SELF-ASSEMBLY OF POLY(ETHYLENE OXIDE)-BLOCK-POLY(ETHYL ACRYLATE)-BLOCK-POLYSTYRENE WITH PHENOLIC RESINS

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SELF-ASSEMBLY OF POLY(ETHYLENE OXIDE)-BLOCK-POLY(ETHYL ACRYLATE)-BLOCK-POLYSTYRENE WITH PHENOLIC RESINS

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ABSTRACT

Mesoporous carbon materials (2-50 nm) have received considerable attention for their remarkable physicochemical properties, which bring about widespread applications, such as absorption, separation, catalysis, drug delivery, and energy conversion and storage. One general route to fabricate mesoporous carbons is through soft-templating, namely cooperative self-assembly of an amphiphilic block copolymer (BCP) with a carbon precursor (e.g. phenolic resin). The precursor is selective to hydrophilic domains to tune the microphase separation of BCP. Typical soft templating involves the use of AB or ABA block copolymers as the template, which in most cases, only spheres, cylinders, and lamellae morphologies were obtained. Switching to an ABC type triblock copolymer provides greater flexibility in the design of the morphology, potentially opening up larger processing windows for bicontinuous morphologies. In this study, we designed and synthesized a new non-frustrated triblock copolymer poly(ethylene oxide)-block-poly(ethyl acrylate)-block-polystyrene (PEO-b-PEA-b-PS) using reversible addition-fragmentation chain transfer (RAFT) polymerization. We discuss efforts to prepare bicontinuous porous carbon thin films through cooperative self-assembly of this novel triblock copolymer with phenolic resins (resol) with different processing methods.
Initially, we spun-cast a series of polymer/resol thin films with variant resol concentrations. These polymer/resol films were processed by three thermal processing steps: thermal annealing to induce ordering of BCP and resol’s crosslinking (120 °C), calcination to remove BCP template to yield mesopores (400 °C), and carbonization to produce mesoporous carbon films (800 °C). After template removal AFM results suggest that a network of homogeneous fibrous nanostructures (~20 nm diameter cylinders) with high porosity (~60%) were produced over a range of resol concentration (25 ~ 33 wt%). Other kinetically trapped structures, such as parallel cylinders and mixed parallel lamella/cylinders are also found at higher resol concentration (40 ~ 60 wt%). These kinetically trapped mesostructures are attributed to the high glass transition temperature of PS segments leading to slower self-assembly ordering rate of BCP than resol’s crosslinking rate.

Next, solvent vapor annealing (SVA) with methyl ethyl ketone (MEK) was performed on as prepared polymer/resol films prior to the thermal processing steps. The MEK solvent vapor plasticized the polymer (i.e. enhancing the mobility of segments) allowing it to self-assemble into a series of highly ordered structures such as parallel cylinders, perpendicular cylinders, and double gyroids, as evidenced by AFM and GISAXS results. Further thermopolymerization of these films produced long range ordered mesostructures through an order-order transition during thermal crosslinking, including a small window of bicontinuous gyroid morphology. It was found that the formation of gyroid phase from order-order transition (cylinder to gyroid) is a strong function of the aging of the resol, as well as the processing conditions, including SVA.
time and resol composition. Subsequent calcination and carbonization of this bicontinuous gyroidal film yielded an ordered bicontinuous gyroidal mesoporous carbon with high porosity (50\%) and narrow pore size distribution (12 ± 2 nm).
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# TABLE OF CONTENTS

| LIST OF FIGURES | xi |
| LIST OF SCHEMES | xv |
| LIST OF TABLES | xvi |

## CHAPTER

### I. INTRODUCTION

1.1 Block Copolymer Self-Assembly

1.1.1 Linear AB Diblock Copolymer

1.1.2 Multiblock Copolymer

1.1.3 Synthesis of Block Copolymers

1.2 Ordered Network Mesostructures

1.2.1 Introduction of Multiply Continuous, Percolating Structures

1.2.2 Network Mesostructures Formed by Block Copolymers

1.3 Ordered Mesoporous Carbon Materials

1.3.1 Hard-Templating

1.3.2 Soft-Templating

1.4 Film Characterization

---

Page

xi

xv

xvi

1

2

6

8

15

15

16

22

23

26

31
1.4.1 Ellipsometry and Ellipsometric Porosimetry (EP) ........................................ 32
1.4.2 Atomic Force Microscopy (AFM) ................................................................. 41
1.4.3 Grazing Incidence Small Angle X-ray Scattering (GISAXS) .................... 44

II. NANOPOROUS NON-WOVEN FIBRIL-LIKE MORPHOLOGY BY COOPERATIVE
SELF-ASSEMBLY OF POLY(ETHYLENE OXIDE)-BLOCK-POLY(ETHYL ACRYLATE)-BLOCK-POLYSTYRENE AND
PHENOLIC RESIN ..................................................................................................... 47

2.1 Introduction ......................................................................................................... 47
2.2 Experimental Section .......................................................................................... 53
   2.2.1 Materials ...................................................................................................... 53
   2.2.2 Preparation of PEO-b-PEA-b-PS Triblock Copolymer ............................ 54
      2.2.2.1 Esterification of PEO$_{45}$-OH with RAFT-COOH ......................... 54
      2.2.2.2 Synthesis of PEO$_{45}$-b-PEA-RAFT ........................................... 55
      2.2.2.3 Synthesis of PEO$_{45}$-b-PEA-b-PS ............................................ 55
   2.2.3 Characterization of Polymer Properties ..................................................... 56
   2.2.4 Films Preparation and Processing .............................................................. 57
   2.2.5 Characterization of Thin Films .................................................................. 58
2.3 Results and Discussion ....................................................................................... 59
   2.3.1 Properties of Synthesized PEO$_{45}$-b-PEA$_{117}$-b-PS$_{99}$ Templates .......... 59
   2.3.2 Fabrication of Mesoporous Films using Thermal Annealing ................. 73
2.4 Conclusions ........................................................................................................ 99

III. BICONTINUOUS MESOPROUS CARBON THIN FILM VIA AN ORDER-ORDER TRANSITION ........................................................................................................ 100

3.1 Introduction ......................................................................................................... 100
3.2 Experimental Section ....................................................................................... 102
3.2.1 Chemicals .................................................................................................................. 102
3.2.2 Films Preparation and Processing ................................................................. 103
3.2.3 Characterization of Thin Films ........................................................................... 104
3.3 Results and Discussion ............................................................................................... 105
  3.3.1 Processing Dependent Morphology ................................................................. 105
  3.3.2 Impact of Resol Age on Morphology ................................................................. 117
3.4 Conclusions ................................................................................................................. 127

IV. CONCLUSIONS AND FUTURE WORK ................................................................. 128

  4.1 Conclusions ................................................................................................................ 128
  4.2 Future work ................................................................................................................. 130
    4.2.1 Exploration of Novel Processing Method to Gyroidal Mesoporous Carbons from OES ................................................................. 130
    4.2.2 Design and Synthesis of Novel Non-frustrated ABC Triblock Copolymer for Gyroidal Mesoporous Carbons ................................................................. 133

REFERENCES .................................................................................................................. 134
LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1 (a) Schematic of equilibrium phases of AB diblock copolymer in bulk; (b) Theoretical phase diagram of AB diblock copolymer predicted by the self-consistent mean-field theory; (c) Experimental phase diagram of polyisoprene-block-polystyrene (PI-b-PS) copolymers.</td>
<td>5</td>
</tr>
<tr>
<td>1.2 Morphologies of linear ABC triblock copolymers.</td>
<td>7</td>
</tr>
<tr>
<td>1.3 Common structures of a chain transfer agent (CTA) agent</td>
<td>11</td>
</tr>
<tr>
<td>1.4 Space-filling models of the $Q^{230}$, $O^{70}$, and $Q^{214}$ network phases in ABC triblock copolymer, poly(isoprene-b-styrene-b-ethylene oxide) (ISO).</td>
<td>17</td>
</tr>
<tr>
<td>1.5 Phase diagram of poly(isoprene-b-styrene-b-ethylene oxide) (ISO) in the vicinity of the order-disorder transition temperature.</td>
<td>21</td>
</tr>
<tr>
<td>1.6 Illustration of the nanocasting strategy for the synthesis of mesoporous carbons...</td>
<td>25</td>
</tr>
<tr>
<td>1.7 Schematic for the preparation of the ordered mesoporous polymers and carbon frameworks.</td>
<td>29</td>
</tr>
<tr>
<td>1.8 Schematic of experimental setup of an ellipsometry experiment.</td>
<td>34</td>
</tr>
<tr>
<td>1.9 Schematic of an experimental setup of ellipsometric porosimetry.</td>
<td>38</td>
</tr>
<tr>
<td>1.10 From ellipsometry data to adsorption isotherm. (A) Refractive index as a function of relative toluene vapor pressure; (B) Relative adsorbed volume of toluene as a function of relative toluene pressure by fitting refractive index using LLEMA model.</td>
<td>40</td>
</tr>
<tr>
<td>1.11 Schematic of an atomic force microscope. The laser emits a beam and reflected by the back of the cantilever. The reflected beam from the cantilever reaches the mirror and reflected to hit on the photo-detector. The signal from the photo-detector goes into feedback loop to control the piezoelectric scanner to adjust the height between the tip and the sample.</td>
<td>43</td>
</tr>
</tbody>
</table>
1.12 Schematic of the geometry of a GISAXS experiment .......................................................... 46

2.1 $^1$H NMR spectra of PEO$_{45}$-RAFT .................................................................................. 63

2.2 $^1$H NMR spectra of PEO$_{45}$-b-PEA-RAFT ...................................................................... 65

2.3 $^1$H NMR spectra of PEO$_{45}$-b-PEA-b-PS ........................................................................ 67

2.4 SEC traces of (i) PEO$_{45}$-RAFT, (ii) PEO$_{45}$-b-PEA-RAFT, (iii) unpurified PEO$_{45}$-b-PEA-b-PS, (iii) purified PEO$_{45}$-b-PEA-b-PS. The vertical lines are guides to the eye to indicate the peak maximum in subsequent SECs. After purification, the mole ratio of PEO:PEA:PS is 1 : 2.6 : 2.2 from $^1$H NMR spectra ................................................ 70

2.5 TGA traces of PEO$_{45}$-b-PEA$_{117}$-b-PS$_{99}$ and resol in the range of 25-900 °C under N$_2$ atmosphere ......................................................................................................................... 72

2.6 A) The thickness of the films ( ■ ) as-spun; (●) after thermopolymerization, at 120 °C; and (▲) after template removal at 400 °C as a function of resol content. B) The thickness contraction of films after thermopolymerization (●), at 120 °C and after template removal (▲) at 400 °C using the as-spun film thickness as reference. .......................... 75

2.7 AFM phase images of PEO$_{45}$-b-PEA$_{117}$-b-PS$_{99}$/resol films under different temperature with growing resol content, (A) F-33-25; (B) F-50-25 ; (C) F-60-25; (D) F-33-120; (E) F-50-120; (F) F-60-120; (G) F-33-400; (H) F-50-400; (I) F-60-400. The size of insets in (D) and (G) is 200 nm × 200 nm. .................................................................................................................. 77

2.8 AFM height image of films (A) F-60-120, (B) F-60-400. For F-60-120 film, the AFM height image (A) shows the bright regions correspond to the platform structure from the AFM phase image, while for F-60-400 film, the AFM height image (B) shows that the platform domains turn out to be lower domains. ............................................. 79

2.9 Surface morphology of F-33-400 calcined film with a network of homogeneous fibrous structure, (A) phase image and (B) height image as shown by AFM, and the associated height profile (C) corresponding to height image in (B). ................................................. 83

2.10 GISAXS patterns of films after thermopolymerization at 120 °C with different resol content (A) 33 wt%; (B) 50 wt%; (C) 60 wt% at incident angle $\alpha_i = 0.10^\circ$ and (D) corresponding 1-D $q_x$ traces of GISAXS scattering patterns along the $q_z = 0.26$ nm$^{-1}$. .................................................................................................................. 86

2.11 (A) Refractive index of films for (■) as-spun; (●) after thermopolymerization, at 120 °C; (▲) after removing template, at 400 °C, as a function of resol content (wt%); (B) Porosity of calcined films as a function of resol content (wt%) at 400 °C using BEMA model and corresponding structures, (I) Fibril-like structure; (II) Parallel
cylinder structure; (III) Mixed cylinder and lamellae structure.

2.12 Adsorption (■) and desorption (●) isotherms of mesoporous calcined films along with different resol content wt%, (A) 33 wt%, (B) 50 wt%, (C) 60 wt%. The corresponding pore size distributions (D) based on the absorption isotherms, (a) 33 wt%, (b) 50 wt%. The pore size distributions curve of calcined film with 60 wt% resol content is calculated due to limited absorption of toluene vapor.

2.13 Film thickness of F-33-400 with respect to relative pressure $p/p_0$, adsorption (■) and desorption (●).

2.14 AFM phase images and cylinder distribution of calcined films with fibril-like structures with Gaussian fit. AFM phase images, (A) F-25-400; (B) F-28.5-400; (C) F-33-400. Cylinder distribution, (D) F-25-400; (E) F-28.5-400; (F) F-33-400.

2.15 Surface morphology of mesoporous carbon pyrolyzed at 800 °C as a function of resol content shown by AFM, phase images (A) 25 wt% resol; (B) 28.5 wt% resol; (C) 33 wt% resol. The topology associate with the pores can clearly be seen in (D) the height images, 33 wt% resol, corresponding to phase image in (C). (E) Height profile of surface topology corresponding to height image in (D).

3.2 AFM phase images of films containing (A) 0 wt%; (B) 25 wt%; (C) 40%; (D) 50%; (E) 60%; and (F) 60 wt% resol after exposure to MEK using short SVA.

3.3 AFM phase images of thermopolymerized films heated at 85 °C for 24 h after application of short SVA time prior to thermopolymerization, containing (A) 25 wt%; (B) 50 wt%; (C) 60 wt% resol.

3.4 AFM phase images of film containing 25 wt% resol exposed to MEK solvent vapor for overnight and processed at different temperature, (A) after long SVA; (B) 85 °C, thermopolymerized; (C) 400 °C, calcined; (D) 800 °C, carbonized.

3.5 Thermopolymerized and calcined film containing 25 wt% after long SVA. (A) GISAXS pattern of thermopolymerized film at incident angle $\alpha_i = 0.10^\circ$; (B) Adsorption (■) and desorption (●) isotherms of mesoporous calcined film with toluene as probe solvent; (C) estimated pore size distribution determined from EP using the Kelvin equation.

3.6 AFM phase images of films containing different resol content at 25 °C, (A) 22.7 wt%; (B) 25.0 wt%; (C) 28.9 wt%; (D) 33.3 wt%; and at 75 °C, (E) 22.7 wt%; (F) 25.0 wt%; (G) 28.9 wt%; (H) 33.3 wt%; and (I) 22.7 wt%; (J) 25.0 wt%; (K) 28.9 wt%; (L) 33.3 wt% after exposure to MEK using long SVA (repeated work). (Scale bar: 250 nm.)
3.7 GISAXS profile for 22.7 wt% resol films after long SVA. The split primary peak is indicative of a mixed parallel and perpendicular orientation of cylinders. ..........................122

3.8 GISAXS profile for 25 wt% resol film after long SVA process obtained at an incident angle of 0.22°. ........................................................................................................124

3.9 GISAXS profile for 28.9 wt% resol film after long SVA process obtained at an incident angle of 0.22°. ........................................................................................................126

4.1 Transmission electron microscopy (TEM) image of ISO + resol hybrid with processing conditions, (a) only THF as the solvent and 1 hour stirring time, limited ordered structure; (b) THF and CHCl₃ as the solvent and 24 hour stirring time, and elevated casting temperatures for solvent evaporation, double gyroid structure. .........132
LIST OF SCHEMES

<table>
<thead>
<tr>
<th>Scheme</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1 Proposed simple mechanism of RAFT polymerization. (I) Initiation and propagation step; (II) pre-equilibrium step; (III) re-initiation step; (IV) main-equilibrium step; (V) termination step.</td>
<td>14</td>
</tr>
<tr>
<td>2.1 The schematic of synthesis of PEO&lt;sub&gt;45&lt;/sub&gt;-b-PEA-b-PS triblock copolymer by sequential RAFT polymerization.</td>
<td>61</td>
</tr>
<tr>
<td>3.1 Schematic representation of the fabrication of mesoporous carbons via cooperative self-assembly induced by a solvent vapor annealing process followed by thermally induced self-assembly, calcination and carbonization.</td>
<td>106</td>
</tr>
</tbody>
</table>


LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
</table>
| 2.1 Characteristics of the purified triblock copolymer | 71

xvi
CHAPTER I

INTRODUCTION

1.1 Block Copolymer Self-Assembly

Block copolymers (BCPs) are hybrid macromolecules composed of two or more chemically distinct polymer segments covalently bound together. The development of this field originated with the discovery of living anionic polymerization by Szwarc et al. in 1956, which enabled the sequential addition of monomers to living polymer chains to produce BCPs.\(^1\) Polymerization of several distinct monomer types (e.g. A, B and C monomers) leads to a number of block copolymer architectures, such as AB diblock copolymers, ABA (or BAB) triblock copolymer, ABC triblock copolymer, (AB)_n star-block copolymer, graft-block copolymer, etc. The complex structures of BCPs consisted of different polymers in sequence have made them many useful properties leading to industrial application for decades, such as foams,\(^2\) adhesives,\(^3\) thermoplastic elastomers,\(^4\) etc. Recently, renewed attention has been attracted to BCPs for their self-assembly behavior leading to the promising applications in nanotechnology, such as biomedicine, catalysts, photoelectric materials, microelectronics.\(^5\)
1.1.1 Linear AB Diblock Copolymer

The simplest block copolymer is a linear AB diblock copolymer, as shown in Figure 1.1a. The self-assembly behavior of linear AB diblock copolymer in bulk, has been most studied both theoretically and experimentally. The self-assembly behavior undergoes a compromise between mixing and separation. Thermodynamic incompatibility between A and B blocks propels a dense aggregation of monodisperse diblock copolymer chains to self-arranged via microphase separation to reach equilibrium in which the contacts between same blocks (A-A or B-B) and distinct blocks (A-B) are maximized and minimized, respectively. The macroscopic phase separation, on the other hand, cannot happen because the blocks are covalently bonded.

Theoretically, for a linear AB diblock copolymer, three parameters govern the microphase separation behavior. These three parameters include the overall degree of polymerization, $N$, and the volume fraction of A (or B) block, $f_A$ (or $f_B$), and the associated segment-segment interaction parameters, $\chi_{AB}$. Here, $N$ is determined by the sum of degree of polymerization of each block, $N = N_A + N_B$; $f_A$ (or $f_B$) is determined by the ratio of polymerization degree of one block to the overall degree of polymerization, $f_A = N_A / N$ ($f_B = N_B / N$); and $\chi_{AB}$, an temperature-dependent interaction parameter, describes the thermodynamic incompatibility between A and B blocks and is given by the following equation:

$$\chi_{AB} = \left(\frac{Z}{k_B T}\right) \left[\frac{1}{2} (\epsilon_{AA} + \epsilon_{BB}) - \frac{1}{2}(\epsilon_{AB})\right]$$
where, \( z \) is the coordination number, meaning the number of nearest neighbors per repeat lattice, \( k_B \) is the Boltzman constant, \( T \) is the absolute temperature, \( \varepsilon_{ij} \) represents the contact energy per repeat lattice site between \( i \) and \( j \) segments. The values of \( \chi_{AB} \) can be either negative or positive. A positive of \( \chi_{AB} \) suggests a repulsive force between A and B segments to drive towards separating, while a negative \( \chi_{AB} \) occurs in some specific A-B interaction (e.g., hydrogen bonding and ionic bonding), indicating an attracting force to propel mixing. Typically, for a common diblock copolymer, such as polystyrene-block-poly(methyl methacrylate) (PS-b-PMMA), in which there is no specific strong interactions, e.g. hydrogen bonding and ionic bonding, the Flory-Huggins interaction parameter, \( \chi_{AB} \), changes with inversely temperature (i.e. \( \chi_{AB} \sim 1/T \)). The tendency of BCPs to phase separation is quantitatively described by the segregation strength \( \chi N \). With decreasing segregation strength \( \chi N \) (i.e. increasing temperature, or decreasing molecular weight, because \( \chi_{AB} \sim 1/T \) and \( N \sim M_n \)), the block copolymer changes from ordered to disordered state due to the increasing product of temperature and conformational entropy and decreasing block incompatibility. The transition is referred to as order-to-disorder transition (ODT), and the temperature, where the ODT occurs, is the \( T_{ODT} \). Since the ODT transition depends on the segregation strength \( \chi N \), typically, three segregation regimes were used to characterize ordering in diblock copolymers: the weak segregation limit (WSL, \( \chi N < 10 \)), and the strong segregation limit (SSL, \( \chi N \geq 100 \)), and the regime between WSL and SSL defined as the intermediate segregation regime (ISR, \( 10 \leq \chi N < 100 \)), as stated by Epps et al.\textsuperscript{11}
The phase behavior of diblock copolymer in bulk is well understood both experimentally and theoretically, as shown in Figure 1.1.\textsuperscript{7,12,13,14} The self-consistent mean-field (SCMF) theory has been developed to predict the phase diagram of AB diblock copolymer, as shown in Figure 1.1b.\textsuperscript{7,15,16} At a fixed $\chi N$ above the ODT, a variety of common periodically ordered phases for AB diblock copolymer can be obtained with increasing composition $f_A$, passing through closely packed spheres (CPS) phase, body-centered cubic (bcc) spheres (S) phase, hexagonally packed cylinders (C) phase, bicontinuous gyroids (G) phase, lamellae (L) phase to inverse morphologies when composition is inverted.\textsuperscript{7} These morphologies and their transition have supported by the later experiment.\textsuperscript{17} Figure 1.1c shows an experimental phase diagram of polyisoprene-block-polystyrene (PI-b-PS) copolymers reported by Khandpur et al.\textsuperscript{17} The overall topology of the experimental phase diagram is obviously similar to the theoretical phase diagram in Figure 1.1b. But there are also some differences. For example, the experimental phase diagram in Figure 1.1c is not perfectly symmetric with respect to $f_A = 1/2$; the metastable phase, perforated layers (PL), is observed in the experimental phase diagram. These differences are attributed to conformational asymmetry as mentioned by Bates et al.\textsuperscript{18}
Figure 1.1. (a) Schematic of equilibrium phases of AB diblock copolymer in bulk. S and S’ = body-centered cubic spherical phase, C and C’ = hexagonally packed cylindrical phase, G and G’ = bicontinuous gyroids phase, and L = lamellae phase. (b) Theoretical phase diagram of AB diblock copolymer predicted by the self-consistent mean-field theory (SCMF).\(^{15}\) \(^{16}\) CPS and CPS’ = closely packed spherical phase. (c) Experimental phase diagram of polyisoprene-block-polystyrene (PI-b-PS) copolymers.\(^{17}\) \(f_A\) = the volume fraction of polyisoprene; PL = perforated lamellae phase. Reproduced with permission from reference 9.
1.1.2 Multiblock Copolymer

Adding additional numbers of blocks (n) in BCPs leads to an increased level of complexity of self-assembly behavior in bulk. For example, ABC triblock copolymer consists of three distinct blocks, A, B and C, which are covalently bonded together, as illustrated in Figure 1.2. This introduction of a third distinct block, C, dramatically expands the spectrum of accessible nanostructured morphologies due to the increased number of tunable parameters: the overall degree of polymerization \(N, N = N_A + N_B + N_C\); two independent volume fractions \(f_A\) and \(f_B\), where \(f_C = 1 - f_A - f_B\), and three different interaction parameters \(\chi\) (\(\chi_{AB}\), \(\chi_{AC}\), and \(\chi_{BC}\)). A wide range of ordered morphologies have been discovered experimentally in ABC triblock melt, including core-shell versions of C and S,\(^{19,20,21,22,23,24,25}\) two-and three-domain L,\(^{11,19,20,21,22,23,26,27}\) three equilibrium network phase (core-shell double gyroid Q\(^{230}\), and alternating gyroid Q\(^{214}\), and orthorhombic O\(^{70}\)),\(^{19,21,26,27,28,29,30}\) and other mixed-phase morphologies,\(^{22,31}\) as depicted in Figure 1.2. While for AB and ABA copolymers, the phase behavior is only governed by three parameters, namely the overall degree of polymerization, \(N\), the relative compositional fraction of A block, \(f_A\), and the Flory-Huggins interaction parameter between A and B segments, \(\chi_{AB}\), as mentioned earlier, and thus very limited number of microphase structures are adopted, typically four familiar structures including lamellae, gyroids, cylinders, and spheres phases.
Figure 1.2. Morphologies of linear ABC triblock copolymers. (a) Lamella phase; (b) core-shell cylinder phase; (c) lamella-cylinder phase; (d) lamella-sphere phase; (e) cylinder-ring phase; (f) cylindrical domains in a square lattice structure; (g) spherical domains in the CsCl-type structure; (h) lamella-cylinder-II phase; (i) lamella-sphere-II phase; (j) lamella-sphere-II phase; (k) core-shell spherical phase; (l) double gyroid phase. Reproduced with permission from reference 9.
1.1.3 Synthesis of Block Copolymers

There are many methods of synthesizing block copolymers. Initially, the preparation of well-defined block copolymers involves the utilization of a living, or at least a controlled chain-growth polymerization method. The living polymerization refers to as a chain growth polymerization where the chain transfer and chain termination are absent. Since the originated discovery of living anionic polymerization by Szwarc et al. in 1956,1 many other living polymerizations (e.g., cationic polymerization,32 ring-opening polymerization,33,34 and condensation polymerization35) have been developed to synthesize BCPs with well-defined architectures, controllable molecular weights, and narrow molecular weight distribution (i.e. polydispersity index, PDI). However, most of these polymerizations methods are limited to some specific monomers or rigorous experimental conditions, thus reducing the probability and facility of synthesizing versatile BCPs.

The discovery of controlled (“living”) free-radical techniques has opened up for BCPs synthesis with further growth and development. The living free radical polymerization (or reversible-deactivation polymerization),36 which contains transfer and termination reactions as conventional free-radical polymerization, is distinct from living polymerization. The live free radical polymerization combines the advantages of radical polymerization, such as the compatibility with a wide range of monomers and facile reaction conditions (unnecessary removal of moisture), and those associated with the living polymerization, such as controllable molecular weight and composition,
and narrow molecular weight distribution (close to 1). Since the first living free radical polymerization using nitroxides to reduce termination reactions, which refers to as nitroxide-mediated radical polymerization (NMP),\textsuperscript{37, 38} many other living free radical polymerization techniques for BCPs have been developed, including atom transfer radical polymerization (ATRP),\textsuperscript{39, 40} reversible addition-fragmentation chain transfer (RAFT),\textsuperscript{41, 42} and some novel ways of combining ATRP and RAFT,\textsuperscript{43, 44} and Cu(0)-mediated radical polymerization.\textsuperscript{45, 46} In this work, we will focus on the RAFT polymerization because of its relative facility and versatility (compatibility of a wide range of monomer and allowance of all modes of polymerizations, including emulsion, suspension, solution and bulk polymerization) compared with other polymerization methods for BCPs.

Since the first report by Thang et al. in 1998,\textsuperscript{41} RAFT polymerization has become the most versatile methods of controlled radical polymerization for BCPs due to its compatibility with a wide range of monomers (including styrene, acrylates, acrylamides, and many vinyl monomers, etc), facile reaction conditions, and controlled molecular weight, as well as relatively narrow polydispersities (between 1.05 to 1.40 for many monomers), which enables its potential applications in both academia and industry.\textsuperscript{47} RAFT polymerization involves the conventional radical polymerization of a monomer in the presence of a chain transfer agent (CTA, or referred to as RAFT agent), which usually contains a thio carbonylthio group with an activating substituent Z and good leaving group R, as illustrated in Figure 1.3.\textsuperscript{41} Generally, a RAFT polymerization
system also includes three other components: a radical source (initiator), monomer, and solvent (not strictly required if the monomer is a liquid).
Figure 1.3. Common structures of a chain transfer agent (CTA) agent. Reproduced with permission from reference 41.
The mechanism of RAFT polymerization is illustrated in Scheme 1.1 consisting of
the following five steps: initiation and propagation, pre-equilibrium, re-initiation, main
equilibrium, and termination. The reaction begins with the decomposition of radical
initiator to produce free radicals (I•), which react with monomers to start the
propagation to yield propagating radical chains of length n, Pm•, as illustrated in step
(I). In the step (II), the polymeric radicals (Pm•) react with RAFT agent (7) to form
radical intermediates (8). These radicals intermediates (8) may undergo two directions,
either to yield the initial polymeric radicals (Pm•) or to form the macro-initiators (9)
and the leaving group (R•). This reversible step is referred to as the pre-equilibrium. In
the step (III), the novel leaving group radicals (R•) can also react with the monomers to
form new polymeric radicals (Pn•), as illustrated in step (III). To distinguish the
original initiation and propagation step, the step (III) is referred to as the re-initiation
step. When the original RAFT agent (7) is totally consumed, the reaction moves into
the step (IV), which is referred to as the main equilibrium step. In this step, the active
polymeric radicals (Pn•) react with macro-initiators (9) to form the dormant species
(10), which can further undergo reaction either towards the (Pn•) or (Pm•). Ideally,
these reversible reactions between active and dormant chains are very fast, which
enables equal opportunities for all polymer chains growth, allowing polymers of low
polydispersity. Also, the unavoidable reactions of termination exist in RAFT
polymerizations system via two active polymer radical chains reacting with each other
to form dead polymers that can no longer react, as illustrated in step (V). From this
mechanism, there are several important requirement in an ideal RAFT polymerization
for the production of polymers having controlled molecular weight and narrow molecular weight distribution: (a) the pre-equilibrium and re-initiation steps are completed very early to ensure that the polymer radical chains to start grow at approximately the same time; (b) high efficiency of re-initiation step by the \( \text{R}^\bullet \) fragment, meaning that the majority of polymer radical chains are formed from the re-initiation step rather than produced from the initiation and propagation step; (c) rapid exchange between the forward and reverse reactions in the main equilibrium step to ensure the number of dormant chains and/or intermediate radical chains are larger than the propagating radicals chains (\( P_m^\bullet \) and \( P_n^\bullet \)).
Scheme 1.1. Proposed simple mechanism of RAFT polymerization. (I) Initiation and propagation step; (II) pre-equilibrium step; (III) re-initiation step; (IV) main-equilibrium step; (V) termination step. Reproduced with permission from reference 47.
1.2 Ordered Network Mesostructures

Ordered network mesostructures, as one kind of multiply continuous, percolating structures, are potentially useful in many applications. In the following part, the multiply continuous, percolating structure and ordered network structure from BCP are introduced.

1.2.1 Introduction of Multiply Continuous, Percolating Structures

In 1976, Scriven first suggested that the bicontinuous, percolating domain structure could arise in complex fluids. In that provisional work, he defined that “a bicontinuous structure is a bicontinuous partitioning in which each subvolume is filled with a distinct, not necessarily uniform composition or state of matter”.

For certain subvolume ratios, he calculated out that the bicontinuous structures have less interfacial area than dispersed spherical structures. In that publication, Scriven also noted that at some certain composition and symmetry, the dividing surfaces could be further reduced by rounding edges and wrapping faces to form a ultimate periodic minimal surface.

In this work, we follow Scriven’s notation and generalized the structures containing two or more continuous, percolating domains as “multiply continuous” structures, as Bates and coworkers put forward.

Since the first introduction of bicontinuous structures by Scriven, a number of multiply continuous structures were identified in polymeric materials, including bicontinuous microemulsions, cocontinuous blends, disordered bicontinuous structure, and bicontinuous ordered network morphologies formed by BCPs.
The multiply continuous, percolating domain structures could be very useful in many technological applications due to their remarkable physical properties. From a mechanical point, the multiply continuous structure allows each domain to contribute to the improvement of the materials in modulus, toughness, stress at failure and creep resistance. Furthermore, the multiply continuous, percolating structure could provide low interfacial area and three dimensional (3-D) connectivity, which can be used to facilitate gas separation, water purification, and ionic transport, etc.

1.2.2 Network Mesostructures Formed by Block Copolymers

It is well recognized that free energy minimization drives BCPs to adopt a variety of periodically ordered morphologies, including body-centered cubic (bcc) spheres (S), hexagonally packed cylinders (C), lamellae (L), and some network phases, such as double gyroid Q, alternating gyroid Q, and orthorhombic O. Among those phases, the ordered network phases have received intensive attention because they are also one kind of multiply, percolating structures that are characterized by two or more independent, interpenetrating microdomains, as shown in Figure 1. These attributes contribute to superior physical properties, such as bicontinuous and 3-D connectivity, percolating path and short diffusion path lengths, and enhanced mechanical stability (e.g., improved Yong’s Modulus), which could be applied to many technological applications such as catalysis, separations, photonic crystal, and solar cells, etc.
Figure 1.4. Space-filling models of the $Q^{230}$, $O^{70}$, and $Q^{214}$ network phases in ABC triblock copolymer, poly(isoprene-b-styrene-b-ethylene oxide) (ISO). Reproduced with permission from reference 26.
The first ordered network phase found in block copolymer morphology was ordered bicontinuous double diamond (OBDD). Such network structure was described as ordered bicontinuous structure initially which was obtained through self-assembly of PS-b-PI starblock copolymer, until Thomas et al. proved that this bicontinuous structure was characterized by $Pn3m$ symmetry that could be represented using (6,4) nets, and referred to it as ordered bicontinuous double diamond (OBDD).

In 1994, Hajduk et al. discovered another equilibrium network morphology in weakly segregated linear PS-b-PI diblock copolymer with $Ia\overline{3}d$ symmetry that could be presented using (10, 3) network lattices, and called it the “gyroid”. Actually, there is another phase that is also called the “gyroid”, but with $I4_{1}32$ symmetry space group. So what’s wrong here? Actually, the name gyroid was initially used by Schoen to describe a Schoen’s G surface with $I4_{1}32$ symmetry. Theoretically, a structure with $Ia\overline{3}d$ symmetry, however, contains two parallel Schoen’s G surfaces. So to distinguish these two structures, researchers have used the term “double gyroid” ($Q_{230}$) to describe a network morphology with $Ia\overline{3}d$ symmetry, and single (or alternating) gyroid ($Q_{214}$) to indicate a network phase with $I4_{1}32$ symmetry. The discovery of alternating gyroid ($Q_{214}$) phase in BCPs was first predicted by self-consistent mean field (SCMF) theory, and later identified in poly(isoprene-b-styrene-b-vinylpyridine) (ISV) triblock copolymer.

Another common network phase in BCPs is orthorhombic $Fddd$ network, which was first discovered by Bates and co-workers in the self-assembly of polyisoprene-b-polystyrene-b-poly(ethylene oxide) (PI-b-PS-b-PEO) triblock
copolymers. This network structure was subsequently referred to as O\textsuperscript{70}, with “O” meaning an orthorhombic unit cell and “70” indicating the number of the space group in the crystallographic tables. The orthorhombic Fddd phase was proved to be a network phase consisting of continuous domains connected with trivalent connectors, and different from other network phases because it is non-cubic structure rather cubic structure. The Fddd network from the self-assembly of BCPs was subsequently predicted by Tyler and Morse in 2005 via self-consistent field theory (SCFT) and later successfully proved in experiment.

In the AB diblock copolymer, the bicontinuous (or network) morphologies only appear over a narrow range of phase window. The phase window for bicontinuous (or network) morphologies is greatly increased for ABC triblock copolymer (triblock terpolymer), which enhances the probability for successful fabrication of materials with bicontinuous structures. One critical factor for obtaining the ABC network structures is to generate a non-frustrated polymer system, in which $\chi_{AC} \gg \chi_{AB} \approx \chi_{BC}$, to prevent non-centrosymmetric nanostructures that can lead to alternating morphologies. The phase diagram of the non-frustrated ABC triblock copolymer is abundant with different network phases, including double gyroid (Q\textsuperscript{230}), orthorhombic (O\textsuperscript{70}), and alternating gyroid (Q\textsuperscript{214}). Figure 1.5 shows the phase diagram the non-frustrated Poly(isoprene-b-styrene-b-ethylene oxide) (ISO) under a certain condition. In this ISO system, five different phases have been identified within the region of phase space bounded by $0.21 \leq f_I \leq 0.58$, $0.27 \leq f_S \leq 0.69$, and $0 \leq f_O \leq 0.35$, including
two-domain lamellae (LAM$_2$), three-domain lamellae (LAM$_3$), double gyroids (Q$^{230}$),
alternating gyroid (Q$^{214}$), and Fddd network (O$^{70}$).
Figure 1.5. Phase diagram of poly(isoprene-b-styrene-b-ethylene oxide) (ISO) in the vicinity of the order-disorder transition temperature. Filled and open circles indicate ordered and disordered states, respectively, within the experimental temperature range from 100 to 225 °C. Different phases are colored with different areas, and overlap areas are identified by the combination of different colors. The dashed line indicates the condition $f_i = f_0$. Reproduced with permission from reference 27.
1.3 Ordered Mesoporous Carbon Materials

Mesoporous carbon materials, as a huge family of carbon materials with pore sizes ranging from 2 to 50 nm, have received considerable attentions because of their potential applications in diverse fields, such as separations, catalysis, water purification, drug delivery, solar cells, but especially energy storage applications. The widespread applications of mesoporous carbons are attributed to their remarkable chemical and physical properties, including high specific surface areas, hydrophobicity of their surface, tunable pore size, excellent thermal and chemical stability, electrical conductivity, high corrosion resistance.

Mesoporous carbon materials were achieved by a variety of methods, such as carbonization of organic aerogels or cryogels, polymer/polymer blends with one thermally decomposed component, catalytic activation using certain metals, etc. However, none of these methods have demonstrated to fabricate mesoporous carbons with monodisperse pores of well-defined size and shape. The design of synthesizing ordered mesoporous carbons (OMCs) with well-defined pore size and structure, as well as controlled high pore volume, large surface area, are very important from a fundamental and application point of view. The synthesis of ordered mesoporous carbons (OMCs) can basically be classified into two approaches, namely hard-templating and soft-templating. Hard-templating method, also referred to as nanocasting strategy, begins with the synthesis of an inorganic mesoporous silica as master template, which then is infiltrated with the carbon
precursor, carbonized, and then the template is removed to yield a replica of the initial mesoporous materials. Alternatively, soft-tempating\textsuperscript{88, 91, 92, 93} provides a more direct approach to obtain the mesoporous carbon, which involves with the cooperative assembly of an amphiphilic surfactant or block copolymer (BCP) with the carbon precursor producing an ordered mesophase, following template removal and subsequent carbonization to yield ordered mesoporous carbon materials.

1.3.1 Hard-Templating

Since the first report on the synthesis of mesoporous M41S silica materials for the sol-gel polymerization of silica precursors using a surfactant assembly in 1992,\textsuperscript{94} many other mesoporous silica materials with diverse pore structures have been developed in presence of various organic structure-directing agents, including surfactants and block copolymers. These mesoporous silica materials with well-defined structures and uniform pores have successfully been utilized as hard template for synthesizing mesoporous carbon materials. Ryoo and coworkers first reported the fabrication of highly ordered mesoporous carbon materials using MCM-48 mesoporous (alumino) silica materials as the template, followed by the introduction of carbon precursors.\textsuperscript{86} In that work, the sucrose which contains the furfuryl alcohol and in-situ phenol resin, as the carbon precursor, was infused into the 3D interconnected pores of the MCM-48 silica template, and subsequently carbonization followed by silica template removal led to the generation of highly ordered mesoporous carbons. Afterwards, many other mesoporous silica templates,
such as the MSU-H, SBA series, and various carbon precursors like phenol-formaldehyde and resorcinol-formaldehyde resins, ethylene and furfuryl alcohol have been used for synthesizing ordered mesoporous carbons. Based on these works, the procedures for nanocasting strategy to prepare ordered mesoporous carbons can be illustrated by five main experimental steps: 1) the preparation of ordered mesophase composites by self-assembly of silica and surfactants; 2) the fabrication of ordered mesoporous silica through the removal of surfactant molecules; 3) the incorporation of proper carbon precursors into the mesoporous silica pores; 4) the carbonization of the carbon precursors; 5) silica templates removal by etching; as shown in figure 1.6.
Figure 1.6. Illustration of the nanocasting strategy for the synthesis of mesoporous carbons. The procedures involve in the preparation of ordered mesophase composites by self-assembly of silica and surfactants, the fabrication of ordered mesoporous silica through the removal of surfactant molecules, the carbon precursor filling into the mesoporous silica pores, the carbonization of the carbon precursors, and silica template removal by etching. Reproduced with permission from reference 102.
The advantages of nanocasting strategy are obvious. It not provides a method to obtain an accurate negative replica from the original template, but makes the synthesizing procedures facile to control since the structures of the template are stable and fixed. However, there are also some drawbacks of the method. As shown in the mechanism, the application of mesoporous silica as template frameworks involving in tedious multi-steps makes the process complicated, time-consuming and costly, which precludes the mass production in industry. Another typical shortcoming comes from the wider pore size distribution and limited pore sizes of mesoporous carbons after template removal due to the limited pore wall thickness compared with the original mesoporous silica. Even though, the nanocasting strategy still open a door for synthesizing ordered mesoporous carbons with a variety of mesostructures, including 1) a bicontinuous cubic structure of \( Ia\overline{3}d \) symmetry;\(^{86,105} 2) \) a cubic structure of \( I4_132 \) symmetry;\(^{86} \) 3) 2) a face-centered structure of \( Fm\overline{3}m \) symmetry;\(^{106} \) 4) a body-centered cubic structure of \( Im\overline{3}m \) symmetry;\(^{106} \) 5) a 2-D hexagonal structure of \( P6mm \) symmetry;\(^{96,107} \) and 6) a cubic structure of symmetry \( Pm\overline{3}n \) symmetry.\(^{107} \) It could be anticipated that ordered mesoporous carbons with novel mesostructures of symmetry would be synthesized through hard-templating method considering the intensive efforts searching on novel ordered mesoporous silica template.

1.3.2 Soft-Templating

The tedious, costly multi-step process of nanocasting strategy for production of ordered mesoporous carbons urges researchers to seek much more direct approaches
to mesoporous carbon materials. The soft-templating method was eventually discovered as a direct synthesis of ordered mesoporous carbons via organic-organic self-assembly process by choosing an appreciate amphiphilic surfactant or block copolymer (BCP) with a suitable carbon precursor.

Liang and coworkers first reported the synthesis of ordered mesoporous carbon films via soft-templating approach using polystyrene-block-poly(4-vinylpyridine) PS-b-P4VP as a template and resorcinol-formaldehyde (RF) as a carbon precursor through a combination of evaporation-induced self-assembly (EISA) and solvent annealing (SVA) process. In that work, the cooperative self-assembly of PS-b-P4VP template and resorcinol precursor was achieved via the hydrogen bonding to form well-ordered perpendicular hexagonal structure in SVA process. Afterwards, many other structure-directing organic surfactant and block copolymer templates, and various carbon precursors have been developed for synthesizing ordered mesoporous carbons via soft-templating approach. Among those works, the organic-organic self-assembly of commercial amphiphilic triblock copolymers poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethylene oxide), (PEO-PPO-PEO) as a soft template and phenolic resins as the carbon precursor are the most attractive because of its versatility for a family of highly ordered mesoporous carbon structures as reported by Meng et al. In terms of that work, the preparation process of ordered mesoporous carbons involves the following five steps as illustrated in Figure 1.7: (1) carbon precursor (e.g. resol precursor) syntheses; (2) cooperative self-assembly of carbon precursor and templates (block copolymers/surfactants) into various 3-D
ordered mesophase through EISA (or SVA) process; (3) thermopolymerization of resol into a stable and crosslinked network at an appropriate temperature range (typically 100 - 150°C); (4) removal of the soft templates at a suitable temperature (350 - 600 °C) under inert atmosphere to form mesoporous polymers; and (5) carbonization above 600 °C under inert atmosphere into the final mesoporous carbon materials. Compared with the hard-templating approach mentioned above, there are many advantages of soft-templating method for the direct synthesis of mesoporous carbon. From the mechanical point, the carbon architectures via soft templates are much more stable because of the 3-D continuous framework. Also, the carbon structures are more tunable and variable, because their formation can be simply adjusted by the temperature, solvent choice, template/precursor ratio, type of template and precursor, etc. Lastly, the entire process is facile, flexible and low-cost, which enables its mass production in industry. However, for successful syntheses of mesoporous carbons via soft-templating approach, the following four requirements are significant: (1) an appropriate cooperative self-assembly system, which means that the carbon precursor and soft template can co-assemble into ordered mesostructures; (2) the stability of template molecules during polymerization of the carbon precursor, but also selective decomposition of template during pyrolysis (i.e. calcination and carbonization) to form mesoporous structures; (3) the capability of carbon precursor of preserving the mesostructure during template removal and carbonization.
Figure 1.7. Schematic for the preparation of the ordered mesoporous polymers and carbon frameworks. Reproduced with permission from reference 108.
The cooperative self-assembly of Pluronics amphiphilic copolymers (PEO-b-PPO-b-PEO) as soft template has been intensively and systematically studied. Though Pluronics have enabled the synthesis of a series of ordered mesoporous carbons of different mesostructures with remarkable properties, such as high specific surface area, tunable pore sizes, large pore volume and thick pore walls, the synthesis of novel and high-performance mesoporous carbons with plentiful mesostructures and large pore sizes are necessary for some applications. The use of non-Pluronic block copolymers offers possibility to synthesize such novel and high-performance mesoporous carbons. Deng et al. reported the synthesis of highly ordered mesoporous carbon materials with ultra-large pores (22.9-37.4 nm) by using PEO-b-PS diblock copolymer as the soft template and resol as the carbon precursor. The organic-organic self-assembly of PEO-b-PS/resol during the solvent evaporation led to the formation of the ordered mesostructures. Apart from tuning the pore size, Deng et al. also prepared ordered mesoporous carbons with fcc structure and large thick pore walls by using poly(ethylene oxide)-b-poly(methyl methacrylate) (PEO-b-PMMA) as the soft template. Such thick pore walls were due to the weakly hydrophilic of PMMA block associated with ester groups, which could partially react with resol via hydrogen bonding, thus resulting in the formation of the thick carbon walls. Subsequently, Deng and coworkers also design the ABC type triblock copolymer PEO-b-PMMA-b-PS with gradient hydrophilicity as the soft template to tune both the wall thickness and pore sizes. Ordered mesoporous carbons with large pore sizes and thick pore walls were successfully synthesized through cooperative
self-assembly of this triblock copolymer and resol. However, only spherical mesostructure was obtained even adjusting the ratio of resol/template at a large range. Recently, Werner and coworkers reported the use of a classical non-frustrated A-B-C type triblock copolymer poly(isoprene-block-styrene-block-ethylene oxide) (ISO) as structure-directing soft template to synthesize order mesoporous carbons. In that work, they successfully synthesized the gyroidal mesoporous carbons with ultra large pore size using non-frustrated (ISO) as soft template and phenol-formaldehyde resol as carbon precursor. On the other hand, RAFT polymerization provides an appropriate replacement for anionic polymerization to non-frustrated triblock copolymer with narrow polydispersity, because RAFT polymerization is a more tolerant controlled free radical polymerization technique which does not require rigorous experimental conditions associated with anionic polymerization. Therefore, it is highly interesting to synthesize novel non-frustrated ABC triblock copolymer by RAFT polymerization to target those abundant network structures to obtain final ordered mesoporous carbons with network structures, i.e. with 3-D continuous, percolating channels.

1.4 Film Characterization

A combination of characterization techniques are utilized to comprehensively understand the properties of thin films, such as film thickness, optical constants, mesoporous structures, porosity, and pore size distribution. The spectroscopic ellipsometer is used to determine the optical properties \((n, k)\) and thickness of the films. From the sorption measurement, the porosity and pore size distribution of mesoporous
calcined films is characterized using ellipsometric porosimetry (EP) techniques. The surface morphology of films is characterized by atomic force microscopy (AFM). And grazing incidence small angle X-ray scattering (GISAXS) is employed to investigate the overall structure of films. Detailed introduction and principles of these characterization methods are illustrated as follows.

1.4.1 Ellipsometry and Ellipsometric Porosimetry (EP)

Ellipsometry, as an optical technique that measures the change in polarization state, is a common method to characterize the thickness and optical properties of thin film, namely refractive index \( (n) \) and extinction coefficient \( (k) \). It is based on the change of polarization state which is quantified by the amplitude ratio, psi \( (\psi) \), and the phase difference, delta \( (\Delta) \) measured from the reflected waves. A typical setup of a basic ellipsometry experiment can be sketched in figure 1.8. First, a light source emits a monochromatic light and passes through a polarizer to give a linearly polarized beam with two electric field components \( E_p \) and \( E_s \) in parallel and perpendicular direction, respectively. Then, this linearly polarized beam goes through an optional compensator until reaches on the surface of the sample. After reflection from the surface of the sample, \( E_p \) and \( E_s \) within the polarized beam experience different amplitude ratio and phase shift, and pass through another optional compensator before being measured by an analyzer (a second polarizer) and finally analyzed by a detector. Upon reflection, the change of amplitudes of components, \( E_p \) and \( E_s \), are represented by two Fresnel reflection coefficients, \( \gamma_s \) and \( \gamma_p \), respectively. These two reflection
coefficient together define a complex reflectance ratio, $\rho$, as given in the following equation:

$$\rho = \frac{r_p}{r_s} = \tan(\Psi)e^{i\Delta}$$

thus, as seen from this equation, the complex reflectance ratio, $\rho$, can also be parameterized by the amplitude component ($\psi$) and the phase difference ($\Delta$). Normally, since the ratio is a complex number which contains two values, amplitude information ($\psi$) and the “phase” information ($\Delta$), the ellipsometry measurement should be both accurate and very sensitive.
Figure 1.8. Schematic of a typical setup of an ellipsometry experiment.
In this research work, a variable angle spectroscopic ellipsometry (VASE) are used, because it combines the advantages of the variable angle of incidence and spectroscopic measurements providing large amounts of data from a given sample. For general scans, three incident angles (65°, 70° and 75°) over the wavelength from 246 nm to 1689 nm were chosen. The data were fitted recursively using a model that contained the silicon substrate, a SiO$_2$ interface layer, and a Cauchy layer that represented the optical properties of the films. A Cauchy relationship is described as below:

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}$$

where $n$ is the refractive index, $\lambda$ is the wavelength, and $A$, $B$, and $C$ are the fitting parameter that used fit the obtained data to determine the refractive index at known wavelength. The Cauchy model is found to be appropriate to characterize the optical constants of polymer/resol thin films and mesoporous calcined films.

In addition to thin film thickness and optical constant, the porosity, the porosity can also be calculated by ellipsometer using Bruggeman effective-medium approximation (BEMA) model given by

$$f_{\text{matrix}} \left( \frac{\bar{\varepsilon}_{\text{matrix}} - \bar{\varepsilon}}{\bar{\varepsilon}_{\text{matrix}}} + \frac{2f_{\text{void}}}{\bar{\varepsilon}_{\text{void}}} \right) + f_{\text{void}} \left( \frac{\bar{\varepsilon}_{\text{void}} - \bar{\varepsilon}}{\bar{\varepsilon}_{\text{void}}} + \frac{2f_{\text{matrix}}}{\bar{\varepsilon}_{\text{matrix}}} \right) = 0$$

where $f_{\text{matrix}} + f_{\text{void}} = 1$, dielectric permittivity $\bar{\varepsilon} = n^2$. Provided that the known refractive index of porous film, void, and pure matrix film, the volume fraction of void, $f_{\text{void}}$ (porosity), can be calculated.
Besides that, the porosity of porous films can also be characterized ellipsometric porosimetry (EP) technique. The EP technique measures the change of the optical characteristics of porous films during vapor adsorption and desorption atmospheric pressure. Giving the known optical properties of the liquid adsorbate, the measured optical constants can be directly converted into the volume fraction of vapor absorbed in the porous film. In this work, the toluene is used as the solvent for sorption in porous calcined films because its boiling point is above the room temperature, and it also displays favorable interactions with the mesopore walls but not (significantly) swell the matrix.\textsuperscript{112, 113}

The EP setup is illustrated by Figure 1.9. It consists of the previously described ellipsometer equipped with a cell containing the porous thin film to analyze, and a mass flow controller (MFC) connected to the cell controlling the flow rate of organic solvent vapor and dry air. The measurement is an in-situ procedure. The cell is initially purged with pure air for over one hour or longer to reach an equilibrium state, followed by tuning the MFC to control the relative flow rate of toluene vapor and air to increase relative partial pressure of vapor step by step until saturation. Upon reaching the saturation point of toluene vapor, the relative vapor pressure is then dropped step by step to undergo desorption in the porous film. The $\psi$ and $\Delta$ are measured during solvent vapor sorption which can be later converted into optical properties and film thickness by fitting an appropriate model. The film porosity the can be calculated from the refractive index of the porous calcined film measured from adsorption curves upon saturation by applying Lorentz-Lorentz effective medium.
approximation (LLEMA) model. The LLEMA model can be described by the following equation,

\[
\frac{V_{\text{tol}}}{V_{\text{film}}} = \frac{(n^2 - 1)}{(n^2 + 2) - \left(\frac{n^2 - 1}{n^2 + 2}\right)}
\]

where \(n\) and \(n_{\text{tol}}\) are the refractive index (at 632.8 nm) of empty porous calcined films and condensed toluene, respectively. Here, the absorbed toluene is supposed to maintain its bulk properties with \(n_{\text{tol}} = 1.496\). LLEMA model assumes the neat porous film is a combination of polymer and voids while the pores can be filled up by toluene when the relative pressure of toluene vapor reaches 1. The ratio of \(V_{\text{tol}}\) to \(V_{\text{film}}\) is the porosity calculated from the LLEMA model when the relative vapor pressure equals to 1.
Figure 1.9. Schematic of an experimental setup of ellipsometric porosimetry.\textsuperscript{114}

Reproduced with permission from reference 114.
In addition to porosity, the pore size distribution (PSD) can also be determined by EP technique via the change of refractive index during absorption isotherms as a function of relative vapor pressure. As described above, normally, the refractive index increases as the relative vapor pressure due to the condensation of toluene in the pores. There is a range of relative pressures at which the refractive index increase quickly with respect to relative pressures due to the occurrence of capillary condensation of toluene. This capillary condensation strongly depends on the pore size, and once the pores are completely filled with toluene, the refractive index remains unchanged with growing relative vapor pressure. According to LLEMA model, the change of refractive index with respect to relative vapor pressure can be transferred to the change of absorbed volume (porosity) as a function of relative vapor pressure, as Figure 1.10A and B shows.
Figure 1.10. From ellipsometry data to adsorption isotherm. (A) Refractive index as a function of relative toluene vapor pressure; (B) Relative adsorbed volume of toluene as a function of relative toluene pressure by fitting refractive index using LLEMA model. The schematics in (B) shows three stages of toluene absorption: (1-2) multilayer absorption, (3) capillary condensation, (4) complete filling of the pores. From the sorption isotherm to pore size distribution. (C) Absorbed volume fraction of toluene with respect to Kelvin radius and relative pressure of toluene; (D) Pore size distribution derived from the sorption isotherm. Reproduced with permission from reference 115. 115
To characterize the pore size distribution (PSD), the Kelvin equation described below is applied to the absorption isotherms to relate the mean radius of curvature of the meniscus $r_k$ (Kelvin radius) to the relative pressure, as illustrated in Figure 1.10C and the following Kelvin equation:

$$\frac{2}{r_k} = \frac{1}{r_1} + \frac{1}{r_2} = -\frac{RT}{\gamma V_L \cos \theta} \ln \left( \frac{p}{p_0} \right)$$

where $r_1$ and $r_2$ are the main radii of curvature of the meniscus, $R$ is the gas constant, $T$ is the Kelvin temperature. Assuming the absorbed toluene maintains its bulk properties, and $\gamma$ is the surface tension of toluene (0.0284 N m$^{-1}$), $V_L$ is the molar volume of the toluene ($1.064 \times 10^{-4}$ m$^3$ mol$^{-1}$), and $\theta$ is the contact angle of the toluene on the calcined resol (~0º). Then the derivative of the void volume with respect to $r_k$ gives an estimate of the pore size distribution, as illustrated in Figure 1.10D.

1.4.2 Atomic Force Microscopy (AFM)

Atomic Force Microscopy (AFM) is used to study the surface morphology of thin films. The basic principle of AFM is shown in Figure 1.11. First, a beam is emitted by a laser and reaches on the back of a cantilever. The cantilever contains a sharp tip, typically with radius on the order of nanometers, at the end of a cantilever (usually a silicon or silicon nitride crystal), which is oscillated just above the surface of a film sample. The interactions between the tip and the sample induce attractive or repulsive forces that lead to a deflection of the cantilever. The cantilever deflection is measured by the change of laser reflected from the top surface of the cantilever. The reflected
laser beam then is reflected by a mirror again until collected on a position sensitive photo-detector (PSD) to analyze the deflection. As the tip tracks the topography of the sample, the height between the tip and the sample might vary. To maintain a constant interactional force between the tip and the sample, the height position is adjusted by a feedback loop. The constant force between the tip and the sample can be controlled by the piezoelectric scanner.
Figure 1.11. Schematic of an atomic force microscope. The laser emits a beam and reflected by the back of the cantilever. The reflected beam from the cantilever reaches the mirror and reflected to hit on the photo-detector. The signal from the photo-detector goes into feedback loop to control the piezoelectric scanner to adjust the height between the tip and the sample.
1.4.3 Grazing Incidence Small Angle X-ray Scattering (GISAXS)

Grazing incidence small angle X-ray scattering (GISAXS) is a versatile analysis technique for the characterization of micro- and nano-structured thin films. It is a powerful tool that combines features from small-angle X-ray scattering (SAXS) and grazing incidence diffraction (GID), which can be used to characterize micro- and nano-scale density correlations and/or the shape analysis at surfaces or internal structures for various kinds of materials such as ceramics, metals, polymers, semiconductors and composites.\textsuperscript{116} Thus, GISAXS is an excellent complementary technique to those conventional nano-scale characterization methods like atomic force microscopy (AFM), scanning electron microscope (SEM), and transmission electron microscopy (TEM).

Figure 1.12 shows a schematic of the geometry of a GISAXS experiment. The sample surface defines the \((x, y)\)-plane with \(x\)-axis parallel to the beam direction and \(y\)-axis perpendicular to it. The direction normal to the surface plane is characterized by \(z\)-axis. As seen in Figure 1.12, a monochromatic x-ray beam of wavevector \(k_i\) ("\(i\)" is referred to as incidence) is first struck on the surface of the sample at a very small incident angle \(\alpha_i\) with respect to the surface. Then, the x-rays beam are scattered along \(k_f\) under an exit angle \(\alpha_f\) and out of plane angle \(2\theta_f\), and the appearing scattering wave vector, \(q\), is defined as below:

\[
q_{xyz} = \frac{2\pi}{\lambda} \left[ \begin{array}{c} \cos(\alpha_f) \cos(2\theta_f) - \cos(\alpha_i) \\ \cos(\alpha_f) \sin(2\theta_f) \\ \sin(\alpha_f) + \sin(\alpha_i) \end{array} \right]
\]
For specular scattering, the wave vector components in x, y, and z axis are \( q_x = q_y = 0 \) and \( q_z \neq 0 \), respectively, while for off-specular scattering, the lateral component is \( q_\parallel = (q_x, q_y) \neq 0 \), probing the in-plane structure. Generally, a two 2-D charge coupled device detector (CCD) is used to record the GISAXS pattern on the \( q_y - q_z \) plane. To avoid the damage or saturation of the detector, the directed and the reflected specular beam are often suppressed by a beamstop.

In this work, GISAXS is used to determine internal morphologies of thin films, as well as top surface morphologies combing with AFM characterization. For analysis, the location of the first-order peak along the \( q_y \) direction is used to calculate the domain spacing of the nanostructure via the equation: \( d = \frac{2\pi}{q_y} \). Higher order peaks at larger \( q \) would appear if the ordering of the films is well-fined and long ranged. These higher order peaks can further help to determine the structures of the films, such as spheres, hexagonal cylinders, lamella, double gyroid or other morphologies.
Figure 1.12. Schematic of the geometry of a GISAXS experiment. Reproduced with permission from reference 117.
CHAPTER II

NANOPOROUS NON-WOVEN FIBRIL-LIKE MORPHOLOGY BY
COOPERATIVE SELF-ASSEMBLY OF POLY(ETHYLENE
OXIDE)-BLOCK-POLY(ETHYL ACRYLATE)-BLOCK-POLYSTYRENE AND
PHENOLIC RESIN


2.1 Introduction

Mesoporous carbon materials, with pore sizes in the range of 2-50 nm, offer a unique combination of properties, such as large surface area, tunable pore size, high electrical conductivity, and excellent thermal and chemical stability, that make these materials promising for a wide range of potential applications; for
example, separations, catalysis, water purification, drug delivery, solar cells, but especially energy storage applications. Templated syntheses provide a common route to the generation of materials with well-defined pore sizes and connectivity. The synthesis of ordered mesoporous carbon materials can be divided into hard-templating and soft-templating. Hard-templating begins with the synthesis of a sacrificial inorganic template, typically silica, that is infiltrated with the carbon precursor, carbonized, and then the template is removed to yield a replica of the initial mesoporous materials. Conversely, soft-templating provides a more direct approach to the mesoporous carbon by organic-organic self-assembly of an amphiphilic surfactant or block copolymer (BCP) with the carbon precursor producing an ordered mesophase.

A common BCP for soft templating is commercial Pluronic (polyethylene oxide-block-polypropylene oxide-block-polyethylene oxide, [PEO-b-PPO-b-PEO]) surfactants. Mixing PEO-b-PPO-b-PEO with highly reactive carbon precursors based on resorcinol and formaldehyde or preformed phenolic resin oligomers can yield highly ordered mesoporous carbon powders and carbon films through cooperative self-assembly. Greater control over the mesoporous structure, such as larger pore sizes and thicker pore walls can be obtained using other amphiphilic BCPs as templates, such as polystyrene-block-poly(vinyl pyridine), polystyrene-block-poly(ethylene oxide), polystyrene-block-poly(methyl methacrylate)-block-poly(ethylene oxide) and poly(methyl methacrylate)-block-poly(ethylene oxide). However, the ordering of these materials, especially in thin films, can be impeded by factors that
impact the mobility, such as large molecular mass of the BCP; the limited mobility of the hydrophobic segments near the glass transition temperature ($T_g$);\textsuperscript{130} or the influence of ionic functionality.\textsuperscript{131}

In these previous examples, the well-ordered block copolymer structure produced primarily dispersed pores, such as spheres or hexagonally packed cylinders, that are by the nature of the template poorly interconnected or have very small windows between the pores.\textsuperscript{132} For applications in separations and energy storage where mass transport is important, interconnecting pores with large window sizes between the mesopores would be desired. Bicontinuous\textsuperscript{56, 133, 134} and network\textsuperscript{26, 49} morphologies associated with BCPs provide excellent ordered nanostructures to promote fast diffusion\textsuperscript{135} through continuous transport pathways. The compositional window for obtaining these morphologies is generally narrow for the neat copolymers, especially for AB diblock and ABA triblock BCPs.\textsuperscript{49} Despite this challenge, there have been numerous examples of successful fabrication of these morphologies with cooperative self-assembly for inorganic materials, such as silica,\textsuperscript{136} aluminosilicates\textsuperscript{137}, titania\textsuperscript{66}, nickel oxide\textsuperscript{138} and gold.\textsuperscript{139} In addition there is one example for fabrication of mesoporous carbon powder with a bicontinuous morphology.\textsuperscript{140} However, difficulties with the direct translation of synthetic conditions from powders to thin films have been reported due to the added constraints associated with preferential wetting at interfaces. This can impact the size of the composition window for pure phases including hexagonally packed cylinders,\textsuperscript{126} but this effect should be most severe for the bicontinuous phase, making the fabrication of monolithic carbon networks with AB and ABA BCPs more difficult.
The phase window for bicontinuous (or network) morphologies is significantly increased for ABC triblock copolymers, which enhances the probability for successful fabrication of these co-continuous nanostructured films.\textsuperscript{134} However, there are very few studies on ABC-type triblock copolymer templates in soft-templating mesoporous carbon materials;\textsuperscript{110} these advances are hindered by challenges associated with the synthesis of the ABC BCP and being able to predict the morphology \textit{a priori}, both for the neat block copolymer and especially the subsequent soft template mixture.

Prediction of the morphologies of neat ABC triblock copolymers is governed by six parameters: two independent volume fractions of the A and B blocks in the triblock, $f_A$ and $f_B$, and three Flory-Huggins parameters, $\chi_{AB}, \chi_{BC}, \chi_{AC}$, and the overall degree of polymerization $N$. One critical factor for obtaining network morphologies is generating a non-frustrated\textsuperscript{19} BCP, where $\chi_{AC} \gg \chi_{AB} \approx \chi_{BC}$, to prevent non-centrosymmetric nanostructures that can lead to alternating morphologies.\textsuperscript{141} One additional advantage with non-frustrated ABC-triblock copolymers is the wealth of different network phases available, including cubic $Q^{230}_2$ core-shell double gyroid, orthorhombic $O^{70}_1$, and cubic $Q^{214}_1$ (alternating gyroid) phases.\textsuperscript{49} Symmetric-asymmetric compositions ($f_A, f_B \neq f_C$) create competing interfacial forces that produce hyperbolic (saddle) surfaces to promote network morphologies.\textsuperscript{26} As proof-of-principle, Wiesner, Bates, and coworkers reported templated inorganic network phases using a non-frustrated symmetric-asymmetric ABC BCP and niobia or aluminosilicate sols\textsuperscript{142} and have more recently applied these BCPs to template
network phases in carbon monoliths, but these have not been applied to the synthesis of mesoporous membranes or films.

One alternative approach to similar highly interconnected morphologies is the fabrication of nonwoven fiber mats by fiber spinning, a top-down approach. These structures would provide facile transport pathways, but a challenge is obtaining sufficiently small pores between the fibers for separations while maintaining high porosity, which typically necessitates small nanofibers. Electrospinning of sol gel or polymeric ceramic precursor solutions enables fabrication of nanofibers that create a non-woven mat, but this is a relatively slow process and requires relatively thick coatings to obtain uniform mats without large area defects. For membranes, this thickness limitation for minimal defects prevents maximizing separation performance as flux decreases as the thickness increases, while defects are detrimental to the selectivity. Thus, the bottom up self-assembly approach to produce network phases should provide significant enhancements in terms of efficiency of membrane formation while also improving performance provides a route to overcome the limitations of the top-down approach.

In order to address the aforementioned shortcomings in AB and ABA soft-templating of mesoporous carbons and attempt to produce bicontinuous mesoporous carbons, we designed and synthesized a new amphiphilic non-frustrated ABC triblock copolymer, poly(ethylene oxide)-block-poly(ethyl acrylate)-block-polystyrene (PEO-b-PEA-b-PS), via controllable reversible addition-fragmentation chain transfer (RAFT) polymerization to use as a soft
templating agent. RAFT\textsuperscript{145} is a more tolerant controlled free radical polymerization technique that does not require the synthetic rigor associated with anionic polymerization, although the polydispersity of BCPs synthesized by RAFT tend to be slightly larger than their anionic counterparts.\textsuperscript{146} The monomers were selected to produce symmetric $\chi$ parameters ($\chi_{AB} = \chi_{BC}$) based on the reported solubility parameters of these polymers.\textsuperscript{147} A composition with a low PEO fraction and near equal hydrophobic segments ($f_{\text{PEA}} \approx f_{\text{PS}}$) was selected to target a network mesophase during the swelling and thermopolymerization of the hydrophilic resol, which is the carbonizable precursor. It will be shown that by simply changing the resol/block copolymer ratio to tune the volume fraction of the hydrophilic phase, different atypical mesostructures can be obtained after template removal. In these systems the high $T_g$ of the PS segment appears to kinetically trap the morphology during the simultaneous thermopolymerization and ordering to yield a network of homogeneous fibrous structures (~20 nm fibrous cylinders) with very low refractive index (\~1.3) and high porosity (\~60\%) for a relatively broad composition window (25 – 33 wt \% resol). This straightforward and simple thermal processing method to yield continuous mesoporous carbon films with nanofibril morphology may provide an attractive alternative to electrospun nanofiber mats\textsuperscript{148} due to their potential for large area film formation, limited thickness requirement to obtain continuous films and smaller fiber diameters.
2.2 Experimental Section

The experimental section is carried out by the following parts, including materials section, preparation and characterization of triblock copolymer and thin film.

2.2.1 Materials

Poly (ethylene glycol) methyl ether (PEO$_{45}$-OH, $M_n$=2000 Da, Sigma-Aldrich), phenol (> 99%, Sigma-Aldrich), formaldehyde (ACS reagent, 37 wt% in H$_2$O, methanol stabilized, Sigma-Aldrich), tetrahydrofuran (THF, >99%, Sigma-Aldrich), N,N'-dicyclohexylcarbodiimide (DCC, >99%, Alfa Aesar), 4-(dimethylamino) pyridine (DMAP, >99%, Alfa Aesar), toluene (>99%, Fisher Scientific), methylene chloride (CH$_2$Cl$_2$, >99%, Fisher Scientific), methyl ethyl ketone (MEK, >99%, Fisher Scientific), sodium hydroxide (NaOH, >99%, EMD Chemicals), hydrochloric acid (HCl, >37%, Fluke Analytical), hexane (>98.5%, Sigma-Aldrich), methanol (>98.5%, Sigma-Aldrich) and ethanol (>98.5%, Sigma-Aldrich) were used as received. S-1-Dodecyl-S’-(a,a’-dimethyl-a”-acetic acid) trithiocarbonate (RAFT-COOH) was prepared using a previously reported method.$^{149}$ Styrene (>99%, stabilized, Alfa Aesar) and ethyl acrylate (EA, >99.5%, stabilized, Acros) were purified by filtering through a column of basic alumina. 2,2-azobis(2-methylpropionitrile) (AIBN, Sigma-Aldrich) was recrystallized by dissolving in methanol at 45°C and recrystallized in a freezer. Resol, a low molecular weight thermally crosslinkable phenolic resin was synthesized
as a carbon precursor by using phenol and formaldehyde (37 wt% in H$_2$O) in a base-catalyzed (NaOH) process as described previously.$^{108}$

2.2.2 Preparation of PEO-b-PEA-b-PS Triblock Copolymer

The amphiphilic triblock copolymer template PEO-b-PEA-b-PS was synthesized by RAFT polymerization by sequential polymerization of ethyl acrylate (EA) and styrene (S) monomer using PEO$_{45}$-RAFT macro-chain transfer agent prepared from the esterification of PEO$_{45}$-OH with RAFT-COOH. Experimental details are described as below.

2.2.2.1 Esterification of PEO$_{45}$-OH with RAFT-COOH

PEO$_{45}$-RAFT agents were prepared by the DCC/DMAP catalyzed esterification of RAFT-COOH with PEO$_{45}$-OH. The procedures were as follows: PEO$_{45}$-OH (9.0 g, 4.5 mmol) was dried by azeotropic distillation with toluene using a Dean Stark trap and reflux condenser at 170 °C. The product was concentrated on a rotovap. To this flask was added RAFT-COOH (2.73 g, 7.5 mmol), DCC (2.06 g, 10 mmol) and DMAP (0.73 g, 2 mmol) and the contents were dried under vacuum. CH$_2$Cl$_2$ was dried by passing through a column of alumina and then added to the flask containing DCC and DMAP under nitrogen. After dissolution of the DCC and DMAP, this solution was added to the flask containing the PEO$_{45}$-OH and RAFT-COOH under nitrogen and stirred at room temperature for 48 h. The content was filtered through a Buchner funnel to remove the insoluble salts. The PEO-RAFT was precipitated by adding the filtrate to hexane. The
precipitated RAFTCOOH was recovered by filtration and dried under vacuum. $^1$H NMR (300MHz, CDCl$_3$=7.26 ppm). δ: 3.64 (2H, -O-CH$_2$-), 3.37 (3H, -O-CH$_3$), 3.26 (2H, -CH$_2$-SC(=S)-), 1.77 (2H, -CH$_2$-CH$_2$-SC(=S)-), 1.69 (6H, -C(CH$_3$)$_2$-), 1.25 (18H, m, -CH$_2$-(CH$_2$)$_9$-CH$_3$), 0.88 (3H, -CH$_2$-CH$_3$).

2.2.2.2 Synthesis of PEO$_{45}$-b-PEA-RAFT

A mixture of the PEO$_{45}$-RAFT macroinitiator (5.0 g, 2.1 mmol), ethyl acrylate (20.0 g, 200.0 mmol), and AIBN (5.0 mg, 30.3 mmol) were dissolved in toluene (20 mL) in a 100 mL round bottom flask and stirred for 20 min and sparged with nitrogen. The solution was then heated to 70 °C for 4 h with a thermostated stir plate. After polymerization, the flask was quenched to room temperature with tap water. Then the viscous solution was diluted in CH$_2$Cl$_2$ (20 mL) and added dropwise to hexane (1000 mL) to precipitate the diblock copolymer, PEO$_{45}$-b-PEA-RAFT. The product was further dried in a vacuum oven overnight at room temperature. Yield: 62.8 %. $M_n$: 9.5 kDa. $^1$H NMR (300MHz, CDCl$_3$=7.26 ppm) δ: 4.10 (2H, -COO-CH$_2$-CH$_3$), 3.64 (2H, -O-CH$_2$-), 3.38 (3H, -O-CH$_3$), 2.30 [1H, -CH$_2$-CH(COO)-CH$_2$-], 1.45-1.91 [2H, -CH$_2$-CH(COO)-], 1.25 (3H, -COO-CH$_2$-CH$_3$).

2.2.2.3 Synthesis of PEO$_{45}$-b-PEA-b-PS

The RAFT agent functionalized diblock copolymer, PEO$_{45}$-b-PEA-RAFT (5.0 g, 0.55 mmol), styrene (25.0 g, 240.0 mmol), and a stir bar were added to a 250 mL round-bottomed flask and sealed with a rubber stopper. The mixture was purged by dry
nitrogen at room temperature for 20 min, followed by heating to 120 °C for 55 min in a thermostated stir plate. Then the reactor was cooled down to room temperature by tap water. The crude product was added dropwise to hexane (1000 mL) to precipitate the polymer. The viscous precipitate was then dried in a vacuum oven overnight. To remove the unfunctionalized PEO45 homopolymer and PEO45-b-PEA-RAFT diblock copolymer, the dried crude product was further washed in cold ethanol (250 mL) in a 300 mL brown bottle twice by shaking the sealed bottle and then stirring the contents for 1 h to dissolve any homopolymer or diblock copolymer. The solution was then filtered to recover the product triblock copolymer and then dried in a vacuum oven overnight to obtain a faint yellow solid. Yield: 9.7 %. M\textsubscript{n}=24 kDa, D=1.2. \textsuperscript{1}H NMR (300MHz, CDCl\textsubscript{3}=7.26 ppm) \(\delta\) : 6.46-7.06 (5H, aromatic), 4.10 (2H, -COO-CH\textsubscript{2}-CH\textsubscript{3}), 3.64 (2H, -O-CH\textsubscript{2}-), 3.38 (3H, O-CH\textsubscript{3}), 2.30 [1H, -CH\textsubscript{2}-CH(COO)-CH\textsubscript{2}-], 1.45-1.91 [5H, -CH\textsubscript{2}-CH(COO)-, -CH\textsubscript{2}-CH(C\textsubscript{6}H\textsubscript{5})-, -CH\textsubscript{2}-CH(C\textsubscript{6}H\textsubscript{5})-CH\textsubscript{2}-], 1.25(3H, -COO-CH\textsubscript{2}-CH\textsubscript{3}), 0.88 (3H, -CH\textsubscript{2}-CH\textsubscript{3}).

2.2.3 Characterization of Polymer Properties

\textsuperscript{1}H nuclear magnetic resonance (\textsuperscript{1}H NMR) (Varian Mercury-300 MHz spectrometer) was used to characterize the PEO45-RAFT, PEO45-b-PEA-RAFT and PEO45-b-PEA-b-PS, using deuterated chloroform (CDCl\textsubscript{3}) as the solvent at 10–15 mg/mL for each analyte. From the \textsuperscript{1}H NMR spectra, the obtained PEO45-b-PEA-b-PS triblock copolymer has number-average molecular weight of 24 kDa, and the approximate volume fraction of PEA and PS block based on published homopolymer
densities reported at 25 °C (\(\rho_{\text{PEO}}=1.095\) g/cm\(^3\), \(\rho_{\text{PSS}} =1.040\) g/cm\(^3\), \(\rho_{\text{PEA}}=1.120\) g/cm\(^3\)).\(^{150}\) The triblock copolymer is named as \(\text{PEO}_{45}-\text{b-PEA}_{117}-\text{b-PS}_{99}\), where the subscript numbers stand for the degree of polymerization for each segment. The molecular weight distribution of polymers was characterized by size exclusion chromatography (SEC) on a waters Breeze system equipped with three Styragel columns at 35°C using THF as eluting solvent. From the SEC traces, the polydispersity of the purified \(\text{PEO}_{45}-\text{b-PEA}_{117}-\text{b-PS}_{99}\) is 1.2 with \(M_n = 26\) kDa against polystyrene standards. Differential scanning calorimetry (DSC, TA Instruments Q200) was performed in hermetic pans to measure the glass transition temperature (Tg) of the triblock copolymer segments. The scan temperature ranged from −50 to 200 °C with a constant heating and cooling rate of 5 °C/min. In the first heating scan, the sample was heated to 200 °C to remove the prior thermal history. The second heating scan was used to determine Tg, which was taken as the midpoint of the inflection tangent. Thermal Gravimetric Analysis (TA-2950) was used to investigate the decomposition temperature of \(\text{PEO}_{45}-\text{b-PEA}_{117}-\text{b-PS}_{99}\) (template) in nitrogen atmosphere. The range of temperature examined was 25-500 °C, and the heating rate was 10°C/min.

2.2.4 Films Preparation and Processing

Mesoporous films were prepared by organic-organic self-assembly of \(\text{PEO}_{45}-\text{b-PEA}_{117}-\text{b-PS}_{99}\) (template) and resol (precursor) at a range of resol wt% from 25 % to 60 %. Silicon wafers with a 300 nm thick native oxide layer (University Wafer) were used as substrates and were cleaned with UV ozone (Jelight Company Inc., Model
No. 42) for 2 h before use. The mixtures of $\text{PEO}_{45}$-b-$\text{PEA}_{117}$-b-$\text{PS}_{99}$ triblock copolymer and resol with different resol wt% were spin coated onto clean silicon wafers from a 10 wt% MEK solution at 3000 rpm for 1 min. Post film fabrication processing involved the following steps. First, the films were heated at 120 °C for 24 h to crosslink the resol and improve the ordering of the mesostructures. Next, the thermo-polymerized thin films were further heated at 400°C for 3 h under N$_2$ atmosphere at a heating rate of 1 °C/min to remove the template (calcination). Finally, the mesoporous carbon films were obtained by heating the calcined films to 800 °C for 3 h at the heating rate of 1 °C/min below 400 °C and 4 °C/min above 400 °C. The obtained films were named as F-P-T, where F refers to fabrication as a film, P refers to weight % of resol in the casting mixture for the film and T is the highest processing temperature observed by the film.

2.2.5 Characterization of Thin Films

The optical properties ($n$, $k$) and thickness of the films were obtained by using a variable angle spectroscopic ellipsometer (VASE, J.A Woollam Co., M-2000). For general scans, multiple incident angles (65°, 70°, and 75°) over the wavelength from 246 nm to 1689 nm were used. The data were fitted recursively using a model that contained the silicon substrate, a SiO$_2$ interface layer, and a Cauchy layer that represented the optical properties of the films. The pore size distribution (PSD) of calcined films was characterized by ellipsometric porosimetry (EP) using toluene as the probe solvent. The adsorption-desorption isotherm of the porous films was determined from the changes in the films’ refractive index under variations of the partial pressure
of probe solvent, toluene. The partial pressure of the toluene was controlled by a pair of mass flow controllers in dry air as described previously.\textsuperscript{113}

Atomic force microscopy (AFM, Dimension ICON, Veeco) was used to characterize the surface morphology of films; 2 μm × 2 μm micrographs were obtained using tapping mode at 0.5 Hz using PPP-NCC-50 tips (Nanosensors). The ordered morphology of the films was investigated using grazing incidence small angle X-ray scattering (GISAXS) at the X9 beamline of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL). The incident X-ray beam was 13.5 keV (wavelength (λ) = 0.0918 nm) at a sample-to-detector distance of 4.73 m. GISAXS profiles for all films were obtained both below and above the critical angle under vacuum.

2.3 Results and Discussion

The results and discussion part include the following parts: properties of synthesized templates, and fabrication of mesoporous films using thermal annealing.

2.3.1 Properties of Synthesized PEO\textsubscript{45}-b-PEA\textsubscript{117}-b-PS\textsubscript{99} Templates

The triblock copolymer template PEO\textsubscript{45}-b-PEA\textsubscript{117}-b-PS\textsubscript{99} with the similar volume fractions of PEA and PS block was synthesized by RAFT polymerization. Within Hildebrand approximation, in which χ\textsubscript{AB} ~ (δ\textsubscript{A}-δ\textsubscript{B})\textsuperscript{2}, where δ\textsubscript{x} is the solubility parameter for homopolymer x, the system must satisfy the condition δ\textsubscript{B}=(δ\textsubscript{A}+δ\textsubscript{C})/2 for the non-frustrated ABC triblock copolymer.\textsuperscript{147} For PEO-b-PEA-b-PS triblock
copolymer, the system meets the condition $\delta_B = (\delta_A + \delta_C)/2$ ($\delta_{\text{PEO}} = 19.9 \text{ MPa}^{1/2}$, $\delta_{\text{PEA}} = 19.0 \text{ MPa}^{1/2}$, $\delta_{\text{PS}} = 18.1 \text{ MPa}^{1/2}$)\textsuperscript{151,152} so PEO-b-PEA-b-PS triblock copolymer is supposed to be non-frustrated. The synthesis procedure starts with the esterification of PEO$_{45}$-OH with RAFT-COOH to yield PEO$_{45}$-RAFT macro-chain transfer agent, 1, followed by sequential polymerization of ethyl acrylate and styrene monomer to obtain diblock copolymer PEO$_{45}$-b-PEA-RAFT, 2, and triblock copolymer PEO$_{45}$-b-PEA-b-PS, 3, respectively (Scheme 2.1).
Scheme 2.1. Schematic of synthesis of PEO₄₅-b-PEA-b-PS triblock copolymer by sequential RAFT polymerization.
The chemical structures of the PEO_{45}-RAFT, PEO_{45}-b-PEA-RAFT, PEO_{45}-b-PEA-b-PS are confirmed by {sup}1{H} NMR spectroscopy. The PEO_{45}-RAFT agents, 1, are prepared by the DCC/DMAP catalyzed esterification of carboxylic acid functional RAFT agent (RAFT-COOH) with the hydroxyl terminated PEO (PEO_{45}-OH). Figure 2.1 is the {sup}1{H} NMR spectra of PEO_{45}-RAFT. Each corresponding peak of the functional groups of PEO_{45}-RAFT is indicated as in the {sup}1{H} NMR spectra, which indicated incorporation of RAFT group to the PEO_{45}-OH termini. The calculated integrals ratio value of signals at 0.88 ppm (a) and 3.64 ppm (b), standing for -CH_{2}-CH_{3} and -O-CH_{2}- in the chemical structure of PEO_{45}-RAFT, respectively, which is 225.06/ 3.02, exceeds the normal value, which should be 178/3. This excess value indicates that residual PEO is present in the PEO_{45}-RAFT.
Figure 2.1. $^1$H NMR spectra of PEO$_{45}$-RAFT
The formation of PEO$_{45}$-RAFT could be further confirmed by successfully synthesis of PEO$_{45}$-b-PEA-RAFT. Polymerization of ethyl acrylate with PEO$_{45}$-RAFT, 1, and AIBN in toluene at 70 °C for 4 h yields the diblock copolymer, PEO$_{45}$-b-PEA-RAFT, 2. Figure 2.2 is the $^1$H NMR spectra of PEO$_{45}$-b-PEA-RAFT. The successful incorporation of EA to the PEO$_{45}$-RAFT chains is demonstrated by the characteristic peaks of -CH$_2$-CH(COO)-CH$_2$- and -CH$_2$-CH(COO)- in EA units found at 2.30 ppm ($f'$) and 1.45-1.91 ppm ($e'$), respectively. Other corresponding peaks of functional groups of PEO$_{45}$-b-PEA-RAFT are also indicated in the $^1$H NMR spectrum. The functional group -CH$_2$-CH(COO)- yields three peaks resulting from the fact that the two hydrogen atoms in methylene region have different environments and the racemic configuration produces another cross peak between these two ones.$^{153,154}$ The calculated integrals ratio value of signals at 4.10 ppm ($d'$) and 3.64 ppm ($a'$), standing for -CH$_2$-CH$_3$ of PEA block and -O-CH$_2$- of PEO block in the chemical structure of PEO$_{45}$-b-PEA-RAFT, respectively, is 3.20/4.00, thus the mole ratio of PEA block and PEO block is 1.6 to 1 and the number-average molecular weight is 9.5 kDa. However, since the PEO-RAFT is not pure and the PEO homopolymer could also be precipitated into hexane, excessive PEO homopolymer is still contained in the precipitated PEO$_{45}$-b-PEA-RAFT.
Figure 2.2. $^1$H NMR spectra of PEO$_{45}$-b-PEA-RAFT.
The PEO\textsubscript{45}-b-PEA-RAFT crude product is used to control the polymerization of styrene at 120 °C for 55 min to yield the triblock copolymer PEO\textsubscript{45}-b-PEA-b-PS, \textit{3}. Since the PEO\textsubscript{45}-b-PEA-b-PS crude product could contain both diblock copolymer and homopolymer, the PEO\textsubscript{45}-b-PEA-b-PS crude product should be purified. Figure 2.3 is the \textsuperscript{1}H NMR spectrum of the purified PEO\textsubscript{45}-b-PEA-b-PS. The successful synthesis of triblock copolymer \textit{3} is proved by the new signals at 6.46-7.06 ppm (b'', e'', d''), which are ascribed to aromatic hydrogen atoms in the styrene units. Other corresponding peaks of functional groups of PEO\textsubscript{45}-b-PEA-b-PS can also be found in the \textsuperscript{1}H NMR spectrum. After purification, the calculated integrals ratio value of signals at 0.88 ppm(a''') and 3.64 ppm (h'''), standing for -CH\textsubscript{2}-CH\textsubscript{3} of RAFT agent and -O-CH\textsubscript{2}- of PEO block in the chemical structure of PEO\textsubscript{45}-b-PEA-b-PS, respectively, 173.5/3 corresponds well very with theoretical value 178/3, meaning that PEO homopolymer is removed from triblock copolymer crude product. The purification of triblock copolymer can be further confirmed by SEC.
Figure 2.3. $^1$H NMR spectra of PEO$_{45}$-b-PEA-b-PS.
The polymerized growth process is confirmed by SEC. Figure 2.4 shows the SEC traces of the products from each step of the synthesis. The elution peaks shifting to the left (higher molecular weight) moving from PEO\textsubscript{45}-RAFT to PEO\textsubscript{45}-b-PEA-RAFT to PEO\textsubscript{45}-b-PEA-b-PS, indicates the step-by-step increase in the number-average molecular weight. Therefore, the successful synthesis of PEO\textsubscript{45}-RAFT, PEO\textsubscript{45}-b-PEA-RAFT and PEO\textsubscript{45}-b-PEA-b-PS is further confirmed. Also, the assertion that the PEO\textsubscript{45}-RAFT contained PEO homopolymer from NMR analysis is further proved by the SEC curve of PEO\textsubscript{45}-b-PEA-RAFT (ii) showing a small peak at PEO position (18.8 min, arrow). The polymerization of the diblock copolymer led to the triblock copolymer. The unpurified triblock copolymer shows a broad peak (from 14.5 min to 18.5 min) with low molecular weight tailing at the PEO\textsubscript{45}-b-PEA-RAFT position from SEC curve (iii) indicating the existence of PEO\textsubscript{45}-b-PEA-RAFT in triblock copolymer. Therefore the triblock copolymer should be purified before further use. Here, cold ethanol is chosen to wash the triblock crude product to purified PEO\textsubscript{45}-b-PEA-b-PS, because both the PEO homopolymer and PEO\textsubscript{45}-b-PEA-RAFT diblock copolymer can dissolve in cold ethanol while the solubility of PEO\textsubscript{45}-b-PEA-b-PS in cold ethanol is very low. The maximum peak position of purified PEO\textsubscript{45}-PEA-b-PS curve (iii) does not shift compared to unpurified PEO\textsubscript{45}-PEA-b-PS curve (iii). Also, the polydispersity of triblock copolymer products changes from 1.30 to 1.20 and the purified PEO\textsubscript{45}-PEA-b-PS shows a narrow peak when compared with PS standards after purification. All of these indicated that washing triblock copolymer crude product in cold ethanol can purify the PEO\textsubscript{45}-PEA-b-PS.
The removal of homopolymer and diblock copolymer in unpurified triblock copolymer product is also proved by $^1$H NMR spectroscopy and SEC traces. The $^1$H NMR spectra of the diblock and triblock copolymers as shown in Figure 2.2 and Figure 2.3, enable the molar composition to be determined from the relative intensity at 3.64 ppm (-O-CH$_2$-) of the PEO block, 4.11 ppm (-COO-CH$_2$-CH$_3$) of the PEA block, and 6.46-7.06 ppm (aromatic) of the PS block (Table 2.1). The fact that molar ratio of PEA block to PEO block increases from 1.6/1 to 2.6/1 indicates that the PEO homopolymer is removed from triblock copolymer. The removal of diblock copolymer in triblock is confirmed by the disappearance of shoulder peak and tailing in triblock copolymer SEC curve. The number-average molecular weight of the triblock is calculated as 24 kDa.
Figure 2.4. SEC traces of (i) PEO$_{45}$-RAFT, (ii) PEO$_{45}$-b-PEA-RAFT, (iii) unpurified PEO$_{45}$-b-PEA-b-PS, (iii) purified PEO$_{45}$-b-PEA$_{117}$-b-PS$_{99}$. The vertical lines are guides to the eye to indicate the peak maximum in subsequent SECs. After purification, the mole ratio of PEO : PEA : PS is 1 : 2.6 : 2.2 from $^1$H NMR spectra (Figure 2.3).
Table 2.1 illustrates the key characteristics of the resulting triblock copolymer, PEO$_{45}$-b-PEA$_{117}$-b-PS$_{99}$ (the subscript indicates the degree of polymerization for each block). One key factor of fabricating mesoporous carbons using soft templating is generation of an open porosity during carbonization by almost complete decomposition of the soft template.$^{108}$ Figure 2.5 illustrates the TGA curves associated with the triblock copolymer and resol. The PEO$_{45}$-b-PEA$_{117}$-b-PS$_{99}$ triblock copolymer starts to slowly decompose at 150 °C, following by a fast decomposition at about 350 °C. Nearly 70% weight of the PEO$_{45}$-b-PEA$_{117}$-b-PS$_{99}$ template is lost upon heating to 400 °C and the template can be completely decomposed above 500 °C. On the other hand, the precursor starts to slowly lost weight when heated even at low temperature, like above 50 °C. When the temperature increases to 70~80 °C, the resol starts to crosslink, leading to a steep weight loss showed in the TGA curve. After fully crosslinking, the resol remains constant showing a plateau in the TGA curve, before further decomposition above 400 °C. Upon heating the resol above 800 °C, the weight loss is almost invariant due to the full carbonization of the resol. From the TGA curves, thus, processing at 400 °C and 800 °C to obtain calcined and carbonized films should thus yield porous films.

Table 2.1. Characteristics of the purified triblock copolymer.

<table>
<thead>
<tr>
<th>$M_n$ (kDa)$^a$</th>
<th>dispersity</th>
<th>$T_g$, PEA (°C)</th>
<th>$T_g$, PS (°C)</th>
<th>$f_{fEO}$</th>
<th>$f_{fPEA}$</th>
<th>$f_{fPS}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>1.2</td>
<td>-24</td>
<td>74</td>
<td>0.08</td>
<td>0.27</td>
<td>0.45</td>
</tr>
</tbody>
</table>

$^a$ Determined on the basis of polystyrene standards.

$^b$ Densities utilized to calculate volume fractions: $\rho_{PEO} = 1.095$ g/cm$^3$, $\rho_{PEA} = 1.12$ g/cm$^3$, and $\rho_{PS} = 1.04$ g/cm$^3$ (at 25 °C)
Figure 2.5. TGA traces of PEO\textsubscript{45}-b-PEA\textsubscript{117}-b-PS\textsubscript{99} and resol in the range of 25-900 °C under N\textsubscript{2} atmosphere.
2.3.2 Fabrication of Mesoporous Films using Thermal Annealing

In order to fabricate mesoporous films, the triblock copolymer and resol are cast as mixtures from solution and methyl ethyl ketone (MEK) is chosen based on Hansen Solubility parameters. Here based on assessment of Hansen Solubility parameters, methyl ethyl ketone (MEK, $\delta_d=16.0$ MPa$^{1/2}$, $\delta_p=9.0$ MPa$^{1/2}$, $\delta_h=5.1$ MPa$^{1/2}$) is chosen because it can dissolve all block segments of PEO$_{45}$-b-PEA$_{117}$-b-PS$_{99}$ and resol.

The thickness of PEO$_{45}$-b-PEA$_{117}$-b-PS$_{99}$/resol films for each processing step is determined by ellipsometry to illustrate how the resol content impacts the film formation and structures, as shown in Figure 2.6 panel A. For the spun-cast films, there is a decrease in thickness with increasing resol content. The thickness of the as-spun F-25-25 is about 550 nm, while the thickness of F-100-25 reduces to 290 nm as resol content increases. This 47% thickness difference between F-25-25 and F-100-25 can be ascribed to the different rheological properties of pure PEO$_{45}$-b-PEA$_{117}$-b-PS$_{99}$ and pure resol in MEK solvent during the spin coating, or to the different ordering of films with changing resol content. After thermal annealing at 120 °C for 24 h, the film thickness decreases due to weight loss of resol caused by crosslinking effect. For example, the film thickness with pure resol changes from 290 nm to 140 nm after thermopolymerization, nearly 52 % contraction (Figure 2.6). For the thermo-polymerized films, the films’ thickness also decreases with increasing resol content like spun-cast films. As there is almost no weight loss of template when films are heated at 120 °C (see Figure 2.5), the weight loss associated with the condensation
of resol in template/precursor systems should increase as the resol content increase. This explains why the thickness contraction goes up with rising resol content (Figure 2.6, panel B). Removal of the template and further crosslinking of the resol through calcination at 400 °C for 3 h under N₂ lead to significant film thickness contraction. For example, the film thickness of 33 wt% resol content decreased from 558.5 nm to 153.4 nm (72.5 % contraction as shown in Figure 2.6 panel B) from as-cast film to calcined film. For calcined films, the film thickness contraction reached a minimum value (about 70%) at approximate 35 wt% resol content. Previously it has been shown that highly ordered mesostructures help to mitigate the contraction of the film during template removal. This effect is also dependent on the morphology and wall thickness. Thus, the minimum in the film thickness contraction suggests the presence of an ordered mesoporous structure in these films with morphology that is composition dependent.
Figure 2.6.  A) The thickness of the films (■) as-spun; (●) after thermopolymerization, at 120 °C; and (▲) after template removal at 400 °C as a function of resol content. B) The thickness contraction of films after thermopolymerization (●), at 120 °C and after template removal (▲) at 400 °C using the as-spun film thickness as reference.
Figure 2.7 shows the AFM phase images of PEO_{45}-b-PEA_{117}-b-PS_{99}/resol films through different processing stages as a function of resol content. For the as-spun films prior to thermal annealing (Figure 2.7, panels A-C), some rods are observed on the surface of films that lack the typical long-range order associated with block copolymer templated mesoporous films. We attribute the limited ordering to the fast evaporation of solvent during spin-coating that leads to vitrification of a non-equilibrium structure. In these AFM phase images, the stiffer PS domains associated with the BCP template appears brighter than the softer resol domain. At low resol content (Figure 2.7, panel A), the continuous phase is the brighter area in the AFM phase image corresponding to the template. However as the resol content increases, the continuous phase switches from the bright domain to the dark domain in the AFM images (Figure 2.7, panel A-C). Moreover, the length of the cylinders becomes shorter as resol content increases. These characteristics substantiate the idea that resol interacting with the PEO segments adjusts the apparent hydrophilic volume fraction. With the change in the majority domain, there should be a transition through an equilibrium network phase when the system is ordered. Nonetheless in this case, this ordering of the as-cast film appears significantly improved in comparison to prior reports for the cooperative assembly of resol with other block copolymers.\textsuperscript{156, 157}
Figure 2.7. AFM phase images of PEO_{45}-b-PEA_{117}-b-PS_{99}/resol films under different temperature with growing resol content, (A) F-33-25; (B) F-50-25; (C) F-60-25; (D) F-33-120; (E) F-50-120; (F) F-60-120; (G) F-33-400; (H) F-50-400; (I) F-60-400. The size of insets in (D) and (G) is 200 nm × 200 nm.
Heating the as-cast films at 120 °C for 24 h leads to a considerable improvement in the ordering as shown in Figure 2.7, panels D-E. After thermal polymerization, the mechanical contrast between the phases decrease, thus it becomes difficult to distinguish the morphology from the AFM phase images. For this reason, the morphology of the F-33-120 film is hard to define (Figure 2.7D) after thermal annealing. However increasing the resol content seems to improve the image contrast, the surface ordering is markedly improved and consists of ordered cylinders without preferential orientation, commonly referred as the fingerprint morphology (see Figure 2.7E). The d-spacing of this fingerprint morphology is $36 \pm 1$ nm. When the resol content is increased to 60 wt%, the surface morphology comprises coexistence of ordered cylinders and featureless plateaus. Interestingly, from the AFM height image, these plateaus are higher domains than the cylinder domains in all cases. Figure 2.8 illustrates the AFM height images of film with 60 wt% resol content after thermopolymerization and calcination. For AFM height images, the bright domains correspond to the higher areas, while the darker areas mean the lower regions. For F-60-120 film (Figure 2.8A), the bright regions correspond to platform structure from AFM phase image, meaning higher domains, while the rods-like structure showed in AFM phase are lower domains here.
Figure 2.8. AFM height image of films (A) F-60-120, (B) F-60-400. For F-60-120 film, the AFM height image (A) shows the bright regions correspond to the platform structure from the AFM phase image, while for F-60-400 film, the AFM height image (B) shows that the platform domains turn out to be lower domains.
The structures formed upon heating are related to the competition between ordering kinetics and crosslinking rate upon thermal annealing. In this case, the glass temperature ($T_g$) of PEO$_{45}$-b-PEA$_{117}$-b-PS$_{99}$ template is higher than the typical Pluronic template due to the PS block in PEO$_{45}$-b-PEA$_{117}$-b-PS$_{99}$, and the number-average molecular weight (24 kDa) is larger than typical Pluronic templates (5.8 kDa). Both these two factors will decrease the chain mobility of the PEO$_{45}$-b-PEA$_{117}$-b-PS$_{99}$ template during the thermal polymerization, which could kinetically trap a non-equilibrium mesostructure.$^{130}$ This could explain the poorly ordered structure in Figure 2.7D that are in contrast to the well-ordered gyroid and network structures formed in monoliths using polyisoprene-block-polystyrene-block-poly(ethylene oxide) as the directing agent.$^{111}$

Removing the template appears to lead to degradation in the ordered surface structures (see Figures 2.7, panel G-I). The structures are highly distorted and a broad distribution of sizes is present. For example for F-50-400 (Figure 2.7, panel H), the remnants of the fingerprint morphology exist, but the surface morphology more resembles a rope laying on a surface with a broad distribution of pores between the cylinders and some apparent clumping of the structure. While for F-60-400 (Figure 2.7I), these cylinders tend to span between flat featureless regions. It is interesting that the orientation of the cylinders appears to shift 90° despite the extended (24 h) crosslinking of the resol prior to calcination. After thermopolymerization, the cylinders are in a fingerprint pattern such that the long axis of the cylinder in general is aligned parallel to the edges of the featureless domains (Figure 2.7F), but these
cylinder-like structures after calcination appear to transverse across these domains. To further examine the morphology, the AFM height image for F-60-400 (Figure 2.8) illustrates a reversal in the heights of the two domains with the plateaus lower than the cylinders. For F-60-400 (Figure 2.8B), the platform domains turn out to be lower domains and the rods be higher domains. These characteristics suggest that these flat plateaus are lamellae sheets aligned parallel with the substrate; these sheets collapse on template removal, which would account for the reversal of the domain heights. In these films, a majority of the pores between the cylindrical nanostructure are larger than 50 nm. Interestingly for F-33-400, a fairly homogeneous fibrous structure is observed in the AFM phase image (Figure 2.7G and 2.9A). This fibril-like structure can be more easily observed in the AFM height images, which show numerous nanopores of different size. The height image of fibrous structure at resol content 33 wt% reveals long fibers of different height that appear to be entangled (Figure 2.9B). A line scan of the AFM height profile (Figure 2.9C) shows the surface fluctuations associated with this fibrous nanostructure. There is a height variation of \(\sim 25 \text{ nm}\), which is similar to the diameter of the fibers. Additionally, the fibers appear to be highly branched unlike the cylindrical structures formed at higher resol loadings. This branching is locally similar to the structure in network morphologies. However, a similar fibril-like structure has also been reported using coil-helical polyethylene-block-poly(g-benzyl-L-glutamate), but these form a flat ribbon morphology due to the \(\alpha\)-helix conformation. Such mechanism is not possible for the PEO\(_{45}\)-b-PEA\(_{117}\)-b-PS\(_{99}\) template, but unusual
structure from kinetically trapped morphologies of block copolymers$^{159}$ has been reported for a variety of systems previously.
Figure 2.9. Surface morphology of F-33-400 calcined film with a network of homogeneous fibrous structure, (A) phase image and (B) height image as shown by AFM, and the associated height profile (C) corresponding to height image in (B).
To better understand these unusual nanostructures, Figure 2.10 illustrates the GISAXS profiles of thermal annealed films at incident angle of 0.1° for the three different resol contents previously described. All these films show diffraction indicative of an ordered structure, but there are no higher order reflections from which a definite space group assignment can be made. For F-33-120, the GISAXS pattern (Figure 2.10A) reveals a primary diffraction peak at $q_x \approx 0.199$ nm$^{-1}$ but this peak is a partial ring with the maximum intensity at $q_z$ associated with the specular reflection. This scattering indicates that the nanostructure orientation favors a parallel structure, but there is significant variation in the orientation. The corresponding AFM phase image (Figure 2.7D) displays fluctuating dark dots and rods. Based on the GISAXS data, these can be attributed to parallel (rods) and tilted cylinders (dots). Increasing the resol content to 50 wt% shifts the diffraction peak to lower $q$ ($q_x \approx 0.183$ nm$^{-1}$) and sharpens the diffraction peak, (Figure 2.10B), which indicates predominately parallel cylinder mesostructure with some tilt. This result is consistent with AFM phase image showing the fingerprint morphology (Figure 2.7E). For F-60-400 film, the GISAXS pattern (Figure 2.10C) reveals that a peak located at $q_x \approx 0.145$ nm along with a shoulder peak at $q_x \approx 0.162$ nm. These two peaks suggest coexistence of phases, which correspond well with the AFM phase images. We attribute the flat plateaus to parallel lamellae coexisting with predominately parallel cylinders. Figure 2.10D illustrates the corresponding 1-D profiles from which the shoulder peak can be better resolved. Moreover, there is a clear shift in the primary peak position to lower $q$ with the addition of resol, which is consistent with resol swelling the domains. This
corresponds to an increase in the \( d_{10} \) spacing from 31.3 nm to 34.2 nm to 43.3 nm for F-33-120, F-50-120 and F-60-120, respectively. These \( d_{10} \) spacings are slightly larger than calculated \( d_{10} \) spacings from the AFM phase images for the more ordered F-50-120 and F-60-120 (31 nm and 37 nm). These \( d_{10} \) spacings are associated with cylinder-to-cylinder spacings \((d_{c-c})\) (36 ± 1 nm and 43 ± 1 nm) calculated from a fast Fourier transform (FFT) of AFM phase images \((d_{10} = \frac{2}{\sqrt{3}}d_{c-c})\).
Figure 2.10. GISAXS patterns of films after thermopolymerization at 120 °C with different resol content: (A) 33 wt%; (B) 50 wt%; (C) 60 wt% at incident angle $\alpha_i = 0.10^\circ$ and (D) corresponding 1-D $q_x$ traces of GISAXS scattering patterns along the $q_z = 0.26$ nm$^{-1}$. 
To further understand these mesoporous structures, ellipsometry is used to characterize the refractive index and porosity of these films. Figure 2.11A shows the refractive index of the films as a function of resol content (wt%) at different processing stages. Before removing template, the refractive indices of these films are very similar (from 1.53 to 1.58) despite their different morphologies because of similar optical properties of pure PEO45-b-PEA117-b-PS99 and pure resol films. However, after removing the template, open porosity is created that dramatically decreasing the refractive index. For example, the refractive index of F-33-120 reduces to 1.29 after removal of template (F-33-400). For the calcined films, the refractive index is relatively constant at low resol content (from 25.0 wt% to 40 wt %), but there is a steep increase in refractive index from 1.33 to 1.6 between 40 and 60 wt% resol (Figure 2.11A). For the low resol content film, the refractive indices are extremely low (1.27-1.33) in comparison to most reported values (1.55-1.71) for mesoporous calcined (polymer resin) films. These low refractive indices are indicative of high porosity as might be expected for the fibril-like morphologies (Figure 2.7G). The steep increase in refractive index from 40 wt% to 60 wt% of resol is correlated with a change in morphology from the branched fibers to the long cylinders to the coexisting cylinders and parallel lamellae. The low porosity for the lamellae is expected as this structure will collapse with template removal; we have also illustrated that the stresses associated with carbonization can collapse long unsupported cylinder structures.
To quantify the porosity of these calcined films, the Bruggeman effective-medium approximation (BEMA) model was used where the measured optical properties (dielectric permittivity $\tilde{\varepsilon} = n^2$) of the film is related to the relative volume fraction, $f_i$, and dielectric permittivity, $\tilde{\varepsilon}_i$, of the constituents of the film, calcined resol and voids, as:

$$f_{\text{resol}} \frac{\tilde{\varepsilon}_{\text{resol}} - \tilde{\varepsilon}}{\tilde{\varepsilon}_{\text{resol}} + \frac{f_{\text{void}}}{2\tilde{\varepsilon}}} + f_{\text{void}} \frac{\tilde{\varepsilon}_{\text{void}} - \tilde{\varepsilon}}{\tilde{\varepsilon}_{\text{void}} + \frac{f_{\text{void}}}{2\tilde{\varepsilon}}} = 0$$

With the known refractive index of calcined pure resol ($n_{\text{resol}} = 1.73$) and void ($n_{\text{void}} = 1$), the volume fraction of void, $f_{\text{void}}$ (porosity), can be calculated by the BEMA. Figure 4B shows the volume fraction of voids in the calcined films at different resol content. The porosity of fiber-like structures at the resol content ranging from 25 wt% to 40 wt% is greater than 50%, which is much higher than normally reported porosity of resol-based templated mesoporous films (about 20%) using other template having common highly ordered structures.\textsuperscript{126, 162, 163} For the mixed rod-like and lamellae structure, the porosity reduces by nearly a factor of three to about 20%, which is similar to prior reports for ordered analogs.\textsuperscript{126}
Figure 2.11. (A) Refractive index of films for (■) as-spun; (●) after thermopolymerization, at 120 °C; (▲) after removing template, at 400 °C, as a function of resol content (wt%); (B) Porosity of calcined films as a function of resol content (wt%) at 400 °C using BEMA model and corresponding structures, (I) Fibril-like structure; (II) Parallel cylinder structure; (III) Mixed cylinder and lamellae structure.
To further investigate the differences of these calcined films, the pore size distributions were examined using ellipsometric porosimetry (EP) technique. First developed by Balkanov and co-workers,\textsuperscript{113} EP involves measuring the change of refractive index, $n$, as a function of varying relative partial vapor pressure ($p/p_0$) of an organic solvent, such as toluene, which wets the wall material to develop the adsorption and desorption isotherms, from which the porosity and pore size distribution (PSD) can be calculated. The relative volume fraction of toluene absorbed ($V_{tol}/V_{film}$) by the porous film is then calculated from the Lorentz-Lorentz effective medium approximation (LLEMA) as\textsuperscript{115,156},

$$
\frac{V_{tol}}{V_{film}} = \frac{(n^2 - 1)}{(n^2 + 2)} - \frac{(n_0^2 - 1)}{(n_0^2 + 2)} \left( \frac{n_{tol}^2 - 1}{n_{tol}^2 + 2} \right)
$$

where $n_0$ and $n_{tol}$ are the refractive index (at 632.8 nm) of empty mesoporous calcined films and condensed toluene, respectively. Here, the absorbed toluene is assumed to maintain its bulk properties with $n_{tol} = 1.496$. Figure 2.12 illustrates the adsorption and desorption isotherms in terms of $V_{tol}/V_{film}$ for three different resol contents. The absorption isotherm of F-33-400 with a fibrous structure (Figure 2.12A) shows a slow increase in $V_{tol}/V_{film}$ with relative partial vapor pressure ($p/p_0$) up to 0.7 where a steep increase associated with capillary condensation within the template mesopores is observed. However, there is no plateau in $V_{tol}/V_{film}$ at high relative partial vapor pressure ($p/p_0$) during absorption, which suggest incomplete pore filling. Similarly, there is no sharp thickness increase (see Figure 2.13) due to release of stress on pore walls from the curvature of the meniscus after the pores are completely filled.\textsuperscript{157} From
the AFM micrographs, there are macropores larger than 50 nm present in this film, but these are likely too large to fully fill with toluene. Incomplete filling is also consistent with the large difference in porosity between BEMA model (about 60%) and using a probe solvent with the LLEMA model (21%). Upon desorption, a hysteresis loop is observed at high relative partial vapor pressure \((p/p_0)\) resulting from the different effective radius of curvature of condensed liquid meniscus for evaporation and capillary condensation.\(^{113}\) For F-50-400 with the cylinder structure, \(V_{\text{tol}}/V_{\text{film}}\) increases monotonically at almost same rate through the whole pressure range and no plateau is observed in either the absorption nor desorption isotherms (Figure 2.12B). These features are consistent with a broad size distribution of pores and incomplete pore filling. Again this is consistent with the different in porosity between EP with the LLEMA model (11%) and BEMA model (40%). Moreover, the hysteresis loop in the desorption curve shrinks as the resol content increases. This feature indicates that the effective radius of curvature of condensed liquid meniscus for evaporation and capillary condensation are similar. Upon increasing resol content to F-60-400, there is almost no change in refractive index of the film with relative partial pressure (Figure 2.12C). This is consistent with the non-porous collapsed lamellae and the even larger pore structure between the cylinders.
Figure 2.12. Adsorption (■) and desorption (●) isotherms of mesoporous calcined films along with different resol content wt%, (A) 33 wt%, (B) 50 wt%, (C) 60 wt%. The corresponding pore size distributions (D) based on the absorption isotherms, (a) 33 wt%, (b) 50 wt%. The pore size distributions curve of calcined film with 60 wt% resol content is calculated due to limited absorption of toluene vapor.
Figure 2.13. Film thickness of F-33-400 with respect to relative pressure $p/p_0$, adsorption (■) and desorption (●).
To approximate the pore size distribution (PSD), the Kelvin equation is applied to the absorption isotherms as:

\[
\frac{2}{r_k} = \frac{1}{r_1} + \frac{1}{r_2} = -\frac{RT}{\gamma V_L \cos \theta} \ln \left( \frac{p}{p_0} \right)
\]

where \( r_k \) is the mean radius of curvature of the meniscus, Kelvin radius, and \( r_1 \) and \( r_2 \) are the main radii of curvature of the meniscus, \( R \) is the gas constant, \( T \) is the Kelvin temperature, \( \gamma \) is the surface tension of toluene, \( V_L \) is the molar volume of the toluene, and \( \theta \) is the contact angle of the toluene on the calcined resol. Assuming the absorbed toluene maintains its bulk properties, \( \gamma \) equals to 0.0284 N m\(^{-1}\), \( V_L \) equals to \( 1.064 \times 10^{-4} \) m\(^3\) mol\(^{-1}\), and the contact angle is \(-0^\circ\), Figure 2.12 D illustrates the PSD for the two films that exhibit significant sorption capacity for toluene. For both cases, the broad peaks indicate a broad pore size distribution ranging from 10 nm upwards.

These characteristics coincide with AFM images (Figure 2.7, panels G-H) showing nanostructures with broad pore size distribution. It should be noted that the Kelvin equation assumes that the pores are cylinders or spheres; while for these structures, the pores are neither. Therefore, the PSD only provides a relative measure of the pore size in these films.

Though sizes of pores for the fibrous structures are very broad, the fibrous cylinders are homogeneous in size with an average width of \( \sim 20 \) nm as illustrated in Figure 2.14. Interestingly, the size and distribution of these fibers appears to be independent of resol content between 25 and 33 wt %. To obtain the data in Figure 2.14, the cylinder fiber diameter from multiple AFM phase images are determined. Interestingly, the distribution of the fiber diameters is relatively homogeneous and
follows a normal distribution. The morphologies of these calcined films are very similar with these fibrous networks (Figure 2.14, panels A-C). The mean diameter of the fibers is 20 nm with a standard deviation near 3 nm in all three cases. This similarity in the fiber diameter is strange considering the swelling in the d-spacing observed for the higher resol content films. One potential explanation is that the fiber shape is being convoluted with the AFM tip shape, but these images are from multiple tips and there is no significant change in the distribution in any case.
Figure 2.14. AFM phase images and cylinder distribution of calcined films with fibril-like structures with Gaussian fit. AFM phase images, (A) F-25-400; (B) F-28.5-400; (C) F-33-400. Cylinder distribution, (D) F-25-400; (E) F-28.5-400; (F) F-33-400.
For many applications, it is desirable to obtain conductive carbon structures. Upon heating to 800 °C in N₂, the phenolic resin is transformed to an amorphous carbon, but additional significant contraction typically occurs at these temperatures.\textsuperscript{162} Figure 2.15 illustrates the surface morphology of carbonized films as a function of resol content. Compared to the calcined films before carbonization with the same resol content (Figure 2.14), the surface morphologies is almost invariant, indicating the thermal stability of these carbonized films. Additionally, the fibrous cylinder structure can still clearly be observed from AFM height image of carbonized film (Figure 2.15D), and the height profile of carbonized film shows height difference $\sim$27 nm (Figure 2.15E). As described before, the height difference is $\sim$25 nm before carbonization. The similar height difference before and after carbonization further suggests the thermal stability of these fibril-like structures. Thus high porosity carbon films consisting of ca. 20 nm fibrils can be readily fabricated using this triblock copolymer, PEO$_{45}$-b-PEA$_{117}$-b-PS$_{99}$, cooperatively assembling with resol. The wide composition window possible to obtain this morphology with limited structural changes provides a robust platform for future exploration of these materials as membranes and electrodes.
Figure 2.15. Surface morphology of mesoporous carbon films pyrolyzed at 800 °C as a function of resol content shown by AFM, phase images (A) 25 wt% resol; (B) 28.5 wt% resol; (C) 33 wt% resol. The topology associate with the pores can clearly be seen in (D) the height images, 33 wt% resol, corresponding to phase image in (C). (E) Height profile of surface topology corresponding to height image in (D).
2.4 Conclusion

A novel triblock block copolymer template (PEO-b-PEA-b-PS) with symmetric volume fraction \( f_{PEA} \approx f_{PS} \) with low hydrophobic cooperatively assembles with resol to form self-assembled nanostructures on simple thermal annealing. The resol content was utilized to control the morphology of these films with poorly ordered (from expected block copolymer phases) structures primarily observed. Among these structures, a network of homogeneous fibrous structure (~20 nm fibrous cylinders) yields high porosity (~60%) films over a relatively wide composition range without significant alteration in the fiber diameter or morphology, which may be promising for reproducibility of high porosity interconnected pore structures in carbon. Heating at 800 °C to carbonize the films does not impact these fibrous structures indicating the highly thermal stability of the mesoporous films. These results provide a simple alternative to fabricate thin films and coatings with a well-defined fibrous network structure that could be potentially applicable to energy and separation applications.
CHAPTER III

BICONTINUOUS MESOPROUS CARBON THIN FILM VIA AN ORDER-ORDER TRANSITION

3.1 Introduction

Chemical and physical properties of ordered mesoporous carbons (OMCs), including high specific surface area, tunable pore size, excellent thermal and chemical stability, electrical and thermal conductivity, are attractive for numerous applications, such as separations, catalysis, energy conversion and energy storage.\textsuperscript{73, 74, 78, 85, 164} Synthesis of OMCs include nanocasting (hard-templating) methods\textsuperscript{165} and soft-templating by organic-organic self-assembly.\textsuperscript{88, 91} The template selection and the ratio of the template/carbon precursor enable a variety of mesostructures to be fabricated, including hexagonal (\textit{p6mm}), body centered cubic (\textit{Im\overline{3}m}), and 3-D bicontinuous (\textit{Ia\overline{3}d}) mesostructures.\textsuperscript{108} For many applications, the bicontinuous (double gyroid) is appealing morphologies due to its interconnected pore geometry in three-dimensional (3D) space.\textsuperscript{56} Several templates have been reported to enable the synthesis of mesoporous carbon powders with gyroid mesostructure\textsuperscript{108, 111, 166} but unlike other mesostructures (\textit{p6mm} and \textit{Im\overline{3}m}),\textsuperscript{167, 168} the gyroid has not be
demonstrated in thin films. For some applications, mesoporous carbon films are desirable due to their structural homogeneity and integrity.\textsuperscript{164}

However, there are additional constraints associated with interfaces that impact the typically narrow phase window for bicontinuous morphologies. The processing window for bicontinuous morphologies can be significantly enlarged using ABC block copolymers (BCPs) as demonstrated by Wiesner and coworkers for mesoporous carbon powders.\textsuperscript{111} However when an analogous triblock copolymer was applied to fabricate thin films, only kinetically trapped morphologies were formed due to competition between ordering and crosslinking kinetics.\textsuperscript{169} For neat block copolymer (BCP) thin films, solvent vapour can generally be used to effectively enhance their ordering (i.e., solvent vapour annealing (SVA)).\textsuperscript{170} The ordering of cylinder forming mesoporous carbon films has been enhanced using SVA with AB BCP/phenolic resin (resol) mixtures.\textsuperscript{156} However for neat BCPs, gyroidal thin films have been illustrated using SVA.\textsuperscript{171,172}

Here, we seek to fabricate highly ordered bicontinuous mesoporous carbon films using the combination of cooperative assembly of poly(ethylene oxide)-block-poly(ethyl acrylate)-block-polystyrene (OES) / phenolic resin (resol) and SVA process techniques. Cooperative assembly has not yet been demonstrated for the synthesis of mesoporous bicontinuous (1a3d) carbon thin film to the best of our knowledge.
3.2 Experimental Section

The experimental section is carried out by the following parts: chemicals, films preparation, processing and characterization.

3.2.1 Chemicals

Methyl ethyl ketone (MEK, >99%, Fisher Scientific), phenol (> 99%, Sigma-Aldrich), formaldehyde (ACS reagent, 37 wt% in H₂O, methanol stabilized, Sigma-Aldrich), sodium hydroxide (NaOH, >99%, EMD Chemicals), hydrochloric acid (HCl, >37%, Fluke Analytical), were used as received. The thermally crosslinkable phenolic resin oligomer (resol) served as a carbon precursor, and its preparation by using phenol and formaldehyde (37 wt% in H₂O) in a base-catalyzed (NaOH) process was previously reported.⁹¹ The amphiphilic triblock copolymer template poly(ethylene oxide)-block-poly(ethyl acrylate)-block-polystyrene (PEO₄₅-b-PEA₁₁₇-b-PS₉₉) with \( Mn = 24 \text{ kDa} \) and polydispersity (\( D \)) =1.2 was synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization. The synthetic routes and post characterization of PEO₄₅-b-PEA₁₁₇-b-PS₉₉ was described in our previous publication.¹⁶⁹ PEO₄₅-b-PEA₁₁₇-b-PS₉₉ (template) and resol (precursor) were dissolved in MEK to make 10 wt% solutions. Clean Silicon wafers (substrate) were prepared by placing them in UV ozone (Jelight Company Inc., Model No. 42) for 2 h.
3.2.2 Films Preparation and Processing

Thin-film samples were prepared on clean silicon wafers by spin-coating at 3000 rpm for 1 min from a 10 wt% MEK solution with mixture of PEO$_{45}$-b-PEA$_{117}$-b-PS$_9$ and resol under different resol wt%. The films thickness varies from 500~620 nm depending on the resol content. Then the films were annealed with MEK vapor in a chamber using mass flow controllers (MKS-146C-FF000-1) in which the dry air was bubbled through MEK solvent to produce mixtures of saturated MEK vapor and dry air stream prior to entering the annealing chamber. The flow total rate of the streams was set constant at the 800 cc/min and the relative partial vapor pressure of MEK was controlled at 1. The volume of MEK solvent could stay in the solvent containing tube for about 4 h under the flow rate. To investigate the influence of SVA time on film structure, two different SVA processing conditions, referred to as short SVA and long SVA time, were employed. For the short SVA, the thin-film samples were solvent vapor annealed at ambient temperature for 3h with a quick removal of the solvent by immediately stopping the mass flow controllers and taking out the samples from the chamber; while for the long SVA, the samples were annealed in MEK vapor for overnight to slowly remove the solvent from the films. Following solvent vapor annealing (SVA), the films were heated at 85 °C for 24 h to crosslink the resol to obtain thermopolymerized films. After that, the thermo-polymerized thin films were further heated at 400°C for 3 h in N$_2$ atmosphere to remove the template using a ramp rate of 1 °C/min. To fabricate the mesoporous carbon thin films, the calcined films were
heated to 800 °C for 3 h at the heating rate of 1 °C/min below 400 °C and 4 °C/min above 400 °C.

3.2.3 Characterization of Thin Films

The thickness and optical properties ($n$, $k$) of the films were measured by a variable angle spectroscopic ellipsometer (VASE, J.A Woollam Co., M-2000) using general scans through multiple incident angles (65°, 70° and 75°) over the wavelength from 246 nm to 1689 nm. A model containing a silicon substrate, a SiO$_2$ interface layer and a Cauchy layer was used to fit the obtained data. The porosity of the calcined films was calculated from the adsorption-desorption isotherm determined from the changes of films’ refractive index under the variations of partial pressure of toluene probe solvent vapor. The partial pressure of the probe solvent was controlled by a partials of mass flow controllers in dry air stream same as the above SVA process.

Atomic force microscopy (AFM, Dimension ICON, Veeco) was employed to characterize the surface morphology of films through tapping mode at 0.5 Hz using PPP-NCC-50 tips (Nanosensors). Grazing incidence small angle X-ray scattering (GISAXS) was conducted to investigate the ordered structure of the films at the X9 beamline of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL). The incident X-ray beam was 13.5 keV with wavelength ($\lambda$) = 0.0918 nm at a distance of 4.73 m from sample to detector. All GISAXS profiles were obtained both below and above the critical angle under vacuum.
3.3 Results and Discussion

The results and discussion part includes the following parts: processing dependent morphology, impact of resol age on morphology.

3.3.1 Processing Dependent Morphology

In this work, OES (PEO\(_{45}\)-b-PEA\(_{117}\)-b-PS\(_{99}\)), non-frustrated\(^{173}\) amphiphilic triblock block (\(f_{\text{PEO}} = 8\%, f_{\text{PEA}} = 47\%, f_{\text{PS}} = 45\%; M_n = 24\) kDa; \(D = 1.2\))\(^{169}\) is used as a template to cooperatively assemble with phenolic resin oligomers (resol), which is the carbonizable precursor. The morphology of the OES/resol mixtures is impacted by the relative resol content similar to homopolymer\(^{173}\) loading in other ABC BCPs. Films were prepared by spin coating, followed by SVA using nearly saturated MEK vapour. The MEK is a good solvent for each segment of the triblock copolymer and resol with a slight selectivity for the PEA segments.\(^{169}\) Two different SVA times (3 h or overnight) were utilized to order the films and are henceforth referred to as short and long SVA, respectively. Post SVA procedures followed standard mesoporous carbon fabrication of thermopolymerization of resol, calcination (template removal) and carbonization as illustrated in Scheme 1. Additional details on the fabrication are included in the experimental section.
Scheme 3.1. Schematic representation of the fabrication of mesoporous carbons via cooperative self-assembly induced by a solvent vapor annealing process followed by thermally induced self-assembly, calcination and carbonization.
Atomic force microscopy (AFM) was employed to characterize the surface morphologies of these films in each processing step. For as-spun films prior to SVA, poorly ordered short cylinder rods are observed on the surface of films (Figure 3.1). These disorganized, but self-assembled structures result from the rapid drying during spin coating that inhibits re-organization into a highly ordered mesostructure.
Figure 3.1. AFM phase images of as-cast PEO$_{45}$-b-PEA$_{117}$-b-PS$_{99}$/resol films with growing resol content, (A) 25 wt %; (B) 50 wt %; (C) 60 wt %.
Exposure to nearly saturated MEK vapour significantly increases the mobility of polymer chains that yields well-organized mesostructures as shown in Figure 3.2, panels A-F. Interestingly, the surface morphologies strongly depend on the film composition, i.e., resol content. For the pure triblock copolymer, the morphology appears to be spheres of PEO as the PEO is the minority component in the triblock copolymer (Figure 3.2A). The addition of resol to 25 wt% results in the distinctive “double wave” pattern consistent with the double gyroid morphology (Figure 3.2B). At 40 wt % resol, concentric rings are observed that are almost onion-like (Figure 3.2C).

Increasing the resol concentration to 50 wt %, the wavy line morphology consistent with the gyroid morphology is observed along with some regions that appear to be transitioning towards parallel cylinders (Figure 3.2D). Further increasing the resol content to 60 wt % also yields an inverse double gyroid structure that is co-existing with parallel cylinders (Figure 3.2E). Continuously increasing the resol concentration to 67 wt %, the parallel cylinders with sharp bends is obtained (Figure 3.2F). These structures are clearly different from the as cast film as sorption of MEK enables reorganization of the BCP. In comparing the two interesting gyroid mesostructures, the interdomain spacing of (100)\(_G\) (i.e., \(d_{(100)G}\) or lattice parameter \(\alpha_G\)) increases from 53 ± 1 nm to 63 ± 1 nm from AFM phase image for 25 wt% and 60 wt% resol, respectively. This approximate 10 nm increase in d-spacing is consistent with swelling of the BCP by the resol.
Figure 3.2. AFM phase images of films containing (A) 0 wt%; (B) 25 wt%; (C) 40 %; (D) 50 %; (E) 60%; and (F) 60 wt% resol after exposure to MEK using short SVA.
However, on heating these films after SVA to thermopolymerize the resol, the structure significantly re-arranges even when low crosslinking temperature (85 °C) is utilized to minimize chain mobility and the highly ordered structures from SVA are lost. The double gyroid morphology transforms to either dot (25 wt % resol) or line (60 wt % resol) pattern as shown in Figure 3.3, panels A and C. While the cylinder structures still exist after thermopolymerization. Thermopolymerization at higher temperatures still results in these morphological transformations. As crosslinking of the resol decreases the concentration of hydroxyl groups, this would expect to decrease the effective Flory-Huggins interaction parameter, $\chi_{\text{eff}}$, based on prior reports associated with hydrogen bonding of additives with PEO.\textsuperscript{174} However, the molecular weight of the resol increases during thermopolymerization and the specific volume of the resol decreases to shift the relative fraction of the block copolymer. These changes in the relative volume fraction and interaction parameter may be responsible for the change in structure on heating due to an order-order transition (OOT),\textsuperscript{175} but kinetically trapped morphologies are also possible during SVA.\textsuperscript{170}
Figure 3.3. AFM phase images of thermopolymerized films heated at 85 °C for 24 h after application of short SVA time prior to thermopolymerization, containing (A) 25 wt%; (B) 50 wt%; (C) 60 wt% resol.
In order to test if these changes in morphology are kinetic or thermodynamic in nature, the SVA conditions are changed for the 25 wt% resol from only 3 h to overnight with a slower removal as well. With this processing, the surface morphology appears to be parallel cylinders instead of the gyroid morphology (Figure 3.4A), which is consistent with a kinetically trapped mesostructure. Parallel cylinders are consistent with the slow evaporation rate\textsuperscript{170} associated with the gradual decrease in solvent during the overnight SVA process when the solvent reservoir is emptied. Additionally, the morphology evolution from gyroid to parallel cylinders with increasing solvent annealing time has been reported for neat BCP systems.\textsuperscript{171, 172} However unlike the transition from gyroid to dot pattern on thermopolymerization at 85 °C, an OOT from parallel cylinder to double gyroid oriented along the (211) direction occurs for this sample (Figure 3.4B). Interestingly, the $d_{(100)G}$ (lattice parameter) of thermopolymerized film is nearly identical to that obtained after solvent annealing for short times (Figure 3.2B). This behavior suggests the structure obtained on thermopolymerization is dependent on the prior mesostructure in the film and implies a delicate balance between thermodynamics and kinetics as the system seeks to transform to a varying equilibrium structure.
Figure 3.4. AFM phase images of film containing 25 wt% resol exposed to MEK solvent vapor for overnight and processed at different temperature, (A) after long SVA; (B) 85 °C, thermopolymerized; (C) 400 °C, calcined; (D) 800 °C, carbonized.
This gyroid mesostructure can be maintained through calcination at 400 °C in N₂ to remove the BCP template (Figure 3.4C). The mesoporous gyroid morphology has pore size of 12 ± 2 nm on the film surface. The film thickness is significantly reduced from 515 nm to 124 nm (76 % contraction) during the calcination process. There are some defects that formed on the surface on calcination that do not appear in the thermopolymerized sample. We speculate that these defects are caused by stresses associated with the calcination process that leads to further crosslinking of the resol along with removal of the BCP template. Upon carbonization at 800 °C, the surface morphology is almost invariant from that of the calcined film (Figure 3.4D), which illustrates the thermal stability of the gyroid morphology.

To further study the double gyroid morphology of the thermopolymerized film (Figure 3.4B), grazing incidence small angle X-ray scattering (GISAXS) is used to elucidate the mesostructure. Figure 3.5A illustrates a typical GISAXS pattern obtained from OES/resol thermopolymerized film before template removal. The GISAXS pattern shows the discrete diffraction spots in semicircular arrangement that are consistent with the gyroid structure possessing $Ia\overline{3}d$ symmetry with preferential alignment of the (211) plane parallel to the substrate, which agrees with the AFM observations (Figure 3.4A). The ratio of the second and first diffraction spots at $q_z=0.24$ is determined to be 1.16 in agreement with the predicted value of $\sqrt{8}/\sqrt{6}$ for the (211) and (220) reflections of the double gyroid structure. From the primary peak position at $\sqrt{6}q^* = 0.245$ nm⁻¹, the $d_{100}$ spacing (lattice parameter) estimated from GISAXS and 62.6 nm ($d_{100}=2\pi/q^*$), which is larger than that determined by AFM (53 ± 1 nm).
Figure 3.5. Thermopolymerized and calcined film containing 25 wt% after long SVA. (A) GISAXS pattern of thermopolymerized film at incident angle $\alpha_i = 0.10^\circ$; (B) Adsorption (■) and desorption (●) isotherms of mesoporous calcined film with toluene as probe solvent; (C) estimated pore size distribution determined from EP using the Kelvin equation.
Additional information about the pore structure is determined using ellipsometric porosimetry (EP) for the films after template removal (calcined) as shown in Figure 3.5, panel B and panel C. The porosity and pore size distribution are determined using Lorentz-Lorentz effective medium approximation and Kelvin equation, respectively.\textsuperscript{113,115} These films exhibit the typical type IV adsorption desorption isotherms of mesoporous materials. The porosity of these mesoporous gyroid is significantly greater (about 50%) than typically observed in other ordered morphologies for mesoporous carbon films.\textsuperscript{126,162} The pore size distribution is broader than typically reported for ordered mesoporous materials as shown in Figure 3.5C. It should be noted that the Kelvin equation is not strictly applicable to the gyroid structure, which may explain the inconsistency in pore size between AFM (12 ± 2 nm) and the mode pore size determined by EP (approximately 30 nm).

3.3.2 Impact of Resol Age on Morphology

In addition to the processing sensitivity, the compositional window for the gyroid morphology using identical SVA processing can be significantly altered by the aging of the resol. Even with storage of the nominally neutral (pH = 7), ethanoic resol solution in a refrigerator (≈ 5 °C), the compositional window for the gyroid after the long SVA procedure is shifted by several percent as 25 wt% resol leads to perpendicular cylinders (if the resol is aged 6 mo.), but the gyroid can be recovered by increasing the resol content to 29 wt %. This sensitivity to the state of the resol along with the ability of the resol block copolymer composite to undergo an order-to-order transition likely
explains why the gyroid has not been previously reported in thin films for soft templated mesoporous carbons.

As shown in Figure 3.6, the gyroid is not obtained for the 25.0 wt % resol film after the long SVA procedure, but instead perpendicularly oriented cylinders are obtained (as will be conclusively shown later). However, increasing the resol content to nearly 28.9 wt % results in the gyroid, and in 33.3 wt% leads to parallel cylinders again. Thus the compositional window for the parallel cylinder is shifted by approximate 8 wt % with aging with respect to the formation of parallel cylinder. This is likely due to the extreme temperature sensitivity of the morphology as shown in Figure 3.6 with the mesostructure after thermopolymerization at 75 °C and 85 °C being somewhat different. As the resol ages, the degree of polymerization increases, which shifts the degree of segregation ($\chi_N$) for the cooperatively assembled blend. As the morphology is strongly temperature dependent, this suggests that the morphology should also be quite sensitive to small changes in the degree of segregation. Of particular interest is the morphology of the 33.3 wt% resol film, where the cylinder (Figure 3.6D) morphology transforms partially to gyroid structure (Figure 3.6L) during thermopolymerization at 85 °C. This OOT phenomenon is very similar to that reported for the previous long SVA, except that the resol content changes from 25.0% to 33.3%. Thus, repeatability of the gyroid structure also depends on specific details associated with the resol. However, the small size, broad molecular weight distribution associated with condensation and the difficulties with eluding resol through a standard GPC column (WARNING: we have ruined a column due to the near irreversible adsorption of resol to the packing material
in THF. No peaks were seen for the resol using an RI detector.) makes quantifying the resol structure extremely challenging.
Figure 3.6. AFM phase images of films containing different resol content at 25 °C, (A) 22.7 wt%; (B) 25.0 wt%; (C) 28.9 wt%; (D) 33.3 wt%; and at 75 °C, (E) 22.7 wt%; (F) 25.0 wt%; (G) 28.9 wt%; (H) 33.3 wt%; and (I) 22.7 wt%; (J) 25.0 wt%; (K) 28.9 wt%; (L) 33.3 wt% after exposure to MEK using long SVA (repeated work). (Scale bar: 250 nm.)
In order to confirm the mesostructures of these films, GISAXS was utilized. The 22.7 wt% resol film after long SVA (Figure 3.6A) is a near random mix of parallel and perpendicular cylinders from GISAXS analysis as shown in Figure 3.7. There is a split first-order peak at 0.196 and 0.23; this ratio of around 1.17 is close to the expected ratio of 1.15 for mixed parallel and perp. The higher order reflection around 0.43 is expected for both parallel and perpendicular cylinders should be observed near 0.4. As the third order reflection for perpendicular cylinders should be around 0.46, this accounts for the broad peak observed near 0.43.
Figure 3.7. GISAXS profile for 22.7 wt% resol films after long SVA. The split primary peak is indicative of a mixed parallel and perpendicular orientation of cylinders.
For the 25 wt % resol film (shown in Figure 3.6B), the GISAXS profile above the critical angle is shown in Figure 3.8. The streaking is consistent with perpendicular cylinders. The higher order reflections at peaks at 0.236, 0.41, 0.47, 0.61, 0.71, and 0.83 are approximately at a ratio of root(3), root(4), root(7), root(9), etc. as would be expected for perpendicular cylinders.
Figure 3.8. GISAXS profile for 25 wt% resol film after long SVA process obtained at an incident angle of 0.22°.
The gyroid morphology shown in Figure 3.6C for the film with 28.9 wt% resol can be confirmed by GISAXS as shown in Figure 3.9. The reflections at 0.142, 0.192, and 0.225 are consistent with the gyroid morphology. Additionally, the broad higher orders probably contain multiple peaks, which would be expected for a gyroid as well.
Figure 3.9. GISAXS profile for 28.9 wt% resol film after long SVA process obtained at an incident angle of 0.22°.
3.4 Conclusions

Long-range ordered gyroidal (cubic; $Ia\bar{3}d$) mesoporous carbon film can be fabricated using OES/resol bi-constituent assembly processed by solvent vapor annealing and post thermal annealing process that induces an order-order transition from parallel cylinder to the double gyroid. Direct solvent vapor annealing of the same composition to gyroid leads to a morphological change to spheres or cylinders on thermopolymerization. After stabilization by thermopolymerization, the gyroid mesostructure can be maintained through calcination and carbonization.
4.1 Conclusions

In this case of study, a novel templated based on a non-frustrated ABC triblock copolymer, PEO$_{45}$-b-PEA$_{117}$-b-PS$_{99}$, has been utilized as a soft template to synthesize bicontinuous mesoporous carbon films via organic-organic self-assembly. The amphiphilic triblock copolymer has low hydrophilic volume fraction (~8%) with nearly same volume fraction of PEA and PS blocks, and is synthesized using RAFT polymerization. The synthesis procedure starts with the esterification of PEO$_{45}$-OH with RAFT-COOH to yield PEO$_{45}$-RAFT macro-chain transfer agent, followed by sequential polymerization of ethyl acrylate and styrene monomer to obtain final triblock copolymer, PEO$_{45}$-b-PEA$_{117}$-b-PS$_{99}$.

Initially, simple thermal annealing and subsequent process of polymer/resol films does not lead to well-ordered mesoporous carbon films due to the high glass transition of PS segments leading to slower self-assembly ordering rate than resol’s crosslinking rate. But among these poorly ordered structures, a network of homogeneous fibrous
structure (~20 nm fibrous cylinders) yields high porosity (~60%) films over a relatively wide composition range (25~33 wt%) without significant alteration in the fiber diameter or morphology.

Alternatively, an introduction of a solvent vapor (MEK) annealing step prior to the thermal annealing steps plasticizes the polymer (i.e. favor high mobility of segments), thus these polymer/resol films form highly ordered structures after solvent evaporation. These well-ordered structures can be controlled by SVA time and resol’s concentration. Further thermal crosslinking of resol produces a small window of ordered bicontinuous gyroid morphology through an order-order transition (from cylinders to gyroids) due to the changes of relative volume fraction and interaction parameter during thermopolymerization of resol leading to a decrease of hydroxyl groups and resol’s volume. Subsequent calcination and carbonization of this thermopolymerized films with gyroid phase results in bicontinuous gyroidal carbon films with high porosity (~50%) and narrow pore size distribution (12 ± 2 nm). Further study shows that the compositional window for the gyroidal mesostructures using identical SVA processing can also altered by the aging of the resol.

These bicontinuous films with organized fibers or gyroid mesostructures are promising for energy and separation applications because of their specific pores size, high porosity, interconnected pores.
4.2 Future work

To continue our research, we will focus on two main directions to get the ordered mesoporous porous carbon thin films.

4.2.1 Exploration of Novel Processing Method to Gyroidal Mesoporous Carbons Using OES Template

Werner and coworkers have recently reported the synthesis of gyroidal mesoporous carbons with ultra large pore size using non-frustrated ABC type triblock copolymer poly(isoprene)-block-poly(styrene)-block-poly(ethylene oxide) (ISO) as structure-directing soft template and phenol-formaldehyde resol as carbon precursor. In that work, the formation of gyroidal mesostructures are achieved by evaporation-induced self-assembly (EISA) process, during which the mixed solution of the carbon precursor and the triblock copolymer is slowly evaporated to dryness, leading the microphase separation of the block copolymer. They also mentioned that the EISA process is very sensitive to the processing parameter as well as the precursor molecules employed. One critical factor of formation of the well-ordered organic-organic hybrid is to ensure the sufficient strong hydrogen bonding between the resol and the PEO hydrophilic segments of the triblock copolymer to provide the sharp interface between the hydrophobic and hydrophilic phases. Initially, they followed the protocols reported in previous literature of synthesizing ordered mesoporous carbons via soft-templating, and only limited ordered structure was obtained (see Figure 4.1a), which is very similar as what we reported using OES as
the soft template. However, when the processing conditions were optimized, for the same ISO/resol hybrid, long-range ordered gyroidal structure was obtained, as Figure 4.1b shows. As stated in that paper, these optimized processing conditions, including longer stirring time (24 h), proper solvent system (THF & CHCl₃) and evaluated casting temperature (50 °C), might make the hydrogen bonding between resol and ISO strong enough to lead to well-ordered structures. Inspired by this idea, in our next work, we will first try to improve our processing method to make ordered mesoporous carbons thin films without SVA for the OES/resol system, including using longer solvent mixing time, finding a proper evaluated spin-coating temperature, and seeking an appropriate solvent system.
Figure 4.1. Transmission electron microscopy (TEM) image of ISO + resol hybrid with processing conditions, (a) only THF as the solvent and 1 hour stirring time, limited ordered structure; (b) THF and CHCl$_3$ as the solvent and 24 hour stirring time, and elevated casting temperatures for solvent evaporation, double gyroid structure.

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4.2.2 Design and Synthesis of Novel Non-frustrated ABC Triblock Copolymer for Gyroidal Mesoporous Carbons

It is recognized that the limited ordered structures of template/resol hybrid after thermosetting of resol comes from slower self-assembly ordering rate than resol’s crosslinking rate, which might be caused by the following three reasons: (1) the high $T_g$ of block copolymers;\textsuperscript{169} (2) not sufficiently high Flory-Huggins interaction parameters among different blocks;\textsuperscript{111} (3) the hydrogen bonding between hydrophilic part and resol is not strong enough.\textsuperscript{111} A good solution to these problems, obviously, is to design and synthesize a novel non-frustrated ABC triblock copolymer with low $T_g$ of each block, sufficient high Flory-Huggins interaction parameters among these three blocks, and appropriate volume fraction of hydrophilic segments of BCP.
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149