA-S. The thin film was casted on a quartz substrate, and placed on a moveable arm. The sample temperature during the run was measured.
by thermocouple which also presses the sample onto the stage. The sample is moved across a temperature controlled hot block which is located between two PDMS oil cooled cold block. The three blocks assembly (cold-hot-cold) thus forms an in-plane temperature gradient. The sample movement across the in plane gradient is controlled by programmed arm at a prescribed velocity. The height of nickel-chrom wire is adjusted to change the temperature gradient $\nabla T$ on the substrate. And the temperature gradient is measured by IR imaging camera (Testo 875 Thermal Imager Kit).

3.4. UV etching

We used ultraviolet radiation to treat PS-b-PMMA thin film due to different sensation between PS and PMMA. UV treated this block copolymer thin film with different time under vacuum condition. After UV etching, wash the film with Acetic acid and then with distilled water. Then dry it in the air. Figure 3-3 show the UV chamber for etching.

Figure 3-3 A kind of UV chamber.
3.5. Fabrication of block copolymer filtration membranes

From now on, I will introduce the processing of fabrication a multilayer block copolymer filtration membranes. It is the key point for this article. Quartz substrate treat by UVO for 2h and than flow coat a poly(sodium-p-styrenesulfonate) (PSS) layer onto it. It is easy to dissolve into water. That is a more useful method for transferring film into water. Oven annealing under vacuum it for 6h at 140°C to remove the solvent. And put it under UVO again for 15min. Flow coated a PS-b-PMMA layer with thickness around 100nm. Cold zone anneal this block copolymer film at maximum temperature $T_{\text{MAX}} \sim 210^\circ\text{C}$ and temperature gradient $\nabla T=35^\circ\text{C/mm}$ with sweep rate 10um/s. After that, float it into water and transfer it onto PES membranes. Put it into UV chamber for 2h and than cut out membrane samples of appropriate dimensions will be placed in an Amicon 8010 stirred cell (Millipore Co., Cambridge, MA) and secured using a silicone O-ring. For filtration part, first, put acetic acid into stirred cell for washing and per-wetting the membranes for 2h. And than use deionized
water washing the acetic acid for 2h. Finally, pull PEO/water solution or oil/water
solution into stirred cell for separation filtration.

3.6. Characterization

3.6.1 AFM

Atomic force microscopy is sensitive method for investigating surface structure of
materials. The normal method applied in polymer films is called tapping mode.
Tapping mode maps topography by lightly tapping the surface with an oscillating
probe tip. The basic working process is demonstrated in Figure3-5. In tapping mode,
the feedback loop keeps a vibrating cantilever at a constant amplitude. The tip on
the cantilever is modulated through mechanical excitation at its resonance. A laser
beam is reflected off of a micro-fabricated cantilever, onto a mirror, then reflected
onto a photodiode array. The laser spot oscillates vertically across the array as a
result of the vibrating cantilever. The tip tracks the topography of the surface and its
oscillation frequency is changed by the presence of relatively harder or softer
features at the surface, giving rise to phase contrast images. Most AFM
measurements are performed on films cast onto flat wafers such as silicon or mica,
and are performed in air at room temperature. In this work, topography at the
surface of nanostructures block copolymer thin films was imaged using a Dimension
Icon atomic force microscope (AFM) (Bruker AXS) in the Peak Force Quantitative
Nanomechanical Property mapping mode.
3.6.2 UV-vis

UV-VIS is the a kind of absorption spectra, which belongs to the electronic spectra and are caused by the transition of the valence electrons. The molecules or ions on the ultraviolet and visible light produced by the absorption of ultraviolet visible spectrum and absorption of material composition, content and structure analysis, determination, inference. The ordinary ultraviolet visible spectrometer, is mainly composed of a light source, monochromator, a sample pool (Xi Guangchi), composed of detector, and recording device. The ultraviolet visible spectrometer design generally try to avoid using lens in the optical path, instead of using mirrors, absorption due to avoid the instrument error. UV visible absorption spectrometer is a kind of use ultraviolet visible spectrometer in the wide, which is mainly composed of light source, monochromator, absorption cell, detector and data processing and recording (computer) parts. The ultraviolet visible spectrometer is used for identification, purity, isomeric compounds determination, determination of steric
hindrance effect, determination of hydrogen bond strength as well as other relevant quantitative analysis.

3.6.3 DLS

Dynamic Light Scattering (DLS), also known as the photon correlation spectroscopy of Photon Correlation Spectroscopy (PCS), quasi elastic light scattering quasi-elastic scattering, measuring changes in light intensity fluctuations with time. The DLS technique for the measurement of particle size, has the advantages of accurate, rapid, reproducible technique, has become a characterization method compared to the conventional nano technology. With the development of update of the instrument and data processing technology, dynamic light scattering instrument now not only has the function of measuring particle size, Zeta potential, ability has the measurement of large molecular weight.
CHAPTER IV
RESULTS AND DISCUSSIONS

4.1. Oven annealing of BCP and BCP/Homopolymer thin film

4.1.1 Block copolymer blending PMMA homopolymer

Oven annealing is the traditional method for inducing self-assembly of PS-b-PMMA thin films. The temperature of oven annealing is more than the glass transition temperature of the block copolymer \( T_{gPS} \sim 110{\degree}C, T_{gPMMA} \sim 124{\degree}C \). In this article, I try to blend different percentage of homopolymer into block copolymer. Figure 4-1 show the 1%PMMA homopolymer in PS-b-PMMA oven annealed at 180{\degree}C for 2h with different thickness.

![Figure 4-1](image-url)
With the thickness increasing, the parallel cylinder will convert to vertical. And the domain size also has a little bit increase. So, we try to measure more percentage of PMMA homopolymer. Figure 4-2 show the different percentage of PMMA homopolymer in PS-b-PMMA and oven anneal at 180°C for 2h.

Figure 4-1 AFM hight image of surface morphology of PS-PMMA with 1%PMMA with different thickness under vacuum oven annealing at 180°C for 2h. The scan size is 2μm.

With the thickness increasing, the parallel cylinder will convert to vertical. And the domain size also has a little bit increase. So, we try to measure more percentage of PMMA homopolymer. Figure 4-2 show the different percentage of PMMA homopolymer in PS-b-PMMA and oven anneal at 180°C for 2h.
The image of surface morphology of block copolymer with homopolymer are the similar to the neat block copolymer. But when the thickness is ultrathin around 80nm and it is easy to get island and hole. Blending 20% PMMA into block copolymer is more parallel cylinder than 5% and 10% PMMA homopolymer. When the PMMA homopolymer increase 15%, we can easy to see that more vertical cylinder changing

Figure 4-2 AFM hight image of PS-b-PMMA with different percentage of PMMA with different thickness and oven annealing at 180°C for 2h. The scan size is 2μm.

The image of surface morphology of block copolymer with homopolymer are the similar to the neat block copolymer. But when the thickness is ultrathin around 80nm and it is easy to get island and hole. Blending 20% PMMA into block copolymer is more parallel cylinder than 5% and 10% PMMA homopolymer. When the PMMA homopolymer increase 15%, we can easy to see that more vertical cylinder changing
to parallel cylinder. So it is easy to say that satisfied the requirement for the filtration membranes’ high throughput we must keep the PMMA homopolymer below 15 percentages. According to the theory of blending homopolymer into block copolymer. The homopolymer will locate at the center of the block copolymer phase. For the image we can get that with the percentage of PMMA homopolymer increase the diameter of the cylinder will also increase. For my research, I need the selective layer around 100nm, the PMMA homopolymer we blended is more important for adjusting the diameter of the cylinder.

In summary, for oven annealing we can use blending PMMA homopolymer to control the diameter of the vertical cylinder. But it has a limit that is we can just blend less than 15 percent of PMMA homopolymer because of the surface morphology. Table 2 show the domain of blending PMMA homopolymer with different content of mixture system.

Table 2 The domain size of different percentage of PMMA homopolymer

<table>
<thead>
<tr>
<th>content of PMMA</th>
<th>Domain size(nm)</th>
<th>expansivity(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>43.73</td>
<td>4.86</td>
</tr>
<tr>
<td>5</td>
<td>45.55</td>
<td>9.23</td>
</tr>
<tr>
<td>10</td>
<td>49.08</td>
<td>17.69</td>
</tr>
<tr>
<td>15</td>
<td>52.94</td>
<td>26.95</td>
</tr>
<tr>
<td>20</td>
<td>57.92</td>
<td>38.89</td>
</tr>
</tbody>
</table>

Form the table, we can control the domain size from 43nm to 58nm. It will cover different requirement of filtration membranes.
In summary, due to blend homopolymer into the block copolymer, we can adjust the domain of the block copolymer to control the size of nanochannels for fabrication of the filtration membranes. We can also use the ImageJ to calculate the percentage of perpendicular cylinder of the surface morphology.

Figure 4- 3 The percentage of PMMA homopolymer with different of domain size.

Figure 4- 4 Calculation of percentage of perpendicular cylinder of bloc copolymer

For the filtration membranes because of different size of diameter can separate different polymer with different molecular weight. Because of different molecular weight has different hydrodynamic radii.

4.1.2 Block copolymer blending PS homopolymer
Most of article always add minority domain, there is another method is adding majority blocks. For this article is blending PS homopolymer. Figure 4-5 shows the surface morphology of PS-b-PMMA blending different percent of PS homopolymer with different thickness. Oven annealing at 180°C for 2h. According to the block copolymer phase separation, when we blended the majority domain of block copolymer is good for inducing the perpendicular cylinder. The results are the similar to the theory of block copolymer phase separation. We can see that the percentage of PS homopolymer is from 1% to 20% , the perpendicular cylinder percent is increasing with adding more PS. And also with the increasing of the thickness, the surface morphology is change a little. But we also can find that for the 15%PS blended into PS-b-PMMA, the percentage of vertical cylinder become more prefect with the thickness increasing. Figure 4-5 show the surface morphology of PS-b-PMMA blending different percent of PS homopolymer with different thickness. Oven anneal at 180°C for 2h.

![Surface morphology images](image-url)
Figure 4-5 AFM height image of PS-PMMA blending different percentage of PS homopolymer with different thickness. Oven annealing at 180°C for 2h.

Table 3 shows the domain size of PS-b-PMMA with blending different percent of PS homopolymer. The percentage of PS homopolymer is from 1% to 20%. And then we calculate the domain size and expansivity. We can find the domain size and the expansivity both increased with the more PS homopolymer we added.

Table 3. Domain size of PS domain with different percentage of PS homopolymer

<table>
<thead>
<tr>
<th>Percent of PS homopolymer(%)</th>
<th>Domain size (nm)</th>
<th>Expansivity(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>42.43</td>
<td>1.75</td>
</tr>
<tr>
<td>5</td>
<td>42.59</td>
<td>2.13</td>
</tr>
<tr>
<td>10</td>
<td>42.4</td>
<td>1.68</td>
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<tr>
<td>15</td>
<td>42.86</td>
<td>2.78</td>
</tr>
<tr>
<td>20</td>
<td>43.18</td>
<td>3.55</td>
</tr>
</tbody>
</table>
4.2. Cold zone annealing of BCP and BCP/homopolymer thin film

Compared with oven annealing, sharp cold zone annealing (CZA-S) as an advanced method to induce the surface morphology of block copolymer has some more advantages.

4.2.1 Neat block copolymer

After Cold Zone Annealing, the PS-b-PMMA block copolymer thin film can produce a cylinder orientation showed in Figure 4-6. It showed the AFM topographical patterns for different thickness. Those films were under sharp temperature gradient (the maximum temperature gradient is 35°C/mm showed by Figure 4-7(b)). With different thickness, the orientation will change. It is ‘hybrid’ morphology: consist of both parallel and vertical cylinders to the substrate and surface. For the 70nm PS-b-PMMA, it shows the mixture orientation with parallel and vertical cylinder. It is obvious that with the thickness increasing, the perpendicular orientation become the main morphology on the top of the thin film. For 100nm PS-b-PMMA thin film, the percentage of perpendicular cylinders is above 90%. And the distant of cylinder-to-cylinder, L0≈40nm (measured by AFM image with software named NanoScope Analysis).
Figure 4-6 AFM height sensor of flow-coated PS-b-PMMA block copolymers with different film thickness after Cold Zone Annealing at 210 °C with speed 10 μm/s. The scan size is 2μm.

Table 4 Film characteristic with different thickness.

<table>
<thead>
<tr>
<th>Thickness(nm)</th>
<th>% perpendicular cylinders</th>
<th>density of pore</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>37.2%</td>
<td>217.25/μm</td>
</tr>
<tr>
<td>85</td>
<td>59.2%</td>
<td>317.97/μm</td>
</tr>
<tr>
<td>100</td>
<td>94.3%</td>
<td>420.77/μm</td>
</tr>
</tbody>
</table>

Figure 4-7 The image of thermal IR imaging camera and with temperature gradient histogram.
The reason of cylinder orientation is due to the different surface energy between polymer-substrate and the polymer-air. Form Figure 4-6, it can indicate that when the thickness thick enough, the difference between interface energy can be ignored because of the perpendicular cylinder is dominant in the AFM images. Among above, there will be a competition between the interaction at the interface. For PS-b-PMMA, the surface energy is influenced by molecular weight and temperature. Because of the different combination of molecular weight and temperature, it can bring different morphology\textsuperscript{40}. At 210-230°C, the free surface is neutral to both PS and PMMA blocks. In my experiment, the temperature was 210°C and the molecular weight is 57k-b-25k, which is similar to Paul F. Nealey’s 46k-b-21k, hence the surface energy at the free surface will expect to be equivalent, resulting perpendicular cylinder with thickness 100nm showed in Figure 4-6.

4.2.2 BCP/PMMA homopolymer

For block copolymer and homopolymer system, cold zone annealing is also a effective method to induce the perpendicular cylinder of surface morphology. We blend PMMA homopolymer, which is the minority phase, into PS-b-PMMA and cold zone anneal with different sweep rate and the maximum temperature is 210°C under sharp temperature gradient (the maximum temperature gradient is 35°C/mm. We use this method blending homopolymer into block copolymer to control the diameter of the perpendicular cylinder.
For the blending system of PS-b-PMMA and PMMA, cold zone annealing is better for oven annealing because of the AFM image of surface morphology. We can find that for the 1% and 5% PMMA homopolymer in BCP, the perpendicular cylinder of the surface morphology is more than 90%. But for the PMMA homopolymer is more than 15%, the ultrathin film is easy to get macro-phase separation. And at the same time, we can calculate the diameter of the cylinder by the software named ImageJ.
For cold zone annealing, we can control the domain size by blending PMMA homopolymer from 42nm to 58nm and also we can choose different PMMA cylinder for different aim.

Compared with oven annealing, figure 4-9 show the domain size of oven annealing and cold zone annealing, we can find that the domain size after cold zone annealing is a little bit smaller than the domain size after oven annealing. And the domain size is proportional to the percentage of blending PMMA homopolymer.

Table 5 The domain size of BCP blending PMMA

<table>
<thead>
<tr>
<th>Percentage of PMMA</th>
<th>Domain size (nm)</th>
<th>Expansivity(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>42.91</td>
<td>2.90</td>
</tr>
<tr>
<td>5</td>
<td>45.38</td>
<td>8.82</td>
</tr>
<tr>
<td>10</td>
<td>47.69</td>
<td>14.36</td>
</tr>
<tr>
<td>15</td>
<td>50.69</td>
<td>21.55</td>
</tr>
<tr>
<td>20</td>
<td>58.24</td>
<td>39.66</td>
</tr>
</tbody>
</table>

For cold zone annealing, we can control the domain size by blending PMMA homopolymer from 42nm to 58nm and also we can choose different PMMA cylinder for different aim.

Compared with oven annealing, figure 4-9 show the domain size of oven annealing and cold zone annealing, we can find that the domain size after cold zone annealing is a little bit smaller than the domain size after oven annealing. And the domain size is proportional to the percentage of blending PMMA homopolymer.
4.3 Effect of CZA-S Sweep Rates on morphology

The Figure 4-10 showed the morphology of PS-b-PMMA thin films that Cold Zone Annealed with different sweep rates. The change from parallel to perpendicular is due to surface flow and relaxation. The rate of CZA-S annealing at 10μm/s showed the maximal vertical ordered orientation. When the sweep rate decrease, the block copolymer has enough time to relax and obtained the similar surface wetting morphology. However, when the blocks under stable larger area equilibrium morphology, it cannot be back perpendicular morphology when it pass through the cold side. It can indicate the morphology of Figure 4-10(b) has fewer defects than that (c). For the morphology both (b) and (c) are better than (a). So (c) do not have enough time to relax with temperature gradient of 35°C/mm and the block copolymer ordering is kinetically hindered. And for block copolymer with sweep rate
at 5μm/s, polymer relaxation leads to have a parallel cylinder. Consequently, as sweep rate of 10 or more, time are sufficient for ordering occurs. Hence, there are an upper and lower critical sweep rate for perpendicular ordering occur. The figure reveal that when cold zone annealing sweep rate is round 10μm/s, there is a well-defined perpendicular ordering of PS-b-PMMA thin film can be produced.

Figure 4- 10 AFM height sensor images with different sweep rate after Cold Zone Annealing at 210°C. The scan size is 2μm. Thickness is 100nm.

(a) 5μm/s  (b) 10μm/s  (c) 15μm/s

Figure 4- 11 AFM height sensor images of PS-b-PMMA with 10%PMMA with different sweep rate after Cold Zone Annealing at 210°C. The scan size is 2μm. Thickness is 100nm.

(a) 5μm/s  (b) 10μm/s  (c) 15μm/s
4.4 UV etching

PS-b-PMMA thin films were exposed to UV with vacuum condition for different time showed by Figure 4-12. After UV etching, wash the film with acetic acid and then with distilled water. Then dry it in the air. We can see that the PMMA phase has different scale of etchable nanochannels with different time.

Figure 4-12 AFM height sensor images of PS-b-PMMA cold zone annealing at 210°C sweep rate is 10 μm/s after UV etch with different time. The scan size is 2μm.

With different time of irradiation, compared with the domain size before UV etching, when the exposure time more than 1.5h, the PMMA phase can be etched completely.
4.5 Fabrication of multilayer filtration membranes.

I will introduce the processing of fabrication a multilayer of block copolymer filtration membranes. It is the key point for this article. Quartz substrate treat by UVO for 2h and than flow coat a poly(sodium-p-styrenesulfonate) (PSS) layer onto it. Poly(sodium-p-styrenesulfonate) is easy to dissolve into water. That is a more useful method for transferring film into water. Oven annealing under vacuum it for 6h at 140°C to remove the solvent. And put it under UVO again for 15min. Flow coated a PS-b-PMMA layer with thickness around 100nm. Figure 4-13 show the processing of flow coating a PS-b-PMMA onto quartz substrate. There is a small gap between the blade and the substrate. Put solution at the gap. The stage with the substrate moved at a specific speed. When the solvent evaporate, there is a PS-b-PMMA thin film on the quartz substrate. Cold zone anneal this block copolymer film at maximum temperature $T_{\text{MAX}} \sim 210^\circ\text{C}$ and temperature gradient $\nabla T = 35^\circ\text{C/mm}$ with sweep rate 10um/s. After that, float it into water and transfer it onto PES membranes. Figure 4-14 show how to transfer PS-b-PMMA thin film onto the PES supporting membranes.

Figure 4- 13 Flow coating PS-b-PMMA onto quartz substrate.
Figure 4- 14 Transfer PS-b-PMMA film from quartz substrate to PES supporting membranes.

And then put it into UV chamber for 2h. Figure 4-5 show the UV treat the PS-b-PMMA film to remove PMMA phase. And than cut out membrane samples of appropriate dimensions will be placed in an Amicon 8010 stirred cell (Millipore Co., Cambridge, MA) and secured using a silicone O-ring. For filtration part, first, put acetic acid into stirred cell for washing and per-wetting the membranes for 2h. And than use deionized water washing the acetic acid for 2h. Finally, pull PEO/water solution or oil/water solution into stirred cell for separation filtration.

After etching, there is some residue on the surface of the hole. So after washing with acetic acid and water, the image of PMMA phase change from black to white. Figure 4-16 show the results.
4.6 Flow rate and effective of separation

As demonstrated in Figure 4-17 show the set-up filtration system. In this part, we can provided pressure by nitrogen cylinder. And use hot stage to increase the temperature at the same time provided the stir. For the PEO/water mixture, the concentration is 1.5g/L, 10psi, under 60rpm stirred. And for oil/water separation filtration. The water/oil=50v:50v, under 10psi and 200rpm stirred.

![Ultrafiltration Cell](image)

Figure 4-17 The ultrafiltration cell for PEO/water separation filtration.
Table 6 The hydrodynamic diameter of different molecular weight PEO

<table>
<thead>
<tr>
<th>Molecular Weight of PEO</th>
<th>6.8K</th>
<th>100K</th>
<th>400K</th>
<th>900k</th>
<th>2000k</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean of diameter (d.nm)</td>
<td>5.44</td>
<td>18.20</td>
<td>28.18</td>
<td>45.6</td>
<td>71.54</td>
</tr>
</tbody>
</table>

Figure 4-18 Hydrodynamic diameter of PEO

For our expectation, we can fabricate different types of multilayer filtration membranes. Such as more than 1 layer selective layer. For the “sandwich membranes”, we can use two or more selective layer to avoid the defect and make sure that all of the polymer in water can be separated. As Figure 4-18 show the pure water filtration is the fastest and no selective film means that no PS-PMMA film on top of PES supporting membranes. And the two layer’s flow rate is obviously slow down than one selective layer separation membrane.
At the same time, we also measure different molecular weight PEO in water. Figure 4-19 show the different molecular weight of PEO solution’s flow rate. We can find that compared with pure water filtration, the flow rate of PEO solution is obviously changed. For the molecular weight of PEO is 100k, it is the smallest in hydrodynamic radii. When the molecular weight is more than 900K, the flow rate will increase. The hydrodynamic radii is much more than the diameter of nanochannel of the filtration membranes. The flow rate will also increase. So we can find from Figure 4-19, the flow rate of separation 900K PEO is more than 400K PEO.
After filtration, we get the solution. And then, we put 1µl solution in a small bottle and evaporated water at 40°C under vacuum. And then calculate the weight of PEO is around 0.8mg. So we got the separating effect is around 50%. For the initial solution the weight of PEO after evaporated water is around 1.5mg.

Figure 4-21 Oil/Water separation (a) The flow rate under 10psi and 200rpm stirred (b) The result of separating effect.

At the same time, we also try to separate the Oil/Water emulsion. Figure 4-21 shows the separation of oil/water. We use cooking Oil: water (50v:50v) emulsion as
initial solution. We can find that after filtration the percolate is mostly like pure water.
The PS-b-PMMA block copolymer with perpendicular cylinder can be a potential choice as a selective layer on the top of filtration membranes. Based on our results, this PS-b-PMMA block copolymer thin film with vertical cylinder can be etched by UV radiation. With the thickness less than 100nm, the percentage of perpendicular cylinder can be more than 90%. The morphology of block copolymer thin film was decided by the Cold Zone Annealing, thickness, temperature gradient, and the type of blending homopolymer. After Cold Zone Annealing, the mixture with PS-b-PMMA block copolymer and homopolymer of PS can have a perpendicular cylinder with domain size around 40nm. And then UV treats these thin films with 1.5h, it will obtain a ~20nm nanochannels. We design this thin film as a selective layer for filtration membranes. Recently, complete the membranes using this thin film for separation of PEO/water. According to this result, it is a new method for separation filtration.
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