CONTROL OF LONG RANGE ORIENTATION IN
ORDERED MESOPOROUS CARBON THIN FILMS

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CONTROL OF LONG RANGE ORIENTATION IN ORDERED MESOPOROUS CARBON THIN FILMS

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Thesis

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Ordered mesoporous carbons are appealing for many application areas, where their function and performance depend critically on structure. Thus, alignment of these mesopores by scalable methods is of notable interest. Cooperative self-assembly provides a facile route to fabrication of ordered mesoporous materials. Heating causes ordering and crosslinking of the carbon precursor (phenolic resin); the relative kinetics of these two processes can lead to complications. Typically, silicon wafers have served as the support for thin films; quartz presents a physicochemically similar surface, but we find significant improvements in ordering of mesoporous carbon films prepared on quartz relative to silicon wafers. The role of annealing temperature on the porosity, pore size distribution and mechanical properties of the mesoporous films supported on quartz substrates are examined using ellipsometry and wrinkling, respectively. We attribute the significant differences between the films processed on silicon and quartz substrates to their relative thermal conductivities and heat capacities that impact the rate. These results illustrate the subtleties associated with the thermally induced self-assembly process for mesoporous carbons and suggest that support selection will significantly impact the ordered mesostructure.

Here, we demonstrate use of a dynamic thermal gradient annealing technique, cold zone annealing (CZA) to obtain 2D cylindrical mesoporous carbon thin films with long range ordered structure and controllable in-plane uniaxial orientation. CZA generates flow in the annealing motion direction from the thermal gradient associated with the CZA to shear-align 2D cylinders along the moving direction. Additionally, the edge of the substrate is approximately 10 °C warmer in the thermal zone, which leads to orthogonal flow from differences in the crosslinking density and can cause cylindrical structure
packing transverse to CZA motion direction. By changing the sample translation velocity from 20 \( \mu \text{m/s} \) to 0.2 \( \mu \text{m/s} \), in-plane cylinders can be arranged in different direction relative to moving direction with high uniformity \((S > 0.95)\). Though pyrolysis leads to a slight loss of directionality, mesoporous carbon films can still exhibit an impressive orientational order factor \((S = 0.89)\). This simple technique is a promising continuous fabrication route to obtaining long-range uniaxially aligned mesoporous carbon thin films over large areas without any physical or chemical templating.

We achieved striking uniaxially aligned well ordered cylindrical mesoporous carbon through simple route with easy process method.
DEDICATION

For my beloved parents,

to whom I owe everything I am today

and my soulmate, who is on the way
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CHAPTER I

INTRODUCTION

1.1 Overview (Application of Mesoporous Carbons)

There has been tremendous interest in porous materials due to their unique nanoscale structure which provides excellent properties such as large surface area (up to 3000 m$^2$/g for porous carbon)\(^1\), enhanced surface reactivity (large free surface energy)\(^2\) and mechanical robustness (volume expansion resistance).\(^3\) Porous materials can be classified by their pore diameters as: microporous (<2nm), mesoporous (2-50nm) and macroporous (>50nm). Mesoporous materials obtained by template routes with high surface area and narrowly distributed tunable pore size promised the stand out performance of this class of material in many areas.\(^4\)

The first report of ordered mesoporous materials were mesoporous silicates obtained from templated supramolecular self-assembly in a sol-gel medium.\(^5\) Afterward this, different mesoporous materials were reported such as mesoporous metals,\(^6\) metal oxides,\(^7\) polymers\(^8\) and mesoporous carbons.\(^9,10\)

Mesoporous carbon garnered our interest for its intrinsic advantages: light weight, corrosion resistance, mechanical robustness and electrical conductivity, abundance and
easy processing. Mesoporous carbon has already played important roles in numerous areas: energy storage electrodes for batteries and supercapacitors, sorbents for separation, heterogeneous catalyst supports, and drug delivery and biological sensors.

1.1.1 Energy Storage

Facing the problems of global warming and shortage of petroleum, energy storage devices such as batteries and capacitors have become urgent topics. The 2\textsuperscript{nd} generation of commercial Lithium-ion batteries using intercalation materials (i.e., LiFePO\textsubscript{4}, LiMn\textsubscript{2}O\textsubscript{4}) as the cathode is no longer able to meet requirements of the current energy market, especially in the field of hybrid electrical vehicles or plug in hybrid electrical vehicles where high energy density package is preferred. Lighter weight and higher energy density batteries are also preferred in the grid for electric storage of renewable energies such as wind or solar.

Low cathode capacitance is the main limitation of lithium batteries nowadays. New battery concepts such as Li-S and Li-Air have shown huge potential for future applications. The theoretical energy density for Li-S (Figure 1.1) and Li-Air cathodes are 2567 Wh/kg and 3500 Wh/kg, respectively; much higher than that for Li-CoO\textsubscript{2} (387 Wh/kg) which is the most popular lithium battery package (1\textsuperscript{st} generation) today.\textsuperscript{13}

Mesoporous carbon is considered the most suitable candidate for the porous
cathode in lithium batteries because of its large surface area, that offers more contact area for electrolytes and electrodes, short and uniform diffusion length due to nano-scale dimensions and mechanical robustness to retain framework during charging and discharging.\textsuperscript{14} In fact, ordered mesoporous carbon with bimodal pore sizes is of particular interest in the field of Li-S batteries for its multi-functioned pores: micropores to house the sulfur and mesopores for electrolytes and fast ion transportation.\textsuperscript{15}

Figure 1.1 A schematic of polymer-coated CMK-3/sulfur to improve the cathode performance. Reproduced with permission.\textsuperscript{16} Copyright 2011, American Chemical Society.

Though Li batteries offered high energy density, there is many cases where high power density supercapacitors are of interest. The two most successful types of electrochemical supercapacitors are: pseudo-capacitors for which mesoporous transition
metal oxides are preferred and electrochemical double layer capacitors (EDLCs, Figure 1.2), using high surface area ordered carbon materials\textsuperscript{17,18} with periodically interconnected porous networks which lead to effective charge storage.\textsuperscript{3} Recent investigation on nanostructure fuel cells has classified it into two main types: exploiting carbon based/carbonaceous supports\textsuperscript{19} or utilizing non-carbonaceous supports.\textsuperscript{20} Again, ordered mesoporous carbon (OMC) showed appealing performance due to its large surface area and electron conductivity in the field.

![Schematic of a commercial spirally wound double layer capacitor.](image)

**Figure 1.2** Schematic of a commercial spirally wound double layer capacitor.

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### 1.1.2 Sensors

Another interesting area that exploits mesoporous carbon materials with its electrochemical properties is biological sensors. In general, an electrochemical biosensor is an analytical device composed of an electrochemical transducer with a close contacted immobilized sensitive biomaterial (typically an enzyme).\textsuperscript{3} Thus a biological
1.1.3 Separations

Activated carbon has been widely used as sorbents in gas masks, water treatment and gas purification. Recently, extraction of a specific component from a mixture such as a side or main product with low energy consumption and sustainable process at ambient conditions has become a hot topic.\textsuperscript{24} To meet the requirements of rapid adsorption of biofuel or adsorptive desulfurization of various fuels (mainly macromolecules), ordered mesoporous carbon materials have been utilized. OMCs provide high adsorption capacity towards many organic compounds and due to its stable chemical and physical properties and interconnected pore structure, OMC is normally reusable. Bennett’s group\textsuperscript{25} reported utilizing CMK-5 as sorbents to adsorb dibenzothiophene (DBT) with high absorbability and recyclability. Additionally, the recovery of DBT from the adsorbents by toluene was almost 100%.

1.1.4 Heterogeneous Catalyst

One of the priorities in current society is finding alternative technologies that are safer, cleaner and more environmentally friendly. To achieve such an objective, renewable heterogeneous catalysts are important topics, it does not only simplify the step of separation of products and catalysts, but also promises the recyclability of the catalysts for a more sustainable process.\textsuperscript{26} Rather than homogeneous catalysts that work
under liquid state, heterogeneous catalysts hold the catalysts at solid state thus sufficient contact area and mass transportation is important. Though microporous materials gained huge success in the field due to their large surface area, adsorption properties and active sites that can be generated in the framework, their small pore size has limited their application to reactants with larger size or meeting the requirement of rapid mass transport.\textsuperscript{27} Moreover, large pore size allows surface modification which may block the micropores thus improved the efficiency of the catalysts.

Figure 1.4 a) The conversion of benzoaldehyde as a function of reaction time during the condensation reaction of benzoaldehyde with ethylene glycol; b) Catalytic activity of the reused OMS/C-SO\textsubscript{3}H microspheres. Reproduced with permission.\textsuperscript{28} Copyright 2012, Wiley-VCH.

A recent publication from Zhao’s group\textsuperscript{28} showed high catalytic conversion (Figure 1.4) using a sulfonated ordered mesoporous silica/carbon material for the condensation
reaction of benzaldehyde with ethylene alcohol. Additionally, this high conversion can be achieved fast and showed adequate recyclability after 10 times.

1.1.5 Drug Delivery

Intensive research conducted on utilizing mesoporous silica nanoparticles (MSN) for drug delivery showed increasing hydrophobic interaction between the surface of MSN and guest molecules can enhance the control of the release pattern. Hydrophobic drug carrier could penetrate the cell walls easily compare to that with hydrophilic surface. Thus, OMC became appealing materials for drug delivery due to its inert chemical properties and hydrophobic nature. Moreover, the large surface area guaranteed sufficient drug loading. A very important aspect for drug delivery is the drug release. The ideal drug releasing systems should maintain therapeutic concentration in the cell for a prolonged time since higher concentration would lead to toxicity while lower concentration would be ineffective. It is believed that the interconnected uniform pores and functionalized surface would improve the stable release; this also makes OMCs a powerful candidate.

1.2 Mesoporous Carbon Synthetic Methods

Among various kinds of mesoporous carbons, two types that exhibit uniform
mesopores attract the most interest: disordered and ordered mesoporous carbon (OMC). Our research focused on the latter: ordered mesoporous carbon material with periodically arranged mesopores. The uniform and tunable pore size and wall thickness of OMC promised identical transport and diffusion lengths for ions thus resulting in consistent and precise device performance.

1.2.1 Methods (Block copolymer template)

Significant research focused on ordered mesoporous carbons during the past years has indicated two synthetic routes based on polymer templates to be the most successful methods to obtain ordered mesoporous carbon. Hard template based on replication of silica and other material framework that were predetermined whereas soft template from direct formation of block copolymer template. Usually there is no significant chemical reaction between carbon precursors and template for hard templating, while chemical interactions such as hydrogen bonding, amphiphilic interaction and ion pairing between carbon precursors and template play an important role in the structure formation in soft templating method.

1.2.1.1 Hard Template

The first ordered carbon material from mesoporous silica templating is reported by
Bein et al.\textsuperscript{33} when they filled MCM-41 (a mesoporous silica material with cylindrical pores) with polyacrylonitrile via radical polymerization followed by carbonization.

But the first report of self-supported highly ordered mesoporous carbon was published by Ryoo et al.\textsuperscript{9} in 1999 when they exploited MCM-48 \textit{(Ia3d)} as a hard template and successfully synthesized CMK-1 (Figure 1.5, left), a cubically structured ordered mesoporous carbon with an average pore size of about 3 nm and narrow pore size distribution from nitrogen adsorption and desorption isotherms. But CMK-1 does not exhibit a true replica structure of MCM-48 ordered silica,\textsuperscript{34} this change of mesostructure was attributed to the displacement of relative position of these two non-interconnected frameworks after removing the silica template.

CMK-3 was then reported by the same group,\textsuperscript{35} which is a real inverse replica of the silica template SBA-15 that has interconnected hexagonal packed cylindrical mesoporous structure (Figure 1.5, right). SBA-15 mesoporous silica sieve was synthesized utilizing triblock-copolymer surfactant poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (Pluronic P123) as template. CMK-3 is composed by hexagonal packed carbon nanorods with bridges from the interconnected micropores of SBA-15.\textsuperscript{36} The authors also pointed out it is possible to tune the mesopore size by tailoring the pore wall thickness of SBA-15 silica template through controlling the ratio of HTAB and surfactants (C\textsubscript{16}EO\textsubscript{8}) in the surfactant mixture in the preparation of the silica template.\textsuperscript{37}
Another achievement made by Ryoo’s group is the fabrication of CMK-5 which exhibited similar structure of CMK-3. Rather than nanorods, CMK-5 is composed by hexagonal packed nanopipes with interconnected bridges. Due to the hollow nanopipes, CMK-5 showed high surface area of 2000 m$^2$/g and a total pore volume of 1.5 cm$^3$/g. This high surface area and large pore volume promised its remarkable performance as
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sorbent or electrodes for batteries.\textsuperscript{14} 

1.2.1.2 Soft Template

Though fabrication of OMC through hard templating has achieved huge success, the requirement of intermediate framework limited its generalization and also complicated the processing conditions. Thus, numerous research has been addressed synthesis of OMCs through direct templating from block copolymer (BCP) which is similar to the synthesis of ordered mesoporous silica.\textsuperscript{4}

Many approaches to OMC via soft template determined mesophase separation successfully but failed during template removal where the mesoporous structure either collapsed or could not be formed due to high carbon yield of templates. The first report of highly ordered mesoporous carbon from soft template route is the polystyrene-b-poly(4-vinylpyridine) (PS-P4VP)/resorcinol-formaldehyde system.\textsuperscript{40} Dai’s group indicated this route as 4 steps (Figure 1.6): 1) PS-P4VP and resorcinol mixture through hydrogen bonding and film coating; 2) determination of cylindrical mesostructure from solvent annealing; 3) utilizing formaldehyde gas polymerization with resorcinol to hold the structure; 4) carbonization of the polymer mixture to the OMC. This striking work not only achieved OMC through soft templating, but also obtained uniaxial alignment of vertical hexagonal packed cylindrical mesoporous structure.
In 2004, Tanaka’s group\textsuperscript{41} obtained OMC through soft templating using a commercial surfactant for the first time. Exploiting Pluronic F127 as template and resorcinol-formaldehyde and triethyl orthoacetate (EOA) as carbon precursors, they obtained hexagonal packed OMC. But the main advance came from Zhao’s group\textsuperscript{42} where they also used Pluronic surfactant (F127, P123 and F108) as template, but phenolic resol as carbon precursor and successfully fabricated OMC with various nanostructures. The five steps involved in the synthesis are summarized in Figure 1.7: 1) the synthesis of phenolic resol oligomer with alkaline catalyst (NaOH); 2) mixture of

Figure 1.6 Schematic of the synthetic procedure used to prepare well-defined carbon nanostructures using the PS-P4VP/resorcinol–formaldehyde system.

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template/resol complex and assembly; 3) thermal polymerization to crosslink the resol and hold the mesostructure; 4) removing the template by pyrolysis; 5) further heating to obtain carbon; or 4) sulfuric acid extraction of hydrogen and oxygen at 2:1 to determined OMC. They also reported through tuning the ratio of PEO to PPO in template and the ratio of template to resol, well defined OMC with different mesostructure can be achieved. This simple method with its large processing window has been widely accepted in producing OMC with soft templating.

Figure 1.7 Preparation of ordered mesoporous polymer and carbon frameworks with resol as carbon precursor. Reproduced with permission.\textsuperscript{42} Copyright 2006, American Chemical Society.
In a recent publication, Bein et al.\textsuperscript{43} indicated the mesophase separation takes place during the thermal polymerization step \textit{via in situ} grazing incident small angle X-ray scattering (GISAXS) measurement. Based on this new mechanism, we considered heating process would affect the structure formation and exploited the phenolic resol- Pluronic P123 methods to study the control of long range orientation of 2D packed ($c2mm$) cylindrical mesoporous carbon FDU-15 films.

Different to hard templating where the nanostructure was held by template frameworks during carbonization, soft templating suffers from pores shrinkage during template removing. To overcome this contraction, a triconstituent method was reported by Zhao’s group\textsuperscript{44} using TEOS and phenolic resol as co-precursor to form carbon-silica walls. The obtained porous material can be converted to OMC by etching the silica with HF or KOH or ordered mesoporous silica (OMS) by heating the carbon at 550 °C under air (Figure 1.8). OMC fabricated through the above method showed the highest surface area and pores volume to our best knowledge in OMC (higher than CMK-5): $2300 \, \text{m}^2/\text{g}$ and $2.1 \, \text{cm}^3/\text{g}$, respectively.
Figure 1.8 Triconstituent co-assembly to ordered mesoporous polymer-silica and carbon-silica nanocomposites, and the corresponding ordered mesoporous silica and carbon frameworks. Reproduced with permission. Copyright 2006, American Chemical Society.

1.2.2 Processing (film)

Though most research has been conducted on preparing ordered mesoporous carbon powders, there is a potential requirement for ordered mesoporous carbon films where easy recyclability, simple assembly, and/or large area fabrication is preferred. Moreover, continuous OMC films can also overcome the barrier caused by interface. Additionally, based on recent study on electrochemical double layer capacitors, OMC films showed remarkable performance since less amount of binder was utilized compared to that of powders. OMC film with binder such as Nafion\textsuperscript{45} has shown a
decrease in current which may cause by decrease in effective surface area of OMC films. Fortuitously, these soft templating syntheses can be in general applied to thin films by minor modifications such as the use of additives or otherwise narrowing of the processing windows.

Due to its simple and ease of operation, spin casting has been widely used as a general laboratory based process to obtain thin films with uniform thickness for relatively small areas on flat substrates. The principle of spin casting is using high angular speed rotation to spin solution off the edge of the substrate. The solvents exploited are usually volatile and the film thickness decreases with increasing rotational speed. Besides the limitation of small area fabrication, spin casting was also considered as a method that would waste massive amount material. To overcome the drawback mentioned above, a doctor-blade technique (flow casting)\textsuperscript{46} was applied. The doctor-blade technique has a minimal material loss and was primarily developed for large area thin film production. Similar as that of spin casting, a volatile solvent was also utilized. Uniform thin films were obtained by shear flow through dragging the solution across the substrate at a fixed speed. But different to spin casting, higher dragging velocity results in a thicker film. Moreover, changing the velocity continuously or discretely, films with gradient or stepped thickness can be cast. A horizontal flat plateau and uniform blade were usually preferred, otherwise heterogeneous thickness may appear. Dip coating is another popular method of producing uniform thin films on flat
substrates for research use. The substrate is first immersed in solution and then pulled up at a constant speed while the thin film is depositing on the substrate. Similar to doctor-blade casting, high velocity leads to thicker films and a volatile solvent is also used in dip coating. Since the substrate is immersed in the solution, it always requires large amount of material and will coat both sides of the substrate simultaneously.

1.2.3 Carbonization

Two different methods have been conducted for carbonization: pyrolysis and sulfuric acid extraction. Pyrolysis is a common way to carbon by heating the material up to 600 °C (or higher)\(^{42}\) under inert gas protection (Nitrogen or Argon). During pyrolysis fast degradation may generate large amounts of gas products that could possibly destroy the nano-structure, therefore a slow ramp rate is preferred prior to reaching the degradation temperature. OMC fabricated by pyrolysis are usually composed of abundant micropores in walls due to the condensation and degradation of materials. Exploiting 48 wt.% sulfuric acid\(^{42}\) can extract hydrogen and oxygen at the ratio of 2:1 from polymer or organics to form carbon, this method led to thick carbon walls and limited micropore formation.\(^{42}\)
1.3 Characterization Methods

A suite of characterization tools: spectroscopic ellipsometry (SE), small angle X-ray diffraction (XRD), grazing incidence small angle X-ray scattering (GISAXS), rotational grazing incidence small angle X-ray scattering, ellipsometric porosimetry (EP), atomic force microscopy (AFM) and transmission electron microscopy (TEM) were utilized to quantify the mesostructure and properties of FDU-15 films in this work.

1.3.1 Spectroscopic Ellipsometry

Ellipsometry is a sensitive, non-destructive and contactless optical technique that utilizes polarized light to determine the optical constants and thickness of thin films. It earns the sensitivity from the determination of the relative phase change in a beam of reflected polarized light. Since ellipsometry refers only to the measurement of the polarization state of a light beam (Figure 1.9), it does not have to measure the absolute intensity of the reflected light, which improves sensitivity and accuracy.
Figure 1.9  Geometry of an ellipsometer experiment, showing the p- and s- direction, a linear polarized incident beam was utilized and reflected off sample and the elliptically polarized light was measured by the detector. Reproduced with permission. Copy right J.A. Woollam CO. INC.

The measured data is the complex reflectance ratio $\rho$ (ratio of Fresnel reflection coefficients $R_s$ and $R_p$, s- and p- are oscillating perpendicular and parallel to the plane of incidence to the sample surface, respectively) which may be expressed as psi ($\Psi$) the amplitude component and delta ($\Delta$) the phase difference by:

$$\rho = \frac{R_p}{R_s} = \tan(\Psi)e^{i\Delta}$$

In general, the $\Psi$ and $\Delta$ cannot be converted directly into the optical constants or the thickness of the samples. Usually, a layer model is established. An iterative procedure with varied unknown optical and/or thickness parameters was used to calculate corresponding $\Psi$ and $\Delta$. The calculated $\Psi$ and $\Delta$ that match the experimental data best provide the final parameters (optical constants, thickness and anisotropy et al.) of the sample. Additionally, an infrared ellipsometer is best for thick films (100 nm - 50 $\mu$m),
while the visible and ultra-violet wavelengths are best for thinner films (0.1nm - 1 μm).

Spectroscopic measurements provide much more information about the samples than single wavelengths, and allow users to acquire data in spectral regions where the measured data are most sensitive to the model parameters which are to be obtained. Moreover, if the optical constant dispersion is known, it can be used to enforce some type of dispersion model (Cauchy or Lorentz et al.) to determine more accurate results.

The combination of variable angle of incidence and spectroscopic measurement provide the ability to acquire large amounts of data from a given sample. More importantly, it can also optimize the condition for data acquisition (at the best incident angle).

1.3.2 Grazing Incidence Small Angle X-Ray Scattering

![Diagram of scattering and GISAXS](image)

Figure 1.10 Schematic of scattering (left) and GISAXS (right) the incident angle $\alpha_i$ range between 0.05 and 1 degree, reproduced with permission;\(^47\) copyright 2012, American Chemical Society.
Grazing incidence small angle X-ray scattering (Figure 1.10, right) is a scattering technique used to determine the nanostructure of both surface and body of thin films. It is a combination of transmission small angle X-ray scattering (TSAXS) and grazing incidence diffraction (GID) and becomes an important aspect of SAXS. It exploits the structure and form factors from TSAXS and the low incident angle (near the critical angle) geometry from GID. Taking advantage of the nearly parallel incident beam, GISAXS explores large area and offers both in-plane and out of plane structure of the samples. As a member of the X-ray scattering family, GISAXS also applies the equation:

\[ q = \frac{4\pi \sin \theta}{\lambda} \]

where q is the scattering vector, \( \lambda \) is the wavelength of incident beam and \( \theta \) is the angle between scattering planes and incident beam. d-spacing then can be calculated by \( q = \frac{2\pi}{d} \). Due to the incident angle, a refraction correction is usually applied to the out of plane component of the scattering vector while the in-plane component is unchanged.

By rotating the sample stage in a certain angular range, preferred orientation of in-plane structure can be obtained by extracting the corresponding peak intensity and plot as azimuthal scan (Figure 1.11) which is similar to that of XRD.
1.3.3 Real Space Micrographs

Though X-ray scattering can measure the nano-structure precisely, real space micrographs is also preferred. Some conventionally used techniques for real space imaging are atomic force microscopy (AFM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

1.3.3.1 Atomic Force Microscopy (AFM)

Atomic force microscopy is a very high-resolution form of scanning probe microscopy (SPM). It is capable of measuring the topography of a sample with vertical features ranging in size from several micrometers to fractions of a nanometer while the
in-plane dimensions of the scanned area was demonstrated on the order of hundreds micrometers to Angstroms. To meet various requirements, different modes were established: contact mode, non-contact mode, tapping mode and peak force.

Figure 1.12  Schematic of AFM using a laser beam to detect the displacement of cantilever.

Tapping AFM obtains topography by tapping the surface with an oscillating tip. This eliminates the shear force that could potentially damage soft samples and reduce resolutions. It can also be applied under air or liquid conditions; it is now the most popular choice for AFM work. Similar to other SPMs, AFM takes advantage of a sharp probe which would significantly affect the resolution moving over the surface. The interaction force (mainly Van der Waals force, attractive) between the sample and tip is detected by the small displacements of the cantilever (Figure 1.12).
1.3.3.2 Transmission Electron Microscopy (TEM)

Electron microscopes are microscopes that exploit an electron beam to illuminate a sample and produce a magnified image. It can be classified as scanning electron microscope (SEM), reflection electron microscope (REM), scanning transmission electron microscope (STEM) and transmission electron microscope (TEM).

TEM is the original form of electron microscope, it utilizes a high voltage electron beam that transmitting through an ultra-thin sample to produce an image by the interaction of beam and sample. The resolution of TEM is tens of thousands times smaller than that of a light microscope at around 0.5 nm.

1.3.4 Pore Size Distribution

Pore size distribution (PSD) and pores volume are important aspects that impact the properties of OMC dramatically. N\textsubscript{2} adsorption and desorption isotherms (BET surface area and BJH pore size distribution), ellipsometric porosimetry (EP)\textsuperscript{49} and specular reflectance porosimetry (SRP)\textsuperscript{50} are commonly used methods to determine PSD for porous materials. N\textsubscript{2} adsorption and desorption isotherms required large amounts of porous materials compare to the others thus it is not suitable for PSD measurements that need to be conducted on thin films. EP and SRP share the similar concept in determination of PSD. In EP (Figure 1.13, left), a flow saturated by a low boiling point
adsorbate was utilized together with a dry air flow. Both were controlled with mass flow controllers. Changing the ratio of the flow in saturated adsorbate and dry air can tune the relative partial pressure ($p/p_0$) of mixed flow in a range of 0.0 - 1.0.$^{51}$

Figure 1.13  Schematic of ellipsometric porosimetry (EP, left) adapted from ref 49 with permission and adsorption and desorption isotherm curve with filling kinetics (right; ■, adsorption; ●, desorption).

Due to wall adsorption and capillary condensation, pores with small size are filled first with increasing $p/p_0$ and emptied with decreasing $p/p_0$ (Figure 1.13, right). Both EP and SRP exploit the idea of the Bruggeman Effective Medium Approximation for a three-component dielectric medium:

$$\frac{n^2 - 1}{n^2 + 2} = (1 - P) \frac{n_{np}^2 - 1}{n_{np}^2 + 2} + P \left( \frac{n_{np}^2 - 1}{n_{np}^2 + 2} \right)$$
where $n_w$ is the refractive index of the wall material (polymer) and $n_p$ is the refractive index of the pores (air or adsorbate). Through the use of two conditions (fulfilled and empty), $n_w$ and $P$ were determined by solving the equation. Thus, the adsorption and desorption process in volumetric change was then converted into detectable refractive index. The PSD was calculated through application of the Kelvin equation from the $p/p_0$ of adsorption isotherms.

$$r_k = \frac{2\gamma V_m}{RT \ln(p/p_0)}$$

where $r_k$ is the Kelvin radius, $\gamma$ is the surface tension of adsorbate, $V_m$ is the molar volume of adsorbate, $R$ is the gas constant, $T$ is the absolute temperature during sorption, and $p/p_0$ is the relative partial pressure of toluene during the adsorption.

The main difference between EP and SRP is how to determine the change in refractive index, the former uses spectroscopic ellipsometry while the latter utilizes reflectance spectra. Again, spectroscopic ellipsometry avoids the need to measure the reflected beam intensity while reflectance spectra allows measuring samples with backside reflection. In our study, we utilized EP to obtain the PSD of mesoporous thin films.
1.3.5 Wrinkling

Taking advantage of early work done by Whitesides et al.,\textsuperscript{52} theoretical and experimental studies of wrinkling have made significant progress. The basic idea of wrinkles is as follows:\textsuperscript{53} when compressing a stiff thin film that is attached to a compliant substrate with a small strain, the film would wrinkle at a characteristic wavelength to minimize the total energy due to the deformation of substrate and bending in the film. The wavelength of wrinkle abided of following equation:

\[
\lambda_f = 3\frac{E_s}{2\pi h} \left( \frac{\lambda}{2\pi h} \right)^3
\]

where \(E_s\) is the strain plane elastic modulus of the PDMS substrate and \(h\) is the thickness of the carbon film.

Figure 1.14 Optical images of various morphological patterns, demonstrating that the wrinkling patterns prefer to orient themselves perpendicular to the axis of principal compressive stress. Reproduced with permission.\textsuperscript{53} Copyright 2011 Wiley-VCH.
Since the stress can be applied in various methods: mechanical compression, thermal expansion and swelling or shrinkage, wrinkles with different shape can be generated (Figure 1.14), this led to multifarious patterns that can be used in tremendous fields. A major advantage of the wrinkle technique is that the elastic modulus of a thin film with a thickness on the order of nanometers can be calculated (from equation above) after measuring the microscale wrinkling wavelength which is easier to be measured. This simple and inexpensive route has been applied on various systems: ultrathin films, carbon nanotubes and porous materials.

In the following chapters, we utilized cooperative self-assembly method reported by Dr. Zhao’s group\textsuperscript{42} to investigate the impact of thermal annealing on 2D in plane packed cylindrical mesoporous carbon thin films. The relative kinetics of two competing processes (heat induced ordering and crosslinking of the phenolic resin) can lead to complications.

In Chapter II, we find significant enhancements in ordering of mesoporous carbon films prepared on quartz compare to silicon wafers. The role of annealing temperature on the porosity, pore size distribution and mechanical properties of the mesoporous films supported on quartz substrates are examined using ellipsometry and wrinkling, respectively. Improved long range order structure is confirmed by GISAXS, AFM and TEM. We attribute the significant differences between the films processed on silicon and
quartz substrates to their relative thermal conductivities and heat capacities. These results illustrate the subtleties associated with the thermally induced self-assembly process for mesoporous carbons and suggest that support selection will significantly impact the mesostructure.

Based on the results from Chapter II, we use a dynamic thermal gradient annealing technique, cold zone annealing (CZA) to obtain 2D cylindrical mesoporous carbon thin films with long range ordered structure and controllable in-plane uniaxial orientation. Rotational GSIAXS is exploited to qualify the directionality of annealed films. CZA generates flow in the annealing motion direction from the thermal gradient to shear-align 2D cylinders along the moving direction. Additionally, the edge of the substrate is approximately 10 °C higher in the thermal zone, which leads to orthogonal flow from differences in the crosslinking density and causes cylindrical structure packing transversely to CZA motion direction. By changing the sample translation velocity from 20 μm/s to 0.2 μm/s, in-plane cylinders can be arranged in different direction relative to moving direction with high uniformity ($S > 0.95$). Though pyrolysis leads to a slight loss of directionality, mesoporous carbon films can still exhibit an impressive orientational order factor ($S = 0.89$).

In Chapter IV, brief summery and unsettled problems are listed, addressing on further investigating of mechanism of this thermal induced cooperative self-assembly behavior and application of the uniaxial aligned ordered mesoporous carbon films.
CHAPTER II

ENHANCING LONG RANGE ORDER IN SOFT TEMPLATED MESOPOROUS CARBON FILMS (FDU-15) ON QUARTZ SUBSTRATES

2.1 Background

Porous carbons are ubiquitous in modern society ranging from the carbon black associated with printer toner\textsuperscript{54} to activated carbon in water purification\textsuperscript{55} to the carbon anode of Li ion batteries.\textsuperscript{56} Recent efforts have demonstrated the need to control both the size and shape of these pores to maximize the performance of porous carbons in emerging applications.\textsuperscript{57} Templated synthesis through self-assembly to create ordered porous carbons provides one facile route to controlling these factors.\textsuperscript{58} Initial reports for fabrication of ordered porous carbons involved hard templating\textsuperscript{9, 10} by which the mirror replica of an inorganic, typically silica, master is created in carbon through infiltration of precursor, carbonization and template removal steps. More recently, several soft templating approaches have been developed that enable a more direct synthesis of ordered porous carbons through templating of carbon precursor with surfactants\textsuperscript{12, 59} or block copolymers.\textsuperscript{40, 60} These templated porous carbons exhibit high surface area that enables significant adsorption of organics from aqueous streams,\textsuperscript{24, 61} high electrical
conductivity\textsuperscript{62} for electrochemical sensors\textsuperscript{63} and supercapacitor electrodes,\textsuperscript{64} while maintaining easily tunable pore sizes.\textsuperscript{65} In most cases, these ordered porous carbons are synthesized in the form of powders, but there are numerous applications where thin film or freestanding membranes would be preferable.

Fortuitously, these soft templating syntheses can be generally extended to thin films.\textsuperscript{40-41, 66} However, minor modifications requiring the use of additives\textsuperscript{41} or otherwise narrowing of the processing windows\textsuperscript{67} have been reported. Recently, Bein and coworkers\textsuperscript{68} demonstrated that the ordering in surfactant templated porous carbon films does not occur during solvent evaporation like for metal oxide films,\textsuperscript{69} but rather the structure evolves as the resol crosslinks during thermopolymerization. This ordering behavior is similar to neat block copolymer systems,\textsuperscript{70} but the neat systems do not have ordering limitations associated with crosslinking. It should be noted that crosslinking of block copolymers themselves has been shown to alter the phase diagram.\textsuperscript{71}

However, the similarity in ordering mechanisms between neat block copolymers and soft template mesoporous carbons suggests that processing ideas developed for block copolymers should be applicable for this system. For mesoporous metal oxide films, orthogonally oriented cylindrical pores can be obtained by surface modification of the substrate\textsuperscript{72} or epitaxy\textsuperscript{73} similar to these techniques being applied to neat block copolymers.\textsuperscript{74} Similarly, the original soft templating reports successfully fabricated cylindrical nanopores with perpendicular orientation by use of solvent vapor
annealing,\textsuperscript{40} which was developed for orienting block copolymer domains in thin films.\textsuperscript{75} Orientation of block copolymers can be controlled simply through selection of the annealing conditions, film formation method and film thickness.\textsuperscript{76} However despite numerous heating protocols from several different groups\textsuperscript{66a, 67-68, 77}, the typical Pluronic P123 directed synthesis of hexagonally packed cylindrical mesoporous carbon films (FDU-15) always exhibit parallel orientation of the pores when using silicon wafers as the substrate.

As the ordering in the film is thermally driven,\textsuperscript{68} how the film is heated could impact the process by which mesostructure evolves. Additionally, recent work has illustrated that the thermal conductivity of the substrate is a critical factor in the domain orientation of block copolymer films.\textsuperscript{78} To examine the role of heating on the mesostructure of mesoporous carbon films fabricated using organic-organic self-assembly, two dense substrates are utilized here to support the mesoporous carbon films: silicon and quartz. Both substrates exhibit similar surfaces (silicon oxide, RMS roughness < 2 nm, and water contact angle <10°), but their thermal conductivities vary by nearly 2 orders of magnitude. In the case of silicon wafers, their high thermal conductivity provides a conduit to deliver heat effectively to the film such that ordering likely occurs from the bottom of the film up. Recently, orienting block copolymer films using zone annealing with thermal gradients have illustrated the importance of substrate thermal conductivity to control the gradient width.\textsuperscript{78}
Here, we seek to alter the ordering process by utilizing quartz as a thermally insulating substrate. Using similar annealing temperatures as reported previously to generate parallel ordered cylindrical mesoporous carbon films on silicon wafers, we demonstrate that using quartz substrates can result in disordered, or highly ordered parallel mesopores depending upon the selection of crosslinking temperature. Moreover, these films can be readily removed from the quartz substrate after carbonization to yield freestanding mesoporous carbon films or attached to elastomers to elucidate mechanical properties through wrinkling.

2.2 Experiment

2.2.1 Materials and Film Fabrication

Phenol–formaldehyde resin (resol) was synthesized from formaldehyde (CH$_2$O, 37 wt.% in H$_2$O, Aldrich) and phenol (C$_6$H$_5$O, Aldrich) under alkaline condition using sodium hydroxide (NaOH, Aldrich) as described previously for organic-organic self-assembly. Following synthesis of the resol and titration to pH ≈ 7 by HCl (1 M), the aqueous solvent was removed by rotary vacuum evaporation lower than 50 °C. The resol was then dissolved at 20 wt. % in ethanol (Aldrich, ACS reagent grade, >99.5%) and NaCl was separated by precipitation. The average molecular weight ($M_n$) of the resol was quantified to be approximately 1400 g/mol using matrix-assisted laser desorption/ionization (MALDI, Bruker Ultra Flex III MALDI-ToF/ToF (tandem time-of-flight))
mass spectrometer). The molecular weight distribution from MALDI is provided in supporting information (Appendix A).

Pluronic P123 (BASF) was utilized as template agent. All chemicals were used without further purification. For fabricating the films, polished quartz wafers (GM Associates, INC) were used as substrates and cleaned using piranha solution (7:3 H₂SO₄:30 % H₂O₂, caution: extremely dangerous) at 90 °C for 30 min, followed by rinsing with deionized water. The cylindrical quartz pieces were 2.5 mm thick and 25.4 mm in diameter. The static water contact angle of quartz and silicon wafers cleaned by this method was determined to be approximately 5°-10° in both cases. Solutions consisting of Pluronic P123 and resol dissolved in ethanol at a molar ratio of phenol: P123 = 1: 0.007 were spin coated on cleaned quartz wafer at 4000rpm with acceleration 1370 rpm/s for 45 s to form the templated films. These films were first aged for 3h at ambient temperature in vacuum, followed by heating in a convection oven at 100 °C, 120 °C, 150 °C or 180 °C for 24 h to order the surfactant template and crosslink (thermopolymerize) the resol. For control experiments, films consisting solely of resol (without Pluronic P123) were prepared in the same manner on quartz. The crosslinked films were pyrolyzed at 350 °C (1 °C/min and held for 3 h at 350 °C) or 800 °C (1 °C/min to 600 °C, 4 °C/min for > 600 °C and held at 800 °C for 3 h) under N₂ atmosphere to remove the Pluronic template. The resultant films were mesoporous polymers or carbons, respectively. The nomenclature for the films is FDU-15-x-y in which x represents
annealed temperature and $y$ is the pyrolysis temperature, in °C. Some mesoporous carbon films were transferred from the quartz substrate to polydimethylsiloxane (PDMS) (Sylgard 184, Dow Corning) to determine elastic modulus via surface wrinkling$^{79}$. The PDMS was cast at a ratio of base: curing agent = 10:1 on flat glass and allowed to partially cure at ambient overnight. A second cure at 120 °C for 2 h, followed by 150 °C for 5 h was utilized to further crosslink the PDMS. The cured PDMS was cut into 25 cm x 25 cm squares for further use. The modulus of the PDMS was determined using a Texture Analyzer (TA-TX Plus) at a strain rate of 0.01 mm/s and found to be 2.69 MPa ± 0.1 MPa.

2.2.2 Characterization

A suite of characterization tools (spectroscopic ellipsometry (SE), X-ray diffraction (XRD), grazing incidence small angle X-ray scattering (GISAXS), ellipsometric porosimetry (EP)$^{49}$, atomic force microscopy (AFM) and transmission electron microscopy (TEM)) were utilized to quantify the mesostructure and properties of FDU-15 films.

2.2.2.1 Spectroscopic Ellipsometry and Pore Size Distribution

A variable-angle spectroscopic ellipsometer (M-2000UI, J.A.Woollam Co., $\lambda = 245$–1690 nm) was used to evaluate the thickness and optical constants of the films using
three incident angles. For measurements of the mesoporous polymer films, translucent cellulose tape (3M scotch) was placed on the backside to scatter the transmitted beam and prevent backside reflections through the transparent quartz substrate. Reflection angles of 65°, 70° and 75° were used, and the data were fit using the Cauchy model, while assuming an optically isotropic material. Introduction of anisotropic optical constants only marginally improves the fit, but the anisotropy is negligible. For measurements of the carbon films with SE, several modifications were made to improve the accuracy of the thickness and optical properties: the ellipsometric measurements were performed at 60°, 70° and 80° over the full range wavelength range along with transmission absorbance through the film and quartz. Both ellipsometric and transmission data were simultaneously fit using a B-spline model, which was later refined using a general oscillator model consisting of Gaussian and Lorentzian oscillators to ensure that optical constants are Kramers-Kronig consistent. In addition to thickness and optical constants, SE was utilized for determining the pore size distribution (PSD) of the mesoporous films by ellipsometric porosimetry (EP). Toluene was chosen as absorbent to fill the pores via capillary condensation. Partial pressure of toluene flow was controlled with mass flow controllers (MKS) by changing the ratio of the flow in saturated toluene and dry air to yield both adsorption and desorption isotherms. The PSD was calculated through application of the Kelvin equation from the adsorption isotherms.
where \( r_k \) is the Kelvin radius, \( \gamma \) is the surface tension of toluene (28.5 mN/m), \( V_m \) is the molar volume of toluene (106.3 mL/mol), \( R \) is the gas constant, \( T \) is the absolute temperature during sorption, and \( p/p_0 \) is the relative partial pressure of toluene during the adsorption. Additionally, the film porosity, \( P \), was estimated from the refractive indices, \( n \), of the neat film and after equilibration with nearly saturated toluene vapor by application of the Bruggeman Effective Medium Approximation and assuming that the neat film was composed of polymer and voids while the pores of the equilibrated film were completely filled by toluene as:

\[
\frac{n^2 - 1}{n^2 + 2} = (1 - P) \frac{n_w^2 - 1}{n_w^2 + 2} + P \left( \frac{n_p^2 - 1}{n_p^2 + 2} \right)
\]

where \( n_w \) is the refractive index of the wall material (polymer) and \( n_p \) is the refractive index of the pores (air or toluene). Through the use of two conditions, \( n_w \) and \( P \) were determined by solving equation 2. Examples for data analysis of the measurements are shown in Appendix A.

2.2.2.2 X-ray Diffraction and Scattering

To elucidate the ordered structure, XRD (D/MAX-2000+ with RA-HF 18 tabletop rotating anode X-ray generator) was used in a \( \theta/2\theta \) geometry with Cu K\( \alpha \) source (\( \lambda = 0.154 \text{ nm} \)) with resolution of \( \Delta q_z = 0.001 \text{ Å}^{-1} \) (convolution of \( \Delta \lambda \) and \( \Delta \theta \)). The angular
range for the diffraction was dependent upon the type of film being examined with $\theta = 0.25^\circ$ to 1.5$^\circ$ for annealed FDU-15 films, $\theta = 0.55^\circ$ to 1.5$^\circ$ for mesoporous polymer films, and $\theta = 0.85^\circ$ to 1.5$^\circ$ for the mesoporous carbon films. However, only periodicities in morphology through the film thickness were determined from XRD. Both in plane and through plane structure of these films was determined from GISAXS (X9 beamline at National Synchrotron Light Source at Brookhaven National Laboratory) using a beam of 13.5 keV ($\lambda = 0.0918$ nm) incident x-rays, focused to a spot 100 $\mu$m wide by 50 $\mu$m tall at the sample position. Scattering data were collected using a two-dimensional charge coupled device (CCD) detector, at a sample-to-detector distance of 1831.5 mm. Samples were measured in vacuum (~40 Pa), with x-ray incident angles both below the film critical angle ($0.07^\circ$) and above the critical angle ($0.12^\circ$, $0.25^\circ$) to elucidate the surface and bulk morphology of the mesoporous films. The GISAXS patterns that are shown in this manuscript are for an incident angle of $0.12^\circ$, but the out-of-plane analysis is based on both angles. Data conversion to from angle to q-space was performed using a silver behenate powder as a standard.

2.2.2.3 Real Space Micrographs

To complement the scattering measurements, real space micrographs of films were obtained using atomic force microscopy (AFM, Dimension ICON, Veeco) and transmission electron microscopy (TEM, JEOL 120keV). The surface morphology of the
porous polymer films of FDU-15-120-350 on quartz and silicon was investigated using AFM. Micrographs were obtained in tapping mode over 1 μm × 1 μm at 0.5 Hz using ACST tips (AppNano). To prepare the carbon film for TEM, the film was floated from the quartz substrate using 10 % KOH (aq) solution similar to previous reports for removal from silicon substrates\textsuperscript{83}. A small piece of the floating carbon film was then collected on a copper grid; the films supported on the TEM copper grid were carefully rinsed by deionized water. The grids were then air dried prior to TEM measurements. Capillary forces associated with the water appear to drive the carbon films to lie flat on the TEM grids to enable imaging through the thickness of the films.

2.2.2.4 Wrinkling

As the carbon films can easily be removed from the quartz substrates using KOH solutions, the films were transferred to PDMS substrates to induce wrinkling\textsuperscript{84}, which was utilized to determine the elastic moduli of the mesoporous carbon films. The transfer from quartz to PDMS involved placing the supported carbon film in intimate contact with PDMS and using vacuum at room temperature to remove any air gap for the PDMS to fully wet the carbon film. Subsequently the PDMS with the supported carbon film was immersed in 10 % aqueous KOH solution for 4-5 h to delaminate from the quartz. The transferred carbon films were rinsed with deionized water several times and dried at ambient temperature. Wrinkling was induced thermally by heating the
carbon film on PDMS at 150 °C for 4 h, then the laminated system was cooled to room
temperature. The wrinkled surfaces were characterized optically using 3-D imaging
microscopy (Zeta-20, Zeta Instruments). The strain plane elastic modulus of the films, $\bar{E}_f$, was determined from the wavelength of the wrinkles, $\lambda$, as:

$$\bar{E}_f = 3\bar{E}_s \left(\frac{\lambda}{2\pi h}\right)^3$$

where $\bar{E}_s$ is the strain plane elastic modulus of the PDMS substrate and $h$ is the
thickness of the carbon film based upon a semi-infinite, linear-elastic solution for the
instability.85

2.3 Result and Discussion

2.3.1 Optical Properties and Nano-Structure of Annealed Samples

Thermopolymerization of the resol leads to an increase in the optical absorption of
the FDU-15 films, which can clearly be seen visually due to the use of quartz as the
substrate. As all films are nearly the same thickness (ca. 700 nm) as determined from SE,
any differences in the adsorption properties would be intrinsic to the crosslinking state.
Figure 2.1 illustrates the impact of annealing temperature on the optical property of the
FDU-15 films as compared to pure resol films. An increase in refractive index related to
film densification as the annealing (thermopolymerization) temperature increases,
however $n$ is approximately 0.06 larger for the resol in comparison to the FDU-15 films.
This increase in $n$ is related to the optical adsorption of the film, which originates from the conjugation of the polymer; this result indicates that the crosslinked network that forms is strongly dependent upon the thermopolymerization temperature despite the long annealing time used (24 h). Interestingly, this temperature dependent adsorption is also observed for pure resol films, so the presence of the surfactant does not appear to be responsible for the differences in the crosslinked network. As the mechanical properties of the wall during carbonization have been found to be important for maintaining the ordered structure\textsuperscript{67}, these differences in the crosslinked network for the resol may be important in determining the final mesostructure of the films.

Figure 2.1 Refractive indices (at $\lambda = 633$ nm) of FDU-15 (■) and pure resol (○) films, after annealing for 24 h.
In addition to crosslinking of the resol, the thermopolymerization temperature is known to impact the ordering of the resultant mesoporous carbons with the ‘best’ order for powders obtained at 120 °C\textsuperscript{86}. Figure 2.2 illustrates the GISAXS patterns for the annealed and thermopolymerized films of FDU-15 on quartz. From examination of the scattering profiles, all four films exhibit a near-hexagonally packed cylindrical mesostructure (c2mm) consistent with FDU-15 as reported previously on a silicon substrate\textsuperscript{68}. Due to pinning of the film to the substrate, there is a slight contraction in the mesostructure in z direction due to shrinkage during crosslinking (with a corresponding expansion of the reciprocal-space GISAXS peaks along q\textsubscript{z}). This non-hexagonal structure is evident from the ratio of d-spacing out-of-plane to that in-plane (d\textsubscript{z} / d\textsubscript{x}) of 1.6 at 120 °C, which is less than \sqrt{3} expected for hexagonal packing based upon the orientation of the mesostructure.
By simulating the positions of the Bragg peaks as described previously\textsuperscript{82,87}, the contraction of the unit cell in the z-direction is found to be temperature dependent with the compression being 0.93, 0.90, 0.87 and 0.73 for 100, 120, 150, and 180 °C, respectively. Additionally, the in-plane lattice parameter increased (14 nm, 14.5 nm, 15.5 nm and 17 nm) as the thermopolymerization temperature increased. These significant
changes in the mesostructure provide some evidence of the importance of heating on the developed morphology. The position of diffraction maxima along $q_x$ are approximately in a ratio of 1:2:3, for all films except FDU-15-180 where fewer higher-order peaks are present. These ratios for reflections are a result of orientation of the film, which limits which diffraction peaks are observed in a given direction, and anisotropic contraction during thermopolymerization (additional discussion is available in Supporting Information (Appendix A)). To explain the decrease in the number of diffraction peaks for FDU-15-180, the relative rates of ordering (chain mobility) and network formation (crosslinking) are important. At 180 °C, the rate of crosslinking appears to approach that of ordering to kinetically trap the mesostructure before defects can be annealed out of the film. We have previously illustrated that for block copolymer templates with relatively high $T_g$ (>100 °C), segments can be kinetically trapped in poorly ordered states due to the sluggish mobility of the template relative to the rate of thermopolymerization \(^88\). Similar reasoning can be applied to the decreased long range order for the FDU-15-180 as assessed by the loss of higher-order reflections in its GISAXS profile relative to analogous films that are crosslinked at lower temperatures. However, there are limited differences in the scattering for the other thermopolymerization temperatures examined despite the significant differences in the optical properties (Figure 2.1).
2.3.2 Optical Properties and Nano-Structure of Template Removed Samples

Figure 2.3 GISAXS patterns for: A, FDU-15-100-350; B, FDU-15-120-350; C, FDU-15-150-350; D, FDU-15-180-350. For both A and B, one diffraction peak \((hk5)\) is missing in comparison to Figure 2.2, while addition peaks are missing in C. More strikingly, no structure remains after template removal for FDU-15-180.
By removing the template at 350 °C, differences in the structures for the different thermopolymerization conditions become more pronounced as shown in Figure 2.3. If only the template is removed, the contrast between cylindrical pores and matrix would be enhanced, but some additional crosslinking of the resol occurs during the template removal.

This later change results in stresses in the system that can distort the ordered mesostructure. For FDU-15-100-350 and FDU-15-120-350, the distortion of the lattice appears to be minimized with similar higher order reflections visible in the GISAXS profiles after template removal (Figure 2.3A and 2.3B) and the analogous thermopolymerized films (Figure 2.2A and 2.2B). Moreover, FDU-15-120-350 appears to be more highly ordered than previously reported analogous films on silicon wafers as evidenced by the increased number of diffraction peaks and the decrease in the width of the primary diffraction peaks. Interestingly for the films annealed on quartz, increasing the temperature for thermopolymerization to 150 °C appreciably impacts the structure after template removal at 350 °C (Figure 2.3C). The GISAXS profiles are still consistent with c2mm space group, but there is a loss of the higher order reflections for FDU-15-150-350.
Table 2.1 Impact of processing conditions on film contraction and refractive index

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<tbody>
<tr>
<td>Contraction†</td>
<td>350</td>
<td>44.0%</td>
<td>44.5%</td>
<td>43.4%</td>
<td>43.4%</td>
</tr>
<tr>
<td></td>
<td>800</td>
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<td>63.5%</td>
<td>65.8%</td>
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<tr>
<td>Refractive Index</td>
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<td>1.688</td>
<td>1.704</td>
<td>1.767</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>2.378</td>
<td>2.140</td>
<td>2.146</td>
<td>2.153</td>
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† Contraction was determined from change in thickness using ellipsometry with comparison to the annealed sample.

More striking is the difference in the GISAXS profiles for FDU-15-180 (Figures 2.2D and 2.3D) where the ordered structure is completely lost upon template removal. Despite these significant differences in the GISAXS profiles, the film shrinkage during template removal is relatively constant at approximately 44% contraction from ellipsometry (Table 2.1). This is slightly larger than the z-contraction determined from changes in the d-spacing in q_z from GISAXS (39%) and XRD (37%) for all the films except FDU-15-180-350. In addition to the z contraction, there is a slight decrease in d_x for all film (except FDU-15-180-350) of approximately 1 nm. Typically for mesoporous metal oxide films, uniaxial contraction is assumed due to pining at the substrate, but there appears to be sufficient mobility for the FDU-15 films to reorganize to relive some stresses associated with crosslinking to allow contraction of approximately 1 nm (6.5–7.1%) in the in-plane d-spacing during template removal. However, the d-spacing through the plane of the film does contract significantly more than in-plane during the
calcination at 350 °C. Additionally, the refractive indices \( n \) of the films are determined from SE with small differences in \( n \) between the films calcined at 350 °C (1.68-1.70) where highly ordered structures are clearly present in the GISAXS patterns, while there is a significant increase in \( n \) for FDU-15-180-350 (1.75). This increase in \( n \) corresponds to decrease in film porosity that occurs as the thermopolymerization temperature is increased. It is intriguing that systems that are better crosslinked initially exhibit lower porosity after template removal.

The porosity of these films (14.6%, 10.9% and 9.6% for FDU-15-100-350, FDU-15-120-350, and FDU-15-150-350, respectively) are less than we have reported previously\(^9\), but the molar ratio of phenol: P123 is only 0.007 here. As this molar ratio decreases from 0.013 to 0.01 to 0.007, the porosity decreases from 19.6 % to 14.0 % to 10.9 % for FDU-15-120-350. It is important to note that the range of compositions available to fabricate the FDU family of mesoporous carbons can significantly impact the properties of the resultant material even if the same space group is produced.

To further investigate the structure of these mesoporous polymer films, ellipsometric porosimetry (EP) is used to estimate the pore size and its distribution in these films. Figure 2.4A illustrates the toluene absorption and desorption isotherms associated for each of the films. The isotherms conform to the standard Type IV isotherms that are typical for mesoporous materials with a clear hysteresis loop between \( p/p_0 = 0.15 \) and 0.35. There are, however, subtle differences in the isotherms
that provide insight into how annealing conditions impact the film morphology after template removal. First, the slope of the isotherms at low partial pressures ($p/p_0 < 0.2$) is significantly greater for FDU-15-100-350 than the other two films. This low partial pressure slope is associated with the surface area of the material from B.E.T. theory$^{91}$; this increase in surface area is likely associated with the presence of micropores in the framework of the mesoporous structure$^{92}$. Additionally, the sigmoidal shape of the adsorption isotherm within the hysteresis loop is significantly broader for the FDU-15-150-350, which suggests a broader pore size distribution for this film in comparison to those thermopolymerized at lower temperatures.

![Figure 2.4 Absorption and desorption curve and pore size distribution for FDU-15 pyrolyzed at 350°C (FDU-100-350 circle, FDU-120-350 triangle, FDU-150-350 square); A, toluene absorption (solid) and desorption (open) curve for template removed FDU-15 film at room temperature (offset has been applied); B, pore size distribution ($r_k$) calculated from the Kelvin equation for template removed FDU-15 polymer film.](image-url)
To better understand the pore structure, the PSD is determined from the adsorption isotherms by application of the Kelvin equation as shown in Figure 4b. The pore size distribution (PSD) is influenced by selection of thermopolymerization temperature; both FDU-15-100-350 and FDU-15-120-350 exhibit a relatively narrow PSD, but the average (mode) pore radius shift from 1.57 nm to 1.92 nm for thermopolymerization at 100 °C and 120 °C, respectively. A much broader PSD is found for FDU-15-150-350 with an average (mode) pore radius of 1.51 nm. This increase in the breadth of the PSD is consistent with a less ordered (more heterogeneous) mesostructure that is determined from GISAXS (Figure 2.3C).

In addition to the porosimetry and GISAXS measurements, the surface morphology of FDU-15-120-350 was examined using AFM as shown in Figure 2.5. Despite the small \( d_x \)-spacing (ca. 14 nm) for the ordered domains, which are similar in size to the curvature of the AFM tip (ca. 10 nm), an ordered mesostructure can clearly be seen in the micrograph. For the film supported on quartz, long-range order of the cylinders is clearly present with well-preserved orientation and long-range order of the self-assembled structure. However, no external field has been applied to produce such an orientation, but rather it appears that large ordered domains can readily form on the quartz substrate. Thus, it is the large grain size that provides for the increase in the number of visible diffraction peaks in GISAXS. The large grain can be clearly ascertained from the FFT of the AFM micrographs as shown in the inset in Figure 2.5. The FFT yields two
crescents whose radii are associated with the average \( d_x \)-spacing, but the azimuthal width of the crescent is associated with the extent of local orientational order (due to the large grain size) of the cylindrical domains. Conversely when an analogous film that has been processed identically except for the support being silicon, only small ordered domains exist similar to those reported previously for mesoporous silica-carbon films on silicon wafers\(^77\). There has been a significant interest recently in obtaining long-range orientation of cylinders in block copolymer films\(^93\) with a variety of techniques examined that are far more complex than simple heating shown here. The large ordered domain sizes associated with FDU-15 on quartz suggests that additional enhancements in the orientation can be readily achieved with one of the aforementioned block copolymer techniques of shear alignment\(^93c\), zone annealing\(^93a\), or epitaxy\(^93b\) while using quartz or another low thermal conductivity substrate. Moreover, the long-range order associated with the FDU-15-120-350 on quartz as assessed by AFM is consistent with the presence of additional higher order reflections in GISAXS in comparison to FDU-15 films supported on silicon wafers.
Figure 2.5  AFM micrographs of mesoporous FDU-15-120-350 on (A) quartz and (B) silicon substrates. Inset illustrates the FFT of the micrograph in A to illustrate the orientation of the cylindrical mesopores.

2.3.3 Mesostructure Determined from GISAXS and TEM

The mesoporous polymer can be converted to carbon by increasing the pyrolysis temperature to 800 °C. Figure 2.6 illustrates the GISAXS patterns for these mesoporous carbon films. All films irrespective of their initial thermopolymerization temperature appear to exhibit a decrease in their higher order peaks in GISAXS, but diffraction peaks associated with the distorted hexagonal packed cylindrical structure clearly remain upon visual inspection. During carbonization, there is an additional decrease in the film thickness (decrease of 63-67 % of initial thickness after thermopolymerization), which is not strongly dependent upon the annealing temperature. There is a concurrent decrease
in the d-spacing associated with the film contraction with a slightly smaller, but similar $d_z$, after carbonization for all 3 films. In contrast, $d_z$ is unchanged in comparison to $d_z$ at 350 °C, which is consistent with uniaxial contraction of the film during carbonization. The compression of the hexagonal unit cell after carbonization is approximately 0.37, which is consistent with the film thickness contraction. This contraction of the film impacts the apparent quality of the diffraction patterns due to pushing the out-of-plane peaks to larger $q_z$. The form factor decreases roughly as $\frac{1}{q_z^2 + q_z^2}$, which can make higher-order peaks appear quite weak. This decrease in scattering intensity due to the large contraction during carbonization makes it difficult to address any potential changes in long-range order perpendicular to the substrate.

Figure 2.6 GISAXS profiles for FDU-15 films after carbonization at 800°C for (A) FDU-15-100-800, (B) FDU-15-120-800 and (C) FDU-15-150-800.

However in examination of the GISAXS profiles after carbonization, both FDU-15-100-800 and FDU-15-120-800 exhibit additional higher order reflections than has been previously reported for carbonized FDU-15 films supported on silicon wafers$^{66a}$. 

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This improved ordering can also be seen through examination of FDU-15-120-800 using TEM as illustrated in Figure 2.7. In this film, the d-spacing is approximately 12-14 nm from TEM, which is consistent with $d_\alpha$ determined from GISAXS (13.5 nm). The critical observation is that the average grain size of the ordered domains in the mesoporous carbon is at least 1 $\mu$m$^2$ from the micrographs examined. With the $d_\alpha$-spacing of $\approx 14$ nm, this domain size corresponds to nearly 80 repeats of the ordered structure for square domains. Also as this micrograph is obtained in transmission through the film thickness, these oriented domains are aligned through the thickness (240 nm) of the film to provide the contrast. Thus the long range order is preserved in these mesoporous carbon films even through carbonization as suggested by large number of higher order reflections present in the GISAXS profiles for FDU-15-100-800 and FDU-15-120-800.
2.3.4 Wrinkling of Highly Ordered Carbon Thin Films

In addition to the structure, the mechanical properties are an important aspect to the suitability of these mesoporous carbons to applications such as membranes, sensor electrodes, and electrodes for supercapacitors. To elucidate the modulus of the carbon films, a metrology based upon wrinkling instabilities is utilized. Figure 2.8 illustrates the structure of the wrinkles obtained for the mesoporous carbon films.

The important feature for elucidating the modulus from the wrinkle pattern is the wavelength of the sinusoidal wrinkles. Elastic moduli of these mesoporous carbon films is approximately 60 GPa, which is approximately 6-7 times that obtained from
nanoindentation for FDU-16-120-800 (cubic array of spherical mesopores) that was processed on silicon. However, the modulus for the FDU-15 films examined here is still only approximately 60% that for glassy diamond-like carbon films as might be expected due to the amorphous and porous nature of FDU-15.

For comparison of the mechanical properties, it is well established that introduction of voids will decrease the modulus of the material, but the scaling of modulus with porosity depends upon the arrangement of the pores in the matrix. To understand the scaling associated with these highly order mesoporous carbons, the porosity of the films is needed. To estimate the film porosity, we assume that the carbonized resol is essentially dense and its refractive index is identical to $n$ for the carbon framework in the mesoporous carbon films. Application of the Bruggeman effective medium approximation (Equation 2) yields the film porosity on the basis of the refractive index of the mesoporous carbon films (Table 2.1). Figure 2.9 illustrates how the modulus of these mesoporous carbon films is impacted by the film porosity. As the films become more porous ($P > 10\%$), there is a significant decrease in the elastic modulus of the film. The rate of this decrease in moduli is significantly greater than expected for ordered porous materials. Nonetheless, the moduli for these mesoporous carbons are significantly greater than previously reported for ordered mesoporous carbons fabricated on silicon. These results illustrate that the enhancements in long-range order of mesoporous films can dramatically increase the modulus of the films by at least of factor of 5. For
applications, this increase in mechanical properties is likely critical to the long-term reliability of mesoporous carbon membranes.

Figure 2.8 3-D optical micrographs of the wrinkle structure for FDU-15-150-800. The sinusoidal structure associated with the wrinkles can be clearly seen.

Figure 2.9 Modulus-porosity scaling relationship for FDU-15 mesoporous carbon films.
To explain the significant differences between mesoporous carbon films prepared on silicon and quartz, the heat transfer associated with the annealing must be considered. In both cases, the transfer from air to the films and substrate should be similar due to the poor thermal conductivity of air. However, the thermal properties of silicon and quartz are quite different. The silicon will heat much faster than quartz due to its lower heat capacity (~20 versus ~45 J mol\(^{-1}\)K\(^{-1}\)) and larger thermal conductivity (~150 versus ~1 W m\(^{-1}\)K\(^{-1}\))\(^99\). As the thermal conductivity of commercial phenolic resins is approximately 0.2 W m\(^{-1}\)K\(^{-1}\), we hypothesize that heat conduction from the silicon to the film will contribute significantly to equilibrating the FDU-15 film. Conversely, the similarities in thermal conductivity between quartz and phenolic resin suggests that the heat will be primarily transported to the FDU-15 film from the air (free convection). Future work will focus on additional substrates of varying thermal conductivity including polymer substrates to enable direct synthesis of free-standing mesoporous carbon films.

2.4 Concluding Remarks

In this section, highly ordered mesoporous carbons films are fabricated on low thermal conductivity quartz substrates were discussed. Despite the physicochemical similarity to silicon, there is a tremendous improvement in the long range ordering of the mesoporous carbon films prepared on quartz. More generally, this illustrates the role of substrate thermal properties, such as thermal conductivity and specific heat capacity,
on the ability to tune mesoporous carbon structures as a processing tool for desired microstructures. This improvement is dependent upon temperature of the thermopolymerization; highly ordered structures are obtained and maintained through carbonization at 100°C and 120 °C, while the ordered structure collapses upon template removal for the film thermopolymerized at 180 °C. Additionally, the thermopolymerization temperature impacts the porosity and pore size distribution. For FDU-15-120-800, TEM illustrates the large ordered grain size extends through the thickness of the film. Finally, the mechanical properties of the mesoporous carbon films were elucidated through transfer from quartz to PDMS and wrinkling of the attached mesoporous carbon film. The moduli of these films are significantly greater than those previously reported for mesoporous carbon films supported on silicon, presumably the improved long-range order also increases the mechanical properties of the films. These results illustrate the importance of the substrate on fabrication of ordered mesoporous carbons films through cooperative self-assembly, which has serious implications for the use of these materials as asymmetric supported membranes.
CHAPTER III

3. LONG RANGE ORIENTATION IN MESOPOROUS CARBON FILMS WITH DYNAMIC THERMAL ZONE ANNEALING

3.1 Background

Ordered mesoporous materials have generated tremendous interest due to their potential application in numerous areas including energy storage \(^3\) electrodes for batteries, \(^{15,14}\) fuel cells, \(^{100}\) and supercapacitors, \(^{83,101}\) sorbents for separation; \(^{102}\) heterogeneous catalyst supports; \(^{28}\) drug delivery; \(^{103}\) and biological sensors. \(^{24}\) From the initial reports of ordered mesoporous silicates, \(^{5}\) there has been interest in extending the framework chemistry to other materials, including metal oxides, \(^{7,104}\) metals, \(^{6}\) and carbons. \(^{10}\) Mesoporous carbons, in particular, have garnered significant interest due to their chemical stability and electrical conductivity, but their commercial applicability has been limited by the processing intensive hard-templating \(^9\) approach, which is based upon infiltrating mesoporous silica with a carbon precursor and removal of the silica template after carbonization. Soft-templating \(^{12,59}\) enables direct fabrication of mesoporous carbons by cooperative assembly of carbon precursors and surfactants. Though most research has focused on powders, mesoporous carbon thin films offer unique advantages including facile self-assembly over large areas, which can be applied
to their application as electrodes\textsuperscript{83} and membranes.\textsuperscript{95} Moreover, considerable advances have been made in tuning mesopores size and geometry,\textsuperscript{4} but controlling the orientation of these pores remains challenging.

For mesoporous silica films, several methods exist to produce uniaxial in plane packed mesopores: rubbed polyimide thin films as patterned substrates,\textsuperscript{105} physical epitaxy on a mesostructured template,\textsuperscript{106} magnetic fields,\textsuperscript{107} and flow casting\textsuperscript{108} can induce uniaxial alignment. However, the quality and extent of the orientation can vary greatly. For mesoporous carbon films, the number of demonstrated methods for orientation is substantially less. Tang \textit{et al.}\textsuperscript{109} fabricated plane packed uniaxial aligned lamella carbon thin films from zone casted poly(butylacrylate-b-acrylonitrile) (PBA-b-PAN), but this method requires high casting temperature and a novel template that must be custom synthesized. Moreover, this structure cannot be readily removed from the substrate without its collapse. One of the first reports of soft templated mesoporous carbons by Dai and coworkers demonstrated striking out-of-plane alignment of cylindrical mesopores in carbon films through controlled solvent evaporation by solvent vapor annealing.\textsuperscript{40} Unfortunately, this method uses a specialty template and the solvent vapor exposure cannot be readily translated to industry.

However, most methods for fabricating ordered mesoporous materials use block copolymers (BCP) as a template for the structure. Numerous routes have been demonstrated for alignment of self-assembled BCP films, including external fields such
as a magnetic field, epitaxy, shear, raster solvent vapor annealing, zone casting, and chemically or topologically patterned substrates. Though these methods enable alignment of 2D packed cylindrical block copolymer structure, they suffer from challenges in their mass adoption, especially for large areas, as they are too complex, too expensive, or require very controlled environments for the alignment. By comparison, a recently developed method for BCP ordering and alignment, termed cold zone annealing (CZA), is a dynamic thermal field annealing technique wherein the sample is passed through a controlled temperature gradient (VT) at a pre-specified rate. CZA is based on the idea of zone annealing or zone refining that was originally developed for refining polycrystalline semiconducting metals by Pfann. Lovinger et al. introduced zone annealing to semicrystalline homopolymers with the polymer morphology being strongly dependent on temperature gradients, growth rate and degree of super-heat. Bodycomb et al., Angelescu et al. and Berry et al. further extended the idea of zone annealing to bulk BCPs as well as BCP thin films. In the CZA methodology, the maximum temperature (TMAX) of the temperature gradient is lower than the order-disorder transition temperature (TODT) of the BCP, but TMAX is above the glass transition temperature (Tg) of the BCP (i.e. Tg < TMAX << TODT). Thus, the thermal field induces polymer mobility, but does not drive the system into a disordered phase. CZA of BCP thin films under a shallow VT (VT < 20 °C/mm) leads to horizontally oriented cylinders with modest orientation control, faster ordering kinetics and improved
long-range order in comparison to uniform oven heating. More recently, Singh et al. demonstrated that CZA annealing of BCP thin films with a much sharper $\nabla T$ ($\nabla T \approx 45 \degree C/mm$) leads to hexagonally close packed vertically oriented cylinders, whereas CZA in conjunction with an induced shear field, self-generated from an elastomeric capping overlayer leads to rapid fabrication of highly oriented horizontal cylinders with an angular spread less than $5\degree$. The most important and practical advantage of the CZA method over other techniques is the facile adaptation to roll-to-roll processing that is highly attractive for industrial scale-up purposes.

BCPs can be designed to directly transform to mesoporous carbons, but a challenge with BCPs is intrinsic limitations associated with obtaining reasonably high segmental block interaction parameter $\chi$, in addition to requiring a large molecular weight ($N$) to microphase separate ($\chi N > 10.49$). As a result of the large $N$, they suffer from large pore sizes and poor segmental mobility. One route to overcome these limitations is through blending with hydrogen bonding additives that selectively interact with one block. Zhao and coworkers demonstrated the cooperative assembly of low molecular weight BCP (Pluronic P123) with phenolic resin oligomer (resol) that leads to well-ordered cylindrical mesostructured blends. Pyrolysis of these polymer blends yields mesoporous carbon (FDU-15) with this route equally applicable to films. Careful examination of the structure formation of these films by Bein and co-workers demonstrated thermal induced self-assembly (TISA), rather than common evaporation
induced self-assembly. This TISA process is analogous to the assembly of neat BCPs and thus we hypothesize that most processing techniques developed for BCP films can be applied to these templated mesoporous carbon films. Here, we apply the CZA technique to FDU-15 films in order to align the cylindrical mesopores. Interestingly, the moving rate during CZA provides a knob to controlled 2D in-plane packed cylinders within a range of 180° (-130° to 50° relative to moving direction) as determined by grazing incidence small angle x-ray scattering (GISAXS). Moreover, near perfect alignment of the cylinders is obtained when the alignment is parallel or transverse to moving direction. With the aim of understanding the mechanism by which the orientation is controlled, ellipsometry is used to map the thickness of the film after CZA. Ellipsometric measurements of film thickness provide evidence for two types of flow (parallel and transverse) generated during CZA that leads to different mesostructure orientation. Most importantly, the high orientational factor (S ~ 0.9) and preferential alignment is maintained through carbonization, although there is some loss in the orientation of the aligned cylinders. The extent of this loss is strongly correlated with the time that the local (i.e., the film area exposed to the hot filament) polymer film was exposed to elevated temperatures. For the best mesoporous carbon film, the orientational order factor is still 0.89 after carbonization. These results demonstrate the potential for developing highly oriented mesoporous films through CZA, important for a number of potential applications of mesoporous films requiring anisotropic transport properties.
3.2 Experiment

3.2.1 Materials and Film Fabrication

The polymer complex was synthesized and cast as mentioned in Section 2.2.1. Phenolic resol was synthesized from formaldehyde (CH$_2$O, 37wt.% in H$_2$O) and phenol under alkaline condition using sodium hydroxide (NaOH) as reported previously. To synthesis FDU-15, Pluronic P123 was added in 20 wt.% resol in ethanol at mole ratio of phenol: P123 = 1: 0.007. The solution was then spin cast on piranha solution treated quartz substrate (G.M. Associates, Inc.) at 4000 rpm. After drying under vacuum for 3 h at ambient temperature, the sample was cold zone annealed at 150 °C with different moving velocities: 0.2 μm/s, 0.5 μm/s, 1.5 μm/s, 2.0 μm/s, 10 μm/s and 20 μm/s.

The cold zone annealing apparatus (Figure 3.1) used here is modified from the design concept demonstrated by Lovinger et al. A low resistance (0.025 Ω cm$^{-1}$) nickel-chrome wire covered with ceramic insulation is utilized to form the hot region. The wire is powered by a high current source (Digital DC Power Supply, Model 1692, B&K Precision Corp.). CZA temperature (Maximum Temperature) can be tuned by adjust the set current. A chiller system (Julabo F12 – ED refrigerated/heating circulator) is exploited to circulate low molecular weight PDMS oil (“Thermal C10” Julabo USA Inc.) at -5 °C which was filled in the two cold blocks. A thermal IR imaging camera (Testo 875 Thermal Imager Kit) was used to characterize the temperature gradient. Further carbonization
was taken at 800 °C (1°C/min to 600°C, 4°C/min > 600 °C and held at 800°C for 3 h) under N₂ atmosphere.

3.2.2 Characterization

Thickness profile was determined by spectroscopic ellipsometer (M-2000UI, J. A. Woollam Co., λ = 245–1690 nm) mapping mode at 65°, 70° and 75° using Cauchy model. Translucent cellulose tape (3M scotch) was placed on backside of quartz to prevent backside reflection. Rotational GISAXS was carried out at X9 beamline at National Synchrotron Light Source at Brookhaven National Laboratory. X-Ray beam with wavelength = 0.0918 nm (13.5 keV) was utilized at incident angle of: 0.07 °, 0.10 ° and 0.15 ° (data shown in this chapter was determined at 0.15 °). The 2D scattering data was collected by a coupled charge device (CCD) detector.
3.3 Result and Discussion

3.3.1 Dynamic Thermal Zone Annealing

Figure 3.1 Schematic of CZA, consist of a syringe pump that translates the sample through thermal zone formed by hot wire in the middle of two cooling stages at a fixed speed.

Figure 3.1 illustrates schematically the cold zone-annealing (CZA) instrument that consists of a heating wire, two cooling stages and a syringe pump to control the translation of the film. This geometry of the heating wire sandwiched by cooling stages yields a sharp thermal gradient (30 °C /mm) on quartz substrates that are coated with an FDU-15 film. The sample is then translated across the thermal zone at a fixed velocity. While in the thermal zone, the film is subjected to a large temperature gradient as illustrated in Figure 3.2.
As the maximum temperature applied during zone anneal (center of hot region) is lower than $T_{\text{ODT}}$ of BCP but higher than $T_g$ for CZA, we selected $T_{\text{MAX}} = 150 \, ^\circ\text{C}$ as this is above $T_g$ for both phenolic resol and P123 and this temperature has been shown to be effective for ordered FDU-15 films. However, this ordering is not reversible due to the crosslinking of resol. Ordering and crosslinking of the resol-Pluronic mixture is effective at temperatures greater than 100 $^\circ\text{C}$, by examination of the temperature profile (Figure 3.2), the effective heating zone is approximately 0.6 cm long that is moving during CZA, which yields an effective heating time of $t = \frac{6 \times 10^5 \, \mu\text{m}}{\text{Velocity} \, (\mu\text{m/s})}$. 

Figure 3.2 Temperature profile of thermal zone.
In order to assess the 3D structure of the films after CZA, grazing incidence small angle X-ray scattering (GISAXS) with sample stage rotated through azimuthal angle \( \phi \) (in plane) is used as illustrated in Figure 3.3. For comparison, the moving direction of sample is defined as \( \phi = 0^\circ \). We define the nomenclature for the CZA annealed FDU-15 films as FDU-15-150-x, where 150 is \( T_{\text{MAX}} \) for the process in degrees Celsius and \( x \) (\( \mu \text{m/s} \)) indicates the moving velocity applied to sample during CZA.
3.3.2 Rotational GISAXS of Annealed Films

Figure 3.4 GISAXS patterns (incident at 0.15°) of CZA FDU-15 films with different moving rate at different azimuthal angles (left $\phi = 90^\circ$, right $\phi = 0^\circ$); (a)
FDU-15-150-20 no clear preferential orientation of in-plane cylindrical structure from these two measurements; (b) FDU-15-150-2.0 with well aligned cylindrical structure along $\phi = 0^\circ$; (c) FDU-15-150-0.5 with well aligned cylindrical structure along $\phi = 90^\circ$.

Figure 3.4 illustrates 2D GISAXS data at $\phi = 90^\circ$ and $0^\circ$ for FDU-15-150 after cold zone annealing at three different moving rates: 20 $\mu$m/s, 2.0 $\mu$m/s and 0.5 $\mu$m/s. These data provide a facile route for preliminary examination of the orientation of in-plane packed cylinders. Due to some uniaxial contraction of the framework from crosslinking of the resol, the cylinders exhibit rectangular packing ($c2mm$) in these films. For CZA, large velocity (20 $\mu$m/s, Figure 3.4a) results in 2D GISAXS patterns that do not significantly differ between $\phi = 0^\circ$ and $90^\circ$. Thus, it is difficult to determine if the cylinders have preferred orientation between $0^\circ$ and $90^\circ$ or if they are randomly oriented from only measuring two angles. Conversely for FDU-15-150-2.0 at $\phi = 0^\circ$, intense higher order diffraction peaks are clearly visible as shown in Figure 3.4b; these diffraction peaks are consistent with the formation of the cylindrical mesostructure associated with FDU-15. However at $\phi = 90^\circ$ for the same sample, the scattering only contains two weak primary peaks, which suggests strong orientation along moving direction. Interestingly by decreasing the CZA velocity by $4 \times$ (FDU-15-150-0.5), the scattering profiles exhibit intense higher order diffraction peaks at $\phi = 90^\circ$, while these
peaks are absent at $\phi = 0^\circ$ (Figure 3.4c). This, therefore, suggests that the cylinders are oriented transverse to the CZA annealing direction. Thus the orientation of FDU-15-150-0.5 film is opposite to the orientation of FDU-15-150-2.0 film, where the former exhibits cylinders oriented orthogonal to the moving direction through the thermal zone, while the later exhibits cylinders oriented parallel to the moving direction. It is important to note that since the incoming X-rays illuminate a large area of the film, these results imply that the CZA orientation effect is persistent over macroscopic length scales.

To better define the orientation of the mesostructure for the different moving rates, the full azimuthal scans from GISAXS can be utilized, which covers 180° spread with data collected every 10°. As all GISAXS patterns (such as illustrated in Figure 3.4) are consistent with only in-plane cylinders (no alignment in the out of plane direction), only the normalized primary peak intensity needs to be examined as a function of the azimuthal angle to provide a quantitative measure of the orientation.\textsuperscript{121} As expected,\textsuperscript{125} these discrete normalized intensities exhibit a normal distribution for their orientation. Thus, we can fit these discrete curves to a Gaussian function ($R^2 > 0.95$) as illustrated in supporting information. From these fits, the preferred direction, $\phi_p$, and angular spread, $\Delta\phi_{\text{FWHM}}$, are obtained, which provide information on the orientation direction and the quality of the orientation, respectively.
Figure 3.5 Normalized primary peak intensity (■) from the azimuthal scan fit to a Gaussian profile (solid line, $R^2>0.95$) for CZA FDU-15 films at different moving rates. The preferential orientation of 2D in-plane packed cylinders shifts to smaller angles as the moving velocity decreases with the full possible range of 180° observed. For clarity, only one peak is shown for each velocity as these profiles are symmetric and the same peak is present at $\phi$ and $\phi \pm 180^\circ$.

Figure 3.5 illustrates the Gaussian profiles associated with the normalized primary peak intensities from the azimuthal scans at different moving rates. All samples examined show a single peak associated with a preferential in-plane orientation of the cylinders. However, the peak position and width varies significantly with moving rate. These data can explain why the 2D GISAXS patterns for FDU-15-150-20 are similar at $\phi$ =
0° and φ = 90° from Figure 2c; the preferential direction of the cylinders is \( \phi_p \approx 47° \), which is nearly halfway between the two angles examined. By decreasing moving rate to 10 μm/s, there is a decrease in the preferred azimuthal orientation angle for the cylindrical mesostructure to \( \phi_p \approx 17° \). From qualitative examination of the 2D GISAXS data for FDU-15-150-2.0 (Figure 3.4b), a preferred orientation parallel to the moving direction is suggested, which is consistent with the quantitative assessment from the azimuthal scans where a preferential orientation direction of \( \phi_p \approx -1° \) is determined (Figure 3.5). Slightly decreasing the velocity further to 1.5 μm/s provides a dramatic shift in preferred direction to \( \phi_p \approx -75° \). Further decreasing to 0.5 μm/s led to a further shift to lower azimuthal angle for the orientation direction of the cylindrical mesostructure (\( \phi_p \approx -85° \)). This orientation is nearly orthogonal to the moving direction as suggested from the qualitative examination of scattering profiles at \( \phi = 90° \) and 0° (Figure 3.4c).

Further decreasing the velocity to 0.2 μm/s shifts the orientation to \( \phi_p \approx -127° \). Thus, a full range of preferred in-plane orientation of the cylindrical mesostructures can be obtained by simple variation in the moving rate between 0.2 μm/s and 20 μm/s. It should be noted that due to symmetry of the cylinders, the orientation can be shifted by 180° in any case. For visualization of the orientation, only one angle is presented to prevent significant overlap of the peaks and difficulty in interpreting data presented in Figure 3.5. Thus for FDU-15-150-0.2, the preferred orientation can also be considered to be \( \phi_p \approx 53° \), which is similar to the orientation of FDU-15-150-20 (\( \phi_p \approx 47° \)). CZA
provides a simple route to long-range orientation of the mesostructure with control of
the preferred angle through the CZA velocity. This is the first report of controllable
in-plane packed cylindrical structure with well defined orientation.

In addition to the peak position, the full width at half maximum of the angular
spread ($\Delta \phi_{\text{FWHM}}$) provides a descriptor for the shape of the peak, which is associated
with the spread of the orientation. Small $\Delta \phi_{\text{FWHM}}$ indicates narrow distribution of the
preferential orientation, which is associated with excellent alignment. It is clear from
Figure 3.5 that FDU-15-150-2.0, FDU-15-150-1.5 and FDU-15-150-0.5 exhibit the best
uniaxial orientation with $\Delta \phi_{\text{FWHM}}$ of 11.4°, 12.9° and 16.7°, respectively. This angular
spread is much narrower than $\Delta \phi_{\text{FWHM}} = 25.2°$ reported by Tang et al. from zone casted
PBA-$b$-PAN. However, the faster velocities examined (10 $\mu$m/s and 20 $\mu$m/s) result in
an increased $\Delta \phi_{\text{FWHM}}$ (26.7° and 27.9°, respectively), which is very similar to the
distribution reported from zone casting. Similarly, decreasing the velocity to 0.2 $\mu$m/s
results in a reduction in the extent of the orientation with an even broader distribution
($\Delta \phi_{\text{FWHM}} = 42.4°$). Thus, there appears to be a sweet spot for the moving rate for CZA of
FDU-15 to provide highly oriented cylindrical mesostructures between 0.5 $\mu$m/s and 2.0
$\mu$m/s.
Although this qualitative analysis of the azimuthal scans can provide significant insight into the efficacy of the alignment at different processing conditions, it is useful to quantify the orientation through the orientational order factor ($S$) for the films. $S$ is estimated based on the average of the second Legendre polynomial. For a totally isotropic or random sample, $S=0$; while for a perfectly aligned sample, $S=1$. These in-plane cylinders provide a simple format to calculate $S$ as:

$$S = \frac{3}{2} < \cos^2 \phi > -1$$

with

$$\langle \cos^2 \phi \rangle = \frac{\sum_{\phi=0^\circ}^{90^\circ} I(\phi) \sin \phi \cos^2 \phi}{\sum_{\phi=0^\circ}^{90^\circ} I(\phi) \sin \phi}$$

where $\phi$ is azimuthal angle, $I(\phi)$ is the intensity of the primary diffraction peak at $\phi$ from
azimuthal scan. Figure 3.6 illustrates the orientational order factor calculated for the different CZA velocities. As expected from our prior discussion of Figure 3.5, FDU-15-150-0.5, FDU-15-150-1.5, FDU-15-150-2.0 exhibit the greatest orientational factor that are close to 1 (0.953, 0.977 and 0.976, respectively), whereas S for FDU-15-150-20 and FDU-15-150-10 are decreased to 0.875 and 0.883, respectively. FDU-15-150-0.2 showed the lowest factor S from the very broad peak. The best oriented samples with S > 0.95 are comparable to the best orientation reported for simple block copolymer films using soft shear or topological epitaxy.

3.3.3 Homogeneity and Heterogeneity of Thickness

However, it is unclear why the orientation direction would change as a result of the velocity of a sharp thermal gradient front. One interesting observation from the FDU-15 films is that macroscopic flow of material occurs during CZA as illustrated in Figure 3.7a. It is important to note that previous studies on CZA annealing did not report material flow due to CZA annealing; here we observed significant material flow caused by CZA that can be seen by naked eye. The yellow flow field due to the condensation of resol and polymer fluid is conspicuous as shown in Figure 3.7a for FDU-15-150-0.5 after CZA. The different color stripes are thickness contour lines. Thus the homogeneity and heterogeneity of FDU-15 films along different direction can be easily observed. To assess these differences, the thickness is measured spatially across the CZA area by
ellipsometry with lines orthogonal (Figure 3.7b), parallel (Figure 3.7c) and 45° (Figure 3.7d) to the moving direction examined. Initially, all films prior to CZA were approximately the same thickness. One commonality in all samples as shown in Figure 3.7b is edge effects where the higher temperature (≈10 °C) at boundary leads to thicker film remaining. We attribute this to enhanced resol crosslinking kinetics at the edges than center area of the film due to the increased temperature at the edge (See supporting information in Appendix B for more details). This difference in crosslink density leads to a differential stress associated with the volumetric contraction of resol during crosslinking. We hypothesize that this stress and the associated viscoelasticity of the resol: pluronic melt drives the flow in this system. This flow phenomenon in the transverse direction is most significant for the slowest moving rate sample FDU-15-150-0.5, where there is an apparent step change in thickness very near the edge. In this case, the slow rate provides significant time for differences in crosslinking to develop and hence more flow occurs in this case. For the other samples, the thickness decreases gradually from the center towards the edge and then there is a sharper increase in thickness at the edge associated with the localized stress induced by the enhanced crosslinking from the higher edge temperature.
Figure 3.7 Image of FDU-15-150-0.5 after CZA. Position dependent thicknesses from ellipsometry of CZA FDU-15 films at different moving rates (■ 0.5 \( \mu \)m/s, ● 2 \( \mu \)m/s, ▲ 10 \( \mu \)m/s, and ▼ 20 \( \mu \)m/s): (b) transverse, (c) parallel and (d) at 45° to the moving direction; the abscissa and origin for the thickness mapping is illustrated in (a) as the white arrow. Dot lines for as cast film, dash lines for uniform annealed samples.

In both Figure 3.7c and 3.7d, all samples exhibit a larger thickness at front edge. This edge is where the wire heating is initially and thus this initial thickness is the
expected film thickness without CZA as the sample is subjected to heating at this location without motion. However as one examines into the CZA area, there is a decrease in thickness that indicates considerable transport of mass caused by CZA induced flow. FDU-15-150-20 shows the most gentle curvature for the parallel direction (Figure 3.7c), which is attributed to the fast moving rate that provides insufficient time for flow to develop (quenched). However in the transverse direction (Figure 3.7b), a small dip in thickness at 1.5 mm suggests more flow toward the tail at the side edge than that of center; this is due to the sharper temperature gradient caused by higher edge temperature. Thus for FDU-15-150-20, though flow along moving direction appears small, it is still able to generate some in-plane orientation as shown in Figure 3.5. However, this orientation is not well developed and likely a result of quenching of the sample due to the fast velocity associated with the CZA front. By decreasing the moving rate to 10 µm/s, the thickness along moving direction (Figure 3.7c) decreased more than at 20 µm/s. After a trough, the thickness slowly increased. In the transverse direction, film thickness decreased continuously to distance = 1.5 mm but to a much greater extent than that of FDU-15-150-20. Like FDU-15-150-20, this drop of thickness in transverse direction came from more flow at the side edge, which was then quenched by the fast moving rate before transverse flow equilibrated. Similar behavior is also observed for FDU-15-150-2.0, but the decreases in thickness are more pronounced. The relative interplay between parallel and transverse flow can also be determined from
Figure 5d. The thickness for FDU-15-150-2.0 is observed to almost oscillate, which is consistent with transverse flow near the edge and parallel flow in the center that lead to decreases in thickness. In examining the thickness profiles, there is a clear trend that the amount of flow (as evidenced by thickness) increases as the CZA velocity decreases. Additionally for these three moving rates, the shape of the topology through the CZA is similar, but the extent of variation is velocity dependent. We attribute the thickness variations in these samples to the flow developed by the temperature gradients that is quenched (vitrified) as the heated zone moves. Interestingly for FDU-15-150-0.5, the behavior appears to be altered with no thickness change in the transverse direction. Moreover, the thickness for this velocity is significantly decreased. We hypothesize due to the slow moving rate that allowed full development of transverse flow from center toward side due to stresses associated with crosslinking at the hot edge. This flow pattern would also be consistent with the observed uniaxial orientation of 2D packed cylinders in transverse direction for this velocity (Figure 3.5). This can help explain the poor orientation observed for the lower velocity of 0.2 µm/s. Two factors likely impact this orientation: first, the slow rate likely does not provide sufficient flow in the moving direction as the resol in the heated zone will be sufficiently crosslinked to limit mobility as the front moves. Second, the slow rate can allow for polymer chain relaxations as further crosslinking occurs, which favor isotropic orientations. Although FDU-15-150-2.0 and FDU-15-150-0.5 both exhibit significant in-plane uniaxial
orientation, the mechanism appears to be different. At 2.0 µm/s and higher moving rate, parallel flow appears to dominate the orientation of cylinders, while transverse flow is dominate for lower velocities. This is consistent with shear induced orientation of P123 and P85 blends by Newby et al.\textsuperscript{126} where the cylinders can be well aligned along shear direction.

3.3.4 Rotational GISAXS of Carbon Films

![Figure 3.8](image)

Figure 3.8 Normalized primary peak intensity (■) from the azimuthal scan fit to a Gaussian profile (solid line, $R^2$>0.95) for CZA FDU-15 carbon films at different moving rates. (0.5 µm/s, 1.5 µm/s, 2.0 µm/s) with azimuthal scan (fit to Gaussian), inset is 2D GISAXS pattern at $\phi = -90^\circ$ for FDU-15-150-0.5-Carbon.
As the alignment for FDU-15-150-2.0, FDU-15-150-1.5 and FDU-15-150-0.5 are competitive with the best alignment for block copolymer, these films have been carbonized to determine how and if carbonization impacts the uniaxial alignment. The 2D GISAXS pattern (Figure 6 inset) for a carbonized film shows a similar structure to our previous reports for mesoporous carbon films. The well-ordered cylindrical porous structure remains after carbonization, but there is significant contraction of the space group due to volumetric change associated with carbonization of the resol. To examine the orientation of these films, azimuthal scans were again utilized with the normalized primary diffraction peak intensity determined as a function of the azimuthal angle as shown in Figure 3.8. The preferential direction is $\phi_p \approx 2^\circ$ $\phi_p \approx -71^\circ$ and $\phi_p \approx -83^\circ$ for FDU-15-150-2.0-Carbon, FDU-15-150-1.5-Carbon and FDU-15-150-0.5-Carbon, respectively. These values are very similar to the analogous cold zone annealed films, which is expected as the crosslinked resol should not dramatically re-organize during carbonization.

However, the extent of the orientation is degraded somewhat as the peaks are broadened for all samples ($\Delta \phi_{FWHM} = 46.2^\circ$ for FDU-15-150-2.0-Carbon, $\Delta \phi_{FWHM} = 34.1^\circ$ for FDU-15-150-1.5-Carbon and $\Delta \phi_{FWHM} = 25.8^\circ$ for FDU-15-150-0.5-Carbon). Nonetheless, FDU-15-150-0.5-Carbon and FDU-15-150-1.5-Carbon still maintains relatively high orientational order factors ($S = 0.888$ and $S = 0.822$). However for FDU-15-150-2.0-Carbon, the orientational order factor is significantly decreased ($S =$
0.696). The extent of change in S upon carbonization can clearly be seen in Figure 3.6 with an increase in the loss of orientation as the moving velocity is increased. This behavior can be rationalized in terms of the effective crosslinking time for resol. Typical heating protocols for fabrication of these ordered mesoporous carbons from resol and Pluronic surfactants involves heating for over 12 h. Based on the moving rate, average of effective heating time for FDU-15-150-2.0 is only 50 min, which is an order of magnitude less than typically utilized and thus it is not surprising that there is a significant decrease in the orientational order factor. However for FDU-15-150-1.5 and FDU-15-150-0.5, this effective heating time is only 67 min and 200 min, respectively. Nonetheless, high S is maintained in both cases. Thus for films, shorter heating protocols (<4 h) may be equally effective for fabricating OMC.

3.4 Concluding Remarks

The in-plane orientation of 2D FDU-15 cylinders has been controlled by CZA. By varying the moving rate, the preferential in-plane orientation can be tuned through the whole 180° range possible from $\phi = 47^\circ$ to $\phi = -127^\circ$ (relative to moving direction). At moving rate of 2 $\mu$m/s, this simple and easy operating process leads to well aligned cylinders parallel to moving direction with a high orientational factor of $S = 0.976$. Moreover, cylinders can be nearly perfectly aligned transverse to the moving direction ($S = 0.953$) by simply decreasing moving velocity to 0.5 $\mu$m/s. We attribute these
alignments to two distinct directional flows that develop from thermal gradients.

Examination of the thickness heterogeneity of films after CZA suggests two different mechanisms during CZA: parallel flow generated by thermal gradient and motion of the heating wire and transverse flow from a second thermal gradient due to higher edge temperature. After carbonization, the preferential orientation remained in cylindrical mesoporous carbon films, but there is some degradation in orientation due to insufficient heating during CZA to crosslink the resol. We consider CZA a simple and powerful method for fabricating well-aligned, self-assembled mesoporous carbon films in large areas.
CHAPTER IV

CONCLUSION AND FUTURE WORK

OMC has garnered intensive attention in numerous areas due to its outstanding properties. Among different synthesis routes, soft templated OMC is most attractive for its simple process and large operation window. FDU-15 is a member of the OMC family that obtained from soft templating with well-defined structure. When fabricates FDU-15 as thin films, it showed in plane layer by layer c2mm packed cylindrical mesestructure. Highly ordered mesoporous carbon films are fabricated here on quartz rather than conventional used silicon. Though quartz and silicon substrates exhibit many similarities, significant improvement in long range ordered structure emerged for ordered mesoporous carbon thin films obtained on quartz. We attributed this improvement to low thermal conductivity of the quartz substrates and related it to annealing temperature since FDU-15 annealed at 180 °C lost its structure during template removal while samples annealed at lower temperatures maintained the framework even after carbonization. Also, we demonstrated the annealing temperature has impacts on the porosity and PSD, too.
TEM image indicated the existence of large grains of highly ordered structure extends through the thickness of the film. Mechanical properties of the OMC films were elucidated through wrinkling by attaching to a PDMS substrate. We consider the high modulus of obtained FDU-15 films coming from its long range order structure. The results of Chapter II illustrated the key roles of the substrate and annealing temperature in manufacturing of highly ordered mesoporous carbon films through cooperative thermal induced self-assembly and inspired us to apply CZA on fabricating -15 carbon films. Utilizing CZA rather than oven annealing resulted in a dramatic uniaxial alignment of the 2D packed cylinders in FDU-15 films. These in plane packed cylinders can be arranged through the whole 180° from $\phi = 47^\circ$ to $\phi = -127^\circ$ (relative to moving direction) by changing the CZA velocity. At 2 $\mu$m/s, the nanostructure was near perfectly aligned ($S = 0.976$) parallel to moving direction while at 0.5 $\mu$m/s packing transverse to moving direction is preferred with a high orientational factor of $S = 0.953$. Further increase or decrease in velocity leads to a reduction of directionality. These alignments were considered to be induced by two types of directional flows: parallel flow developed by dynamic thermal gradient (dewetting of polymer complex) and transverse flow generated by heterogeneous crosslink density. The uniaxial alignment maintained in OMC films after carbonization. But due to insufficient crosslink of resol, -15-150-2.0-carbon lost the orientation significantly compare to that of -15-150-1.5-carbon and FDU-15-150-0.5-carbon. We consider CZA a simple and
powerful method for fabricating well-aligned, self-assembled mesoporous carbon films over large areas.

Apparently, the thermal annealing step would significantly affect the structure formation of FDU-15 thin films. Being explained as a thermal induced self-assembly with hydrogen bonds, the mechanism details still remain challenging. Two hypotheses are raised here: the formation of micelle during heating process as that in solution of the template or the curing induced self-assembly as reported by Balsara et al. 128

Also, substrate confinement would affect the chain rearrangement, thus the film thickness would also has influence on formation of nanostructure. This effect can be addressed by study the self-assembly of FDU-15 films with different thickness. Though we have reported the uniaxial alignment of 2D packed cylindrical mesoporous carbon thin films, the mechanical and electrochemical property need to be further investigated.

Encouraged by results above, we are currently looking forward a facile method for fabricating OMC films with controllable long range orientated mesoporous structure and flexibility in large area through roll to roll process. Flexible substrate such as Kapton (Polyimide) will not only simplify the procedure but also allowed pre-shaping of the final carbon films. Triconstituent co-assembly44 which has been demonstrated as the route to obtain OMC with largest surface area and pore volume will be utilized here.
The OMC loading is limited by commercial thick Kapton film that yields about 65% in mass as carbon after carbonization. This massive carbon yield reduces the flexibility of final product. The addition TEOS (precursor for silica) and alternating template P123 by F127 would also cause problem such as decreases the mobility of the mixture complex. Moreover, the moving velocity 2.0 μm/s is too slow for industrial use. So we are considering using rubbing\textsuperscript{129} to assist the alignment of OMC thin films during roll to roll processing. Preliminary study showed the OMC films maintained decent flexibility (Figure 4.1) and a surface area of 260 m²/g (ca. 14wt% OMC). The pore size distribution determined from BJH approach illustrated the similar results as powders and demonstrated the method is applicable on Kapton.

Figure 4.1  Photograph of carbon roll with flexibility.
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APPENDICES
APPENDIX A

SUPPORTING INFORMATION FOR CHAPTER II

1. Molecular weight distribution of resol

![Molecular weight distribution of resol as determined by MALDI](image1.png)

Figure S1. Molecular weight distribution of resol as determined by MALDI

2. Specular ellipsometry
Figure S2. $\Phi$ (dot) and fitting (line) for FDU-15-100.

Figure S3. $\Delta$ (dot) and fitting (line) for FDU-15-100.
Figure S4. Refractive index $n$ and adsorption coefficient $k$ for FDU-15-100. Black for refractive index and blue for adsorption coefficient.

Figure S5. $\Phi$ (dot) and fitting (line) for FDU-15-100-350.
Figure S6. △ (dot) and fitting (line) for FDU-15-100-350.

Figure S7. Refractive index n and adsorption coefficient k for FDU-15-100-350.

Black for refractive index and blue for adsorption coefficient.
Figure S8. $\Phi$ (dot) and fitting (line) for FDU-15-100-800.

Figure S9. $\Delta$ (dot) and fitting (line) for FDU-15-100-800.
Figure S10. Transmission intensity (dot) and fitting (line) for FDU-15-100-800.

Figure S11. Refractive index \( n \) and adsorption coefficient \( k \) for FDU-15-100-800.

Black for refractive index and blue for adsorption coefficient.
FDU-15-100 and FDU-15-100-350 are fitted by Cauchy model while FDU-15-100-800 is fitted by GenOsc model with transmission data. The fits are pretty good with low MSE.

![Graph of refractive index over time](image)

**Figure S12.** Adsorption and desorption curve for FDU-15-150-350.

Refractive index was selected at $\lambda = 632\text{nm}$, which is wavelength of HeNe laser that was conventional used. The adsorption and desorption isothermals reached equilibrium very fast, the steps indicated the change in $p/p_0$. final refractive index is slightly higher than that of initial because of the very small pores are hard to empty.

3. X-ray diffraction

As GISAXS is not typically readily available in the laboratory setting, we have also characterized the films using a laboratory source x-ray diffractometer (XRD) to illustrate the differences in ordering as the thermopolymerization temperature is varied on quartz
substrates. Figures S13-S14 illustrate the diffraction as a function of annealing temperature. The poorly ordered structure obtained from heating at 180°C, but differences between the other temperatures are not as apparent. The temperature dependent d-spacing is clearly evident, but these data may be misinterpreted without the q_x data as there is a difference in the in plane unit cell parameter as well. Thus for soft-templated mesoporous carbon films, it is important to be careful of the structural claims from only 1-D scattering data.

Figure S13. XRD of annealed FDU-15 films on quartz
Figure S14. XRD of FDU-15 films on quartz after template removal at 350 °C.

4. GISAXS data analysis

Packing symmetry is determined by simulating the positions of Bragg peaks in \((2\Theta, \alpha_i)\) space for comparison with experimental data (as a function of incident angle \(\alpha_i\)). Data for all samples are consistent with parallel cylinders, where the out-of-plane symmetry is hexagonal (an ABA stacking sequence). The real-space lattice vectors are

\[
\mathbf{i}_1 = \{a, 0, 0\}, \quad \mathbf{i}_2 = \{0, b, 0\}, \quad \mathbf{i}_3 = \{0, 0, c\}.
\]  

(1)

Parallel cylinders are defined with the lattice parameters \(a=1, b=XX\; \text{nm}, c=\sqrt{3}b*f\), where \(XX\) denotes the in-plane periodicity (ranges from 13-17 nm), and \(f\) denotes the level of compression (contraction) \((f=1\) is perfect hexagonal symmetry, \(f<1\) is a compressed unit cell). The unit cell is described with a two-point basis \((x_j, y_j, z_j)\),
Positions of cylinders within the unit cell are described by the set of \( j \) vectors \( \mathbf{r} = x_1 \mathbf{a}_1 + y_1 \mathbf{a}_2 + z_1 \mathbf{a}_3 \). Reciprocal lattice vectors are computed in the usual way, i.e.,

\[
\mathbf{q} = 2\pi \left( \mathbf{a}_1 \times \mathbf{a}_2 \right) / \left( \mathbf{a}_1 \cdot \left( \mathbf{a}_2 \times \mathbf{a}_3 \right) \right)
\]

Scattering vectors are \( \mathbf{q} = h \mathbf{a}_1 + k \mathbf{a}_2 + l \mathbf{a}_3 \), where \( h, k, \) and \( l \) are the Miller indices. A reflection is allowed from plane \((h,k,l)\) when the structure factor is non-zero,

\[
S(\mathbf{q}) = \sum_j e^{-i\mathbf{q} \cdot \mathbf{r}_j}
\]

For each allowed reflection, there are two Bragg peaks in \((2\Theta, \alpha)\) space:

\[
\alpha_f^{(a)} = \arcsin \left( \frac{g_x^2}{k} \right) + \sin^2 \alpha_i - 2 \frac{g_x}{k} \sqrt{n^2 - 1 + \sin^2 \alpha_i}
\]

\[
\alpha_f^{(b)} = \arcsin \left( \frac{g_x^2}{k} \right) + \sin^2 \alpha_i + 2 \frac{g_x}{k} \sqrt{n^2 - 1 + \sin^2 \alpha_i}
\]

\[
2\Theta_f^{(a,b)} = \arccos \left( \frac{\cos^2 \alpha_f^{(a,b)} + \cos^2 \alpha_i - (q_{par}/k)^2}{2 \cos \alpha_f^{(a,b)} \cos \alpha_i} \right)
\]

Parameters \( q_{par} \approx 4\pi \theta / \lambda \) and \( q_z \) are in-plane and out-of-plane components of the scattering vector, respectively, \( k = 2\pi / \lambda \) is the wave vector modulus, and \( n \) is the refractive index of the film.

Figure S15 shows a comparison between the experimental data and predicted peak positions for FDU-15-100. The O’s and X’s are the solutions to Equations (4) and (5), respectively. The scattering length density for the carbon films is assumed to be approximately \( 9 \times 10^{10} \text{ cm}^{-2} \), as determined previously. There is good agreement between the predicted diffraction peak locations and those observed experimentally.

Figures S15-S18 illustrate the GISAXS with predicted peaks for the as heated samples.
Figures S19-S21 illustrate the GISAXS with predicted peaks for the carbonized samples.

Figure S15. Comparing predicted peak positions with experimental data for FDU-15-100. \((b = 14 \text{ nm, and } f = 0.93)\).

Figure S16. Comparing predicted peak positions with experimental data for
FDU-15-120. \((b = 14.5 \text{ nm}, \text{ and } f = 0.90)\).

\begin{align*}
\alpha_i &= 0.12 \text{ deg} \\
\alpha_i &= 0.25 \text{ deg}
\end{align*}

Figure S17. Comparing predicted peak positions with experimental data for FDU-15-150. \((b = 15.5 \text{ nm}, \text{ and } f = 0.87)\).

\begin{align*}
\alpha_i &= 0.12 \text{ deg} \\
\alpha_i &= 0.25 \text{ deg}
\end{align*}

Figure S18. Comparing predicted peak positions with experimental data for FDU-15-180. \((b = 17 \text{ nm}, \text{ and } f = 0.73)\).
Figure S19. Comparing predicted peak positions with experimental data for FDU-15-100-800. ($b = 13.5$ nm, and $f = 0.375$).

Figure S20. Comparing predicted peak positions with experimental data for FDU-15-120-800. ($b = 13.5$ nm, and $f = 0.38$).
Figure S21. Comparing predicted peak positions with experimental data for FDU-15-150-800. (b = 14.5 nm, and f = 0.36).
APPENDIX B

SUPPORTING INFORMATION FOR CHAPTER III

1. GISAXS patterns at different incident angle (0.07 and 0.15)

Figure S22. FDU-15-150-2, 0.07 (left) and 0.15 (right)

Figure S23. FDU-15-150-0.5-carbon 0.07° (left) and 0.15° (right).
The nanostructure of surface and film are same base on different incident angles. No extra peaks show up, due to the small incident angle (0.07°). A reflection is allowed as mentioned in Appendix A.

2. Rotational GISAXS patterns
Figure S24. Rotational GISAXS patterns at each angle for FDU-15-150-2.0.
Figure S25. Rotational GISASXS patterns at each angle for FDU-15-150-0.5-carbon (preferred direction is set to be $0^\circ$).
3. Rotation GISAXS data and Gauss fitting

Figure S26. Primary peak intensity and Gauss fitting for FDU-15-150-20

Figure S27. Primary peak intensity and Gauss fitting for FDU-15-150-10
Figure S28. Primary peak intensity and Gauss fitting for FDU-15-150-20

Figure S29. Primary peak intensity and Gauss fitting for FDU-15-150-1.5
Figure S30. Primary peak intensity and Gauss fitting for FDU-15-150-0.5

Figure S31. Primary peak intensity and Gauss fitting for FDU-15-150-0.2
Figure S32. Primary peak intensity and Gauss fitting for FDU-15-150-2.0-carbon

Figure S33. Primary peak intensity and Gauss fitting for FDU-15-150-1.5-carbon
Figure S34. Primary peak intensity and Gauss fitting for FDU-15-150-0.5-c-arbon

Figure S35. Photograph of samples annealed at different velocities.