Challenges in Fabrication of Mesoporous Carbon Films with Ordered Cylindrical Pores *via* Phenolic Oligomer Self-Assembly with Triblock Copolymers

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ABSTRACT Mesoporous phenol formaldehyde (PF) polymer resin and carbon films are prepared by a solution self-assembly of PF oligomers with amphiphilic triblock copolymers. After thermopolymerization of the PF to cross-link the network, the films show an ordered morphology as determined by X-ray diffraction and grazing incidence small-angle X-ray scattering (GISAXS). Our results show that the amphiphilic triblock copolymer template greatly influences the stability of the final porous mesostructures. The pyrolysis of the two-dimensional (2-D) hexagonal films with *p6mm* symmetry templated by Pluronic F127 yields a disordered porous structure following the template removal. Conversely, films templated by Pluronic P123 can exhibit well-ordered cylindrical pores after the template removal, but the solution composition range to yield ordered cylindrical mesopores is significantly reduced (nearly 70%) for thin films in comparison to bulk powders. We propose two dominant difficulties in fabricating well-ordered cylindrical mesopores in films: first, the stress from contraction during the pyrolysis can lead to a collapse of the mesostructure if the wall thickness is insufficient, and second, the surface wetting behavior in thin films leads to a small compositional range.

KEYWORDS: mesostructure · phenol formaldehyde resin · self-assembly · mesoporous materials · thin film

Sol−gel chemistry and self-assembly processes have been successfully combined to enable the controllable fabrication of materials on nanometer scale.[1] Soft chemistry of inorganic or hybrid networks templated by structure-directing agents yields materials organized at the mesoscopic scale (2−50 nm).[2−4] These general approaches have been utilized to synthesize ordered mesoporous metal oxides,[5,6] metal sulfides,[7,8] and metals.[9,10] However, the direct synthesis of mesoporous carbons has only recently been explored. Using an organic−organic self-assembly approach, mesoporous carbonaceous materials were synthesized by using cetyltrimethylammonium bromide (CTAB) or hexadecyltrimethylammonium bromide (HTAB) as a template but failed to form ordered mesostructures analogous to the mesoporous silicates.[11,12] However, evaporation-induced self-assembly (EISA) of low-molecular-weight and water-soluble phenolic resin (resols) and commercially available triblock copolymers can yield highly ordered mesoporous polymers and carbon materials.[13−16] In this method, the ordered hybrid mesophase forms through organic−organic self-assembly during solvent evaporation, followed by thermopolymerization of the resols around the template to solidify the framework. Simply adjusting the ratio of phenol/template and the template composition can produce different mesostructures, including two-dimensional (2-D) hexagonal (*p6mm*), 3-D body center cubic (*Im*3*m*), 3-D bicontinuous (*Ia*3*d*), and lamellar (*Lam*) mesostructures.[14] Mesoporous polymer resins can be converted to glassy carbons by pyrolysis under inert atmosphere above 600 °C to yield powders,[14] fibers,[17] monoliths,[18] and films.[19]

High-temperature pyrolysis leads to a reduction in the spacing of the mesostructure. The contraction during carbonization is generally more severe than that typically observed for mesoporous silicates or other metal oxides.[20] This effect becomes even more significant in films due to the uniaxial contraction in the direction normal to the substrate, leading to changes in the symmetry of the mesostructure.[21] For example, the 2-D hexagonal phase (space group *p6mm*) transforms to a *c2mm* rectangular mesostructure.[22,23] However, the fabrication of the 2-D hexagonal (*p6mm*) mesostructure in carbon films can require additives or

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Received for review September 24, 2009 and accepted December 2, 2009.

10.1021/nn9012884

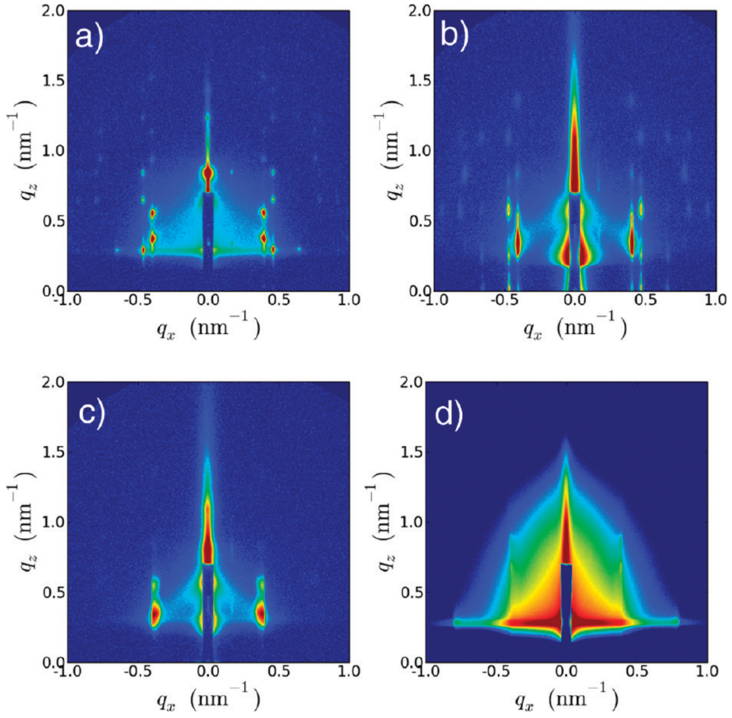

Figure 1. GISAXS patterns for (a) the as-made FDU16 film and (b) the FDU16 film after pyrolysis at 350 °C using a Pluronic F127/phenol molar ratio of 0.006/1. GISAXS patterns of (c) the as-made and (d) pyrolyzed FDU15-350 films prepared by using F127/phenol molar ratio of 0.012/1.

other special processing to obtain well-ordered structures in comparison to the methodologies that can be employed for cubic mesoporous films. It is possible to fabricate well-ordered mesoporous films with vertically aligned hexagonal pores through self-assembly and solvent annealing of a resorcinol and a diblock copolymer mixture, followed by polymerization of the resorcinol with formaldehyde vapor and carbonization at 800 °C.[24] This method, which is one of the first reports for soft templating of mesoporous carbons, illustrates that the *p*6*mm* mesostructure can be fabricated in mesoporous carbon thin films. However, Tanaka and co-workers utilized resorcinol/formaldehyde−Pluronic F127 mixtures to synthesize mesoporous carbon films with well-ordered face-centered orthorhombic structures,[19] but poorly ordered films are obtained when using analogous mixtures containing a different composition to induce a transition from cubic to hexagonal mesophase.[20] A simple change in the processing, addition of triethyl orthoacetate (EOA) as a carbon co-precursor with resorcinol/formaldehyde, can result in well-ordered mesoporous films with cylindrical pores.[20] Similarly, recently, Nishiyama and co-workers described a vapor-based method using benzyl alcohol to fabricate very thin carbon films with ordered cylindrical mesopores, which was not possible to obtain using conventional soft-templating approaches.[25] These results suggest that the formation of ordered cylindrical mesopores in carbon thin films is highly dependent upon processing, although it should be noted that these are known processes to yield highly ordered hexagonally packed mesoporous carbon films.

It is unclear why well-ordered hexagonal phases in mesoporous polymer resin/carbon films formed through organic−organic self-assembly can be more difficult to fabricate in comparison to their powder analogues depending upon the processing route. Here we attempt to provide insight into the origins of these difficulties by examining organic−organic self-assembly of resol with Pluronic (F127 and P123). Through global (GISAXS) and local (cross-section TEM) analysis of the films, the mesostructures are comprehensively assessed. We find that, although both templates initially yield well-ordered mesostructured films, synthesis conditions that result in thin wall thickness lead to films with poorly defined pores. We propose a mechanical-based mechanism to explain the differences in the structural stability of ordered cylindrical mesopores during template removal.

RESULTS AND DISCUSSION

Comparison of Cubic and Hexagonal Symmetries. The interfaces of films impose geometric constraints on self-assembly that are absent in bulk powders. Cubic (*Im*3*m*, FDU16-350) and 2-D hexagonal (*p*6*mm*, FDU15-350) mesostructured powders can be readily obtained using Pluronic F127.[14] To examine how geometric constraints impact the mesostructure, these same solutions are applied to create films approximately 1−1.5 μm in thickness. Well-defined scattering profiles are observed for the as-made (Figure 1a) and after template removal (Figure 1b) of the FDU-16 film. However, instead of cubic *Im*3*m* structure for the FDU-16 powder, a face-centered orthorhombic symmetry (*Fmmm*)[19] is determined from fitting the GISAXS profiles using NANOCELL as included in Supporting Information.[26] Although films and powders are made from the same solution, different phase behavior and mesostructure are observed. The scattering of the bulk powders are included in the Supporting Information. This *Fmmm* mesostructure in the film results from uniaxial contraction of *Im*3*m* symmetry normal to the substrate during thermopolymerization and pyrolysis.[27] Additionally, the contraction of the film (27% from *d* spacing change, 33% from decrease in thickness determined from ellipsometry) is significantly greater than that for the powder (≈14% from SAXS). This difference is not surprising based upon prior reports of the large contraction in mesoporous carbon films.[19]

The 2-D hexagonal FDU15 film with a F127/phenol molar ratio of 0.012/1 shows different behavior than the FDU16; the as-made film exhibits a *c*2*mm* structure as determined from GISAXS (Figure 1c), which is in agreement of the transformation of the *p*6*mm* to *c*2*mm* observed previously for mesoporous silica films. Thus, an ordered mesostructure is initially formed in the film, but it is significantly distorted by the template removal at 350 °C (Figure 1d). This is counter to the well-ordered mesopores found in the powders from the same solution (see Supporting Information). For the film, there are no oscillations in the scattering intensity along q_z at $q_x = 0$, which would correspond to the through-plane correlations of cylindrical mesopores oriented parallel to the substrate. However, there are two weak streaks in the GISAXS profile at fixed q_x. One explanation for this scattering pattern is perpendicularly oriented cylinders; the lack of expected oscillations in q_z at fixed q_x ($\neq 0$) can result from differences in the finite heights of the cylindrical pores.[28] However, scattering from the as-made film suggests predominately in-plane orientation of the cylindrical mesodomains, but other orientations are present as evidenced by the weak ring in the GISAXS profile (Figure 1c). These results suggest that the (near) perpendicular orientation of the mesostructure is preserved during template removal at 350 °C, while there is a loss of the parallel mesostructure under the same conditions. The origins of the change from a predominately parallel orientation of mesopores in the as-made films to perpendicularly aligned pores upon template removal are not clear. This change in structure would not be seen from simple XRD measurements and could likely be related to previous reports of a strong dependence on the carbon precursor (phenol, resorcinol, phloroglucinol) on the ordering of the obtained structure.[17] One property that could provide insight to the change in structure is the porosity of this film, which from ellipsometric porosimetry is 12%, which is significantly smaller than that reported for silica analogues (approximately 35%) in the literature.[29] This low porosity suggests potential collapse of the mesostructure during pyrolysis; a partial collapse of mesopores aligned parallel to the substrate would be consistent with the loss of diffraction along $q_x = 0$ upon template removal. Additionally from ellipsometry, the film thickness is reduced from 1537 to 593 nm during template removal, a contraction of 61%. Figure 2 shows cross-section TEM images of highly ordered FDU16-350 (Pluronic F127/phenol: 0.006/1) film viewed along 100 (Figure 2a) and 101 (Figure 2b) directions of the *Fmmm* mesostructure. Conversely, the vast majority of the FDU15 (Pluronic F127/phenol: 0.012/1) film contains disordered, irregularly shaped pores; a representative micrograph is shown in Figure 2c; this is consistent with the lack of diffraction along $q_x = 0$ and the relatively poorly defined GISAXS patterns. However, some small regions of the film show well-defined nearly vertically aligned (perpendicular to the substrate) cylindrical mesopores (Figure 2d). This ordered mesostructure within the film is a minor phase, but this morphology is consistent with the streaks in the GISAXS profiles.

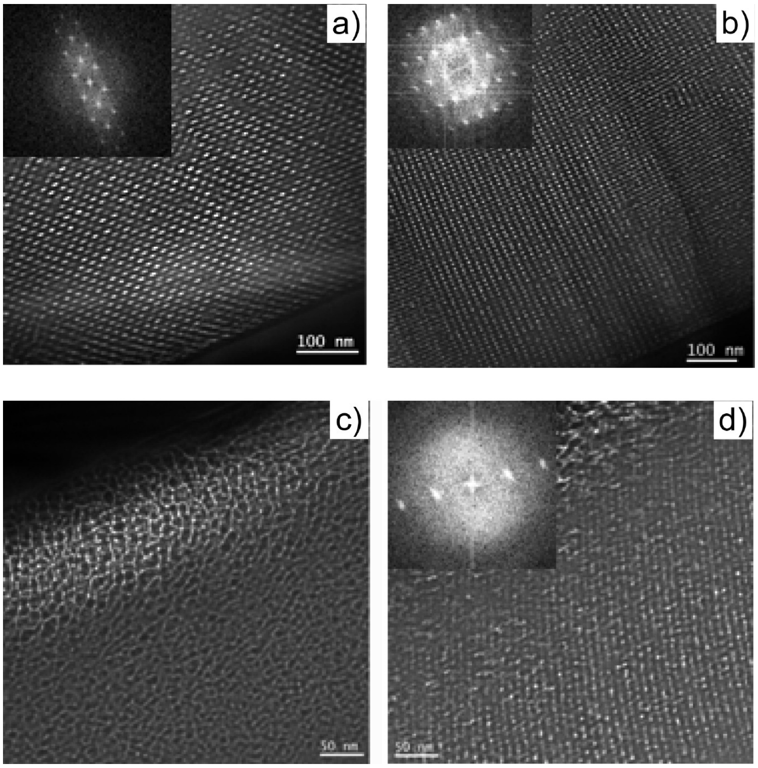

Figure 2. TEM micrographs of the highly ordered mesoporous polymer resin FDU16-350 film prepared with Pluronic F127/phenol molar ratio of 0.006/1, viewed along (a) [101] and (b) [100] directions. The silicon substrate is in the lower right corner of both micrographs for FDU16. The mesoporous polymer resin FDU15-350 film prepared with Pluronic F127/phenol molar ratio of 0.012/1 after pyrolysis at 350 °C primarily shows (c) disordered pore structure, but some regions of the film contain (d) ordered mesopores that are oriented perpendicular to the silicon substrate. The substrate is in or near the upper left corner of both images from FDU15.

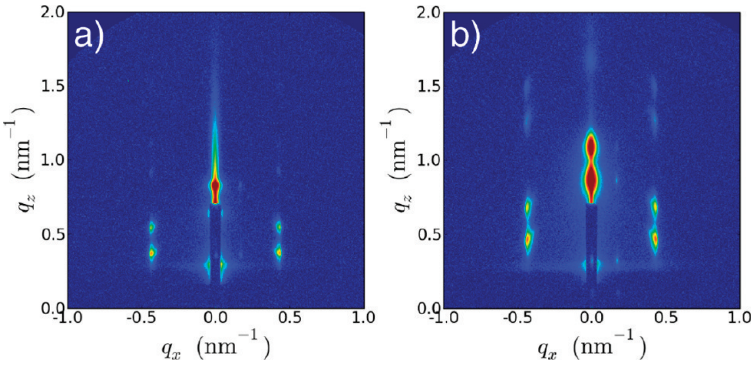

Figure 3. GISAXS patterns for the as-made (a) and pyrolyzed at 350 °C (b) mesoporous polymer resin films prepared with Pluronic P123/phenol molar ratios of 0.01/1. Note that a well-ordered *c2mm* mesostructure remains after template removal.

Recently, the assembly of crystalline titania nanoparticles with amphiphilic surfactants to create ordered mesoporous films has been reported using KLE surfactants, but it is noted that well-ordered mesoporous

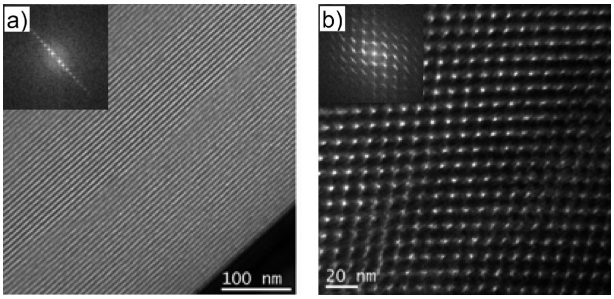

Figure 4. Cross-section TEM micrographs of the mesoporous polymer films with rectangular structure (*c*2*mm*) synthesized by using Pluronic P123 as a template after pyrolyzed at 350 °C in nitrogen with P123/phenol ratio of 0.01/1 (substrate in lower right). The micrographs show both the (a) (110) and (b) (001) planes.

films could not be obtained using Pluronic surfactants.[30] To test if the Pluronic family of surfactants is, in general, unable to create well-ordered mesoporous films from co-assembly with resol, another Pluronic surfactant, P123, is utilized. Pluronic F127 and P123 have the same middle block length (PPO_{70}) but dramatically different hydrophilic end blocks (PEO_{106} for F127 and PEO_{20} for P123), although a similar molar ratio of surfactant to phenol can be used for both surfactants to template hexagonal mesostructured powders.[14] Figure 3 illustrates the GISAXS profiles of the FDU15 films (Pluronic P123/phenol: 0.01/1). The as-made film (Figure 3a) shows a well-defined *c*2*mm* mesostructure similar to the film templated by Pluronic F127. However, after template removal, the well-ordered *c*2*mm* mesostructure is retained when using Pluronic P123 (Figure 3b). The mesostructure contracts normal to the film surface during template removal as evidenced by the shift in the diffraction along q_z; however, there is minimal change in the diffraction location in q_x, which is consistent with near-uniaxial contraction. From ellipsometry, the film contracts 27% during the template removal process at 350 °C, which is substantially less than observed for the Pluronic F127 templated FDU15 film (61%). However, the porosity of the Pluronic P123 templated FDU15 film from ellipsometric porosimetry is 14%, which is still quite low for ordered mesoporous materials. Cross-section TEM images (Figure 4) illustrate the ordered mesostructures viewed along the [100] and [110] directions for the ordered *c*2*mm* film. The highly aligned stripe-like morphology viewed from the (110) plane (Figure 4a), and the near-hexagonal structured mesopores along the (001) plane (Figure 4b) are observed across the whole film thickness at a P123/phenol ratio of 0.01. Additionally, the pore morphology is quite symmetric across the radius of the pore as the contraction of this film is quite limited (only 27%). The unit cell parameter measured from these TEM micrographs is approximately 9.0 nm, which is in good agreement with that from the XRD (8.6 nm calculated from *d* spacing of 7.4 nm based upon the geometry). These micrographs demonstrate that cylindrical mesopores can be formed using resol as a precursor.

To understand why ordered *c*2*mm* composite films (template + resol) lead to a relatively disordered porous structure when using Pluronic F127 while a highly ordered mesostructure is maintained with Pluronic P123, the difference in the template structure must be examined. Recall that the hydrophobic PPO segment length is identical for Pluronic F127 and P123, but F127 contains approximately 5 times more PEO (PEO_{106} for F127 and PEO_{20} for P123). As such, the mass fraction of resol increases substantially when using Pluronic P123 as the template if the same space group is formed. This difference results in hexagonal mesoporous silica templated by Pluronic P123 to exhibit significantly thicker walls than analogous mesostructures templated by F127.[31] Additionally, the small regions of near-perpendicular pore orientation in the film templated by F127 are peculiar. The perpendicular pore orientation is generally difficult to form due to preferential segregation of one segment of the template to the free surface and substrate.[32] However, mechanically, perpendicular pores are aligned to the stress direction that is created during template removal. For the perpendicular orientation for the cylindrical pores, the contraction occurs along the axial direction, so the forces do not act across the radius of the pore and any contraction in the length of the cylindrical mesopores requires contraction of the dense matrix surrounding them. The large contraction, low porosity, and the presence of a limited number of perpendicularly oriented mesopore arrays suggest that the lack of a well-defined ordered mesostructure throughout the FDU15 film templated by F127 is a result of significant stress and the mechanically weak polymer framework. The wall thickness of the mesostructure templated by P123 is significantly greater, which would act to decrease the local stress during template removal. As a range of different resol/pluronic ratios can be used to synthesize FDU15 powders, this provides a route to systematically investigate the role of wall thickness on the stability of cylindrical mesopores in FDU15 films.

Stability of Cylindrical Mesopores in Polymer Resin Films Templated by Pluronic F127. From the known synthesis conditions for FDU15 using F127, the molar ratio of Pluronic F127 to phenol can be reduced down to as low as 0.008 from the 0.012 utilized previously. This change in composition should act to increase the pore wall thickness, which could better dissipate the stresses and potentially stabilize the parallel c2*mm* morphology. The XRD patterns for as-made films (F127/phenol ratios of 0.012, 0.01, and 0.008) show a single diffraction peak at 2θ of ≈0.76. The GISAXS profile confirms the presence of an ordered *c*2*mm* mesostructure in the as-made films (see Supporting Information). However, no diffraction peak is detected after the removal of the template for any of these ratios. For the film prepared with F127/phenol ratio of 0.008, there is a change in the GISAXS profile (Figure 5) after the template removal in

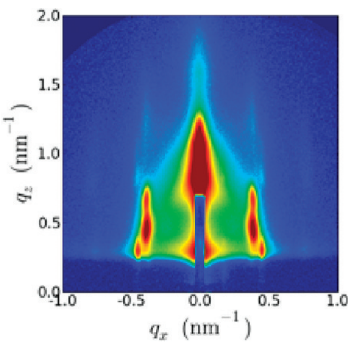

Figure 5. GISAXS pattern of the mesoporous polymer resin films prepared with Pluronic F127/phenol molar ratio of 0.008/1 after being pyrolyzed at 350 °C.

comparison to the sample with the ratio of 0.012 (Figure 1d). At this lower F127/phenol ratio, the scattering becomes slightly better resolved and appears to be consistent with parallel orientation of cylindrical pores, but the diffraction peaks are still highly smeared along q_z. This suggests that the ordering of the mesopores is not well-defined through the thickness of the film, but the mesopores are ordered in-plane.

To examine the local structure of these films, cross-sectional TEM is again utilized. As the F127 template fraction is decreased, the resultant film becomes denser and the pores smaller. Despite the apparent improvement in the mesostructure as determined by GISAXS, the pores are not well-ordered overall in these films at Pluronic F127/phenol ratios of 0.01 and 0.008. This disordered structure is reminiscent of the reported collapse of the 2-D hexagonal structure in mesoporous silica films when contacted by water.[33] The authors attribute this loss in the ordered structure to the large capillary forces during water adsorption within the pores. The stresses that evolve during pyrolysis likely also lead to collapse of the mesostructure in our case. This collapse is not complete, however, as a small portion of the film at a F127/phenol ratio of 0.01 contained cylindrical pores that are ordered. These mesopores are oriented perpendicular to the substrate like those at F127/phenol ratio of 0.012 shown in Figure 2d. Further decreasing the F127/phenol ratio to 0.008, we observed parallel aligned cylinders in some regions of the film (Figure 6), which is consistent with the GISAXS data. The cylindrical mesostructure does not form across the whole film thickness with an irregularly shaped, slightly porous region occurring in the middle domains of the film. In this case, the pore wall thickness is larger than the previously examined compositions (ratios of 0.012 and 0.010), where small regions of vertically aligned mesopores are present. This increase in the thickness when decreasing the F127/phenol ratio is well-established for mesoporous powders formed through organic–organic self-assembly[14] and is a result of more carbonizable material being present in the film. No perpendicular cylindrical domains were observed at this lower ratio (0.008:1) in TEM analysis. The partial stabilization of small parallel cylindrical pore domains suggests that further decreasing the Pluronic F127 to phenol ratio could potentially lead to large ordered domains.

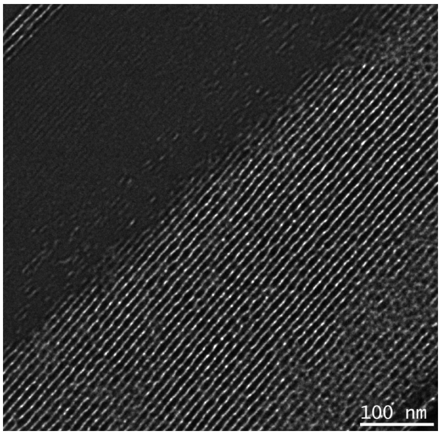

Figure 6. Cross-section TEM image of the mesoporous polymer resin films prepared with Pluronic F127/phenol molar ratio of 0.008/1 after pyrolyzed at 350 °C.

However, decreasing the F127/phenol ratio to 0.006 results in a phase transformation from *c*2*mm* to *Fmmm* in the mesoporous films. As shown previously, this composition yields a well-ordered mesoporous film (Figures 1b and 2a,b). An improved structural stability of the orthorhombic mesostructure in comparison to the rectangular phase is expected. Previously, it has been shown for silica films templated by the same block copolymer that the cubic (orthorhombic) mesostructures have improved thermal stability because of their larger pore walls in comparison to hexagonal (rectangular) structures.[27] This is consistent with the results reported here for the polymer resin films.

Since the morphology change from hexagonal to orthorhombic occurs when decreasing the Pluronic F127 to phenol ratio from 0.008 to 0.006, it does not appear that a well-ordered mesoporous polymer resin film with parallel hexagonal pores can be easily formed with this template. However, previously, Tanaka and coworkers demonstrated that addition of EOA as a carbon co-precursor enables well-ordered cylindrical mesopores using Pluronic F127 as the template,[20] but how this additive enables the ordered structure to be formed is unclear. Based on the results here, we suspect that EOA acts to increase the modulus of the carbonizable polymer to enable the framework to withstand the stresses during template removal.

Cylindrical Mesopores Templated by Pluronic P123 in Polymer Resin Films. Unlike films templated by F127, Pluronic P123 can be used to synthesize mesoporous films with well-ordered cylindrical pores, as shown in Figure 4. FDU15 powders can be synthesized using P123/phenol ratios between 0.008 and 0.016,[14] but it is unclear if well-ordered FDU15 films can be obtained over this full range. Figure 7 shows the GISAXS profiles of two films at different ratios. At the low P123/phenol ratio of 0.008,

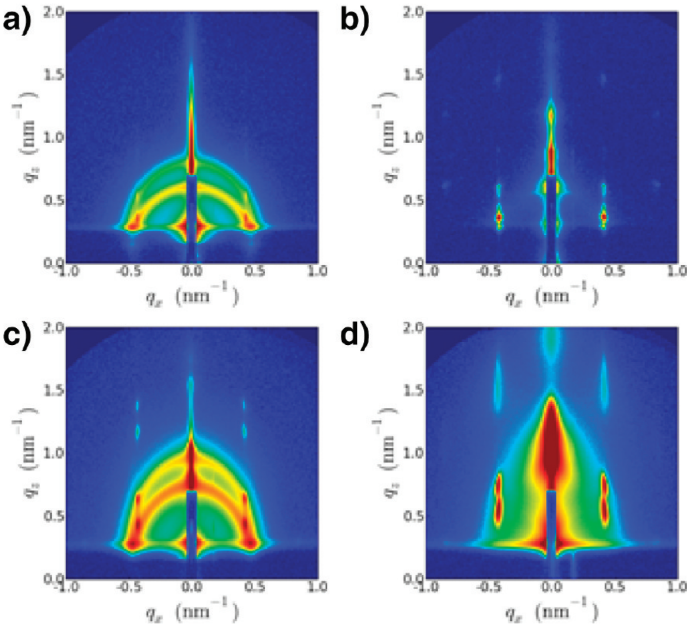

Figure 7. GISAXS patterns for the as-made (a,b) and pyrolyzed at 350 °C (c,d) mesoporous polymer resin films prepared with Pluronic P123/phenol molar ratios of (a,c) 0.008/1 and (b,d) 0.014/1.

the scattering shows both well-defined diffraction spots for a parallel oriented *c*2*mm* mesostructure and a ring that corresponds to *p*6*mm* morphology lacking defined orientation (Figure 7a). For the P123/phenol ratio of 0.014, a well-defined *c*2*mm* phase is present, but there is an additional spot in the GISAXS pattern along $q_x = 0$ (Figure 7b). We attribute it to the presence of a second phase consisting of parallel aligned lamellae sheets. Additionally, XRD profiles of the as-made films with P123/phenol ratios of 0.015 and 0.016 show three diffraction peaks at a ratio of 1:2:3, which is consistent with parallel aligned lamellae sheets (see Supporting Information). Thus, it appears the phase diagram boundary for the thin film has been shifted in comparison to bulk powders for the co-assembly of resol and Pluronic P123.

After pyrolysis at 350 °C for 3 h, a ring pattern remains in the GISAXS profile after template removal along with diffraction spots corresponding to *c*2*mm* morphology at a P123/phenol ratio of 0.008 (Figure 7c). The film at this composition is ordered but lacks long-range orientation of the mesopores. Upon template removal of the mixed phase consisting of cylindrical and lamellae domains for the as-made film at P123/phenol ratio of 0.014 (Figure 7b), only scattering from a *c*2*mm* phase is observed (Figure 7d). The lamellae morphology is not stable after removal of the template and is not observed after pyrolysis at 350 °C. A summary of the thin film morphologies observed for the different copolymer/phenol ratios is listed in Table 1.

Further increasing the fraction of phenol in the initial nanocomposite (Pluronic P123 to phenol ratio of 0.008/1) results in a change in the mesostructure; in comparison to the powder analogues, which exhibit well-ordered *p*6*mm* mesostructure, the film shows a large number of disordered worm-hole-like mesopores, as shown in Figure 8a. These worm-like mesopores are consistent with the scattering ring in its GISAXS pattern (Figure 7c). Some well-ordered mesopores are formed near the surface of the film (Figure 8b). The presence of the mixed phase demonstrates a change in the phase diagram for the surfactant/resol system when confined to a film geometry in comparison to the bulk powder. It is noted that a mixed phase is commonly observed at compositions near transitions from one morphology to another for mesoporous carbon powders.[14] This change of "phase behavior" in the thin film is likely due to preferential wetting of the surface and substrate interface by a component, similar to that for the block copolymer thin films.[34]

Similarly, by increasing the P123/phenol ratio to 0.014, well-ordered pores are not found throughout the film, as shown in Figure 9. There are some regions of ordered mesopore arrays with apparent hexagonal symmetry after pyrolysis at 350 °C (Figure 9a); these pores are found to extend through the thickness of the film. However, small disordered pores are observed in other regions of the film (Figure 9b). This behavior is attributed to the formation of a mixed mesophase as determined from GISAXS (Figure 7b); increasing the Pluronic P123/phenol ratio to 0.015 results in a lamellar morphology for the as-made film and subsequent removal of the template results in a collapsed mesostructure. It is important to note that all of the compositions examined using Pluronic P123 as the template result in well-ordered *p*6*mm* mesostructure for bulk powders (Table 1).

However, intermediate compositions of the P123/phenol ratio yield a well-ordered mesoporous film with large-domain periodicity, as shown in Figure 10. At a P123/phenol ratio of 0.012, relatively symmetric cylindrical pores are observed similar to the well-ordered

TABLE 1. Compositional Dependence on Morphology after the Template Removal at 350 °C

molar ratio of surfactant/phenol	surfactant	thin film structure[a]	powder structure[b]
0.006	F127	*Fmmm*	*Im*3*m*
0.008	F127	*DIS*[c]/‖*c*2*mm*	*Im*3*m*/*P*6*mm*
0.01	F127	*DIS*/⊥*P*6*mm*	*P*6*mm*
0.012	F127	*DIS*/⊥*P*6*mm*	*P*6*mm*
0.008	P123	*WLM*/‖*c*2*mm*	*P*6*mm*
0.01	P123	‖*c*2*mm*	*P*6*mm*
0.012	P123	‖*c*2*mm*	*P*6*mm*
0.013	P123	‖*c*2*mm*	*P*6*mm*
0.014	P123	‖*c*2*mm*/*LAM*	*P*6*mm*
0.015	P123	*LAM*	*P*6*mm*
0.016	P123	*LAM*	*P*6*mm*

[a] As determined from combined GISAXS and cross-section TEM. [b] As reported by Zhao and co-workers (refs 13 and 14). [c] DIS = disordered structure, LAM = lamellae mesostructure, WLM = worm-like micelle.

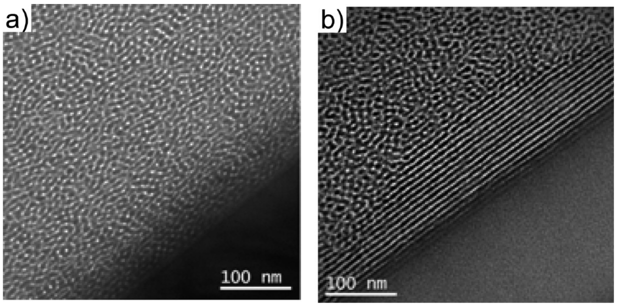

Figure 8. Cross-section TEM micrographs of the mesoporous polymer films synthesized with Pluronic P123/phenol ratio of 0.008/1 after pyrolyzed at 350 °C. The silicon substrate is in the (a,b) lower right of the micrographs.

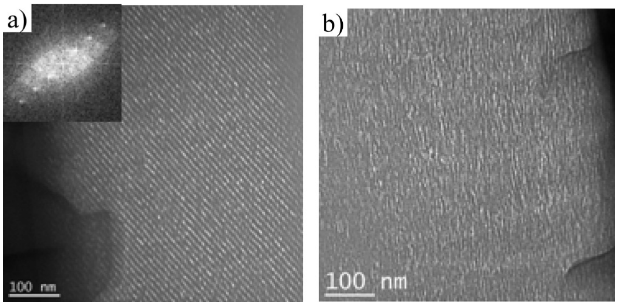

Figure 9. Cross-section TEM micrographs of the mesoporous polymer films synthesized with Pluronic P123/phenol ratio of 0.014/1 after pyrolyzed at 350 °C. The silicon substrate is in (a) the lower left and (b) upper right of the micrographs.

structure reported previously. TEM images along the (110) and (001) planes are shown in Figure 10a,b, respectively. At a ratio of 0.013, the well-ordered *c2mm* mesostructure is still present along both the (110) and (001) planes, as illustrated in Figure 10d,e, respectively. One apparent change at this larger Pluronic P123/phenol ratio is that the cross section of the pore is no longer symmetric (Figure 10f); the mesopore dimension in the plane of the film (7.2 nm) is significantly larger than that out of plane (1.2 nm). The asymmetric elliptical mesopores and more distinct *c2mm* (rectangular) morphology in Figure 10f is consistent with an increase in film contraction as the ratio increases.

The pore size of these well-ordered mesoporous films is further assessed using ellipsometric porosimetry (EP) (see Supporting Information for details). By assuming that all of the pores within the film can be accessed by toluene vapor, the total porosity of the films can be calculated from the EP measurement. Our results show that the ordered mesoporous films have porosities of 14, 19.4 and 19.6% for P123/phenol ratio of 0.01, 0.012, and 0.013, respectively. This increase in total porosity as the ratio is consistent with progressively thinner walls. However, despite using the same template, the average pore size decreases systematically as the P123/phenol ratio increases. For the well-ordered film samples, the average pore size decreases from 3.3 to 3.0 and 2.9 nm as the ratio increases from 0.01, 0.012, and 0.013, respectively. This decrease is consistent with contraction of the mesopores that is dependent upon the wall thickness; thinner walls lead to more contraction during the template removal.

The composition range for the fabrication of ordered cylindrical mesoporous films using Pluronic P123 as a template is decreased to 0.01−0.013 of P123/phenol ratio for films from 0.008−0.016 for powders. This corresponds to nearly 70% decrease in the compositional window for the fabrication of cylindrical meso-

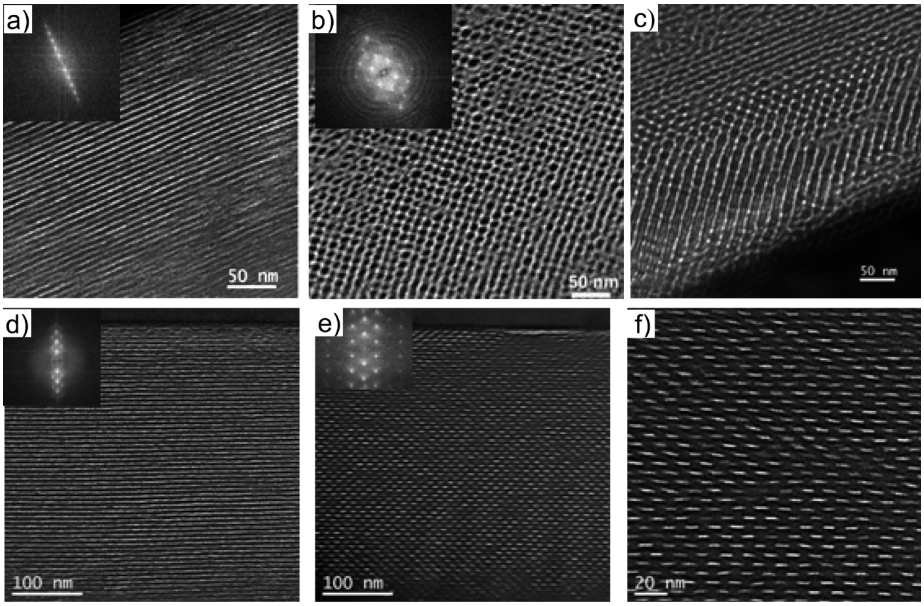

Figure 10. Cross-section TEM micrographs of the mesoporous polymer films with rectangular structure (*c2mm*) synthesized by using Pluronic P123 as a template after pyrolyzed at 350 °C in nitrogen with P123/phenol ratio of (a−c) 0.012/1 ((a) substrate in upper left, (b,c) substrate in the lower right) and (d−f) 0.013/1 (substrate at the top of micrographs). The micrographs show both the (a,d) (110) and (b,c,e,f) (001) planes.

porous films in comparison to powders. Moreover, stable, well-ordered *c2mm* films with mesopores running parallel to the substrate could not be obtained using Pluronic F127 as a template. These results illustrate the importance of both interfacial effects such as wetting/component segregation (limited composition window) and mechanical integrity of the mesostructure to withstand stresses during template removal and carbonization. Although these results are specific for the resol/Pluronic system, these concepts may also be applicable to other soft-templating systems based upon some reported issues in the literature with obtaining a well-ordered hexagonal phase in mesoporous carbon films depending upon the processing.[20,25]

CONCLUSIONS

Highly ordered mesoporous polymer resin films with cylindrical pores have been successfully synthesized by using resol as a precursor and Pluronic P123 as a template. However, the change in sample geometry from powders to thin films can significantly alter the mesostructure even when using identical processing conditions. For example, Pluronic F127 is found to not be an appropriate template for ordered cylindrical mesopores in thin films. A distorted *p6mm* mesophase is formed in the as-made organic−organic nanocomposite films, but the ordered structure mostly collapses upon template removal at 350 °C. However, well-ordered orthorhombic mesoporous films can be easily obtained by using Pluronic F127 as a template. A thicker wall in the polymeric framework for the *p6mm* mesostructure can be obtained by using Pluronic P123 as a template; in this case, well-ordered cylindrical mesopore arrays can be retained after the template removal at 350 °C. Part of the reported difficulties in obtaining ordered cylindrical mesopores in carbon films appears to be correlated with insufficient wall thickness to withstand the uniaxial stress derived during the template removal. An additional complication in obtaining ordered cylindrical mesopores in carbon films is that the composition window for the fabrication using Pluronic P123 is significantly reduced (approximately 70%) in comparison to that for the bulk powders. These results illustrate that interfacial wetting, component segregation, and mechanical integrity of the mesostructure are important factors for the synthesis of ordered cylindrical mesoporous carbon films by using organic−organic self-assembly.

METHODS

Chemicals. Triblock copolymers, Pluronic F127 (M_w = 12 600, $PEO_{106}-PPO_{70}-PEO_{106}$, BASF) and Pluronic P123 (M_w = 5800, $PEO_{20}-PPO_{70}-PEO_{20}$, BASF) were purchased from Aldrich and directly utilized as templates for the mesostructures. (Certain commercial products or equipment are described in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that it is necessarily the best available for the purpose.) Sodium hydroxide (NaOH, Aldrich) catalyzed condensation of phenol (C_6H_6O, Aldrich) and formaldehyde (CH_2O, 37 wt % in H_2O, Aldrich) was used to synthesize the resol precursor as described previously.[14]

Preparation Methods. Resol, a low-molecular-weight, water-soluble phenolic resin, was prepared from polymerization of phenol and formaldehyde using a base catalyst.[14] Mesostructured polymer resins were templated by using Pluronic F127 or P123 with molar compositions in the range of phenol/formaldehyde/NaOH/F127 (molar ratio) = 1:2:0.1:0.006−0.012 or phenol/formaldehyde/NaOH/P123 = 1:2:0.1:0.008−0.016.[14] The Pluronic template and resol were each individually dissolved in ethanol and then mixed together in the desired ratio. After stirring at room temperature for 10 min, a homogeneous solution was obtained. The films were fabricated by spin-coating the solution onto clean silicon wafer at 4000 rpm for 45 s. The films were aged at room temperature for 1 to 4 h, followed by thermal treatment in an oven at 120 °C for 24 h to cross-link the phenolic resin. For nomenclature, the films after this 120 °C thermopolymerization are called as-made films. The as-made films were then pyrolyzed in a tubular furnace under ultrapurified nitrogen atmosphere with a flow rate of 140 cm^3/min at 350−600 °C for 3 h, with a heating rate of 1 °C/min. The solution remaining after spin-coating was poured into dishes to evaporate ethanol at room temperature for 5−8 h, followed by heating in an oven at 120 °C for 24 h. The as-made products were scraped from the dishes and crushed into powders. Pyrolysis was carried out at the same condition as the films.

Characterization Techniques. The small-angle X-ray scattering (SAXS) analysis on pyrolyzed powder samples was performed on a Nanostar U small-angle X-ray scattering system (Bruker, Germany) using Cu Kα radiation (40 kV, 35 mA). The scattering angle, θ, was converted to scattering vector, q, by the equation of $q = 4\pi \sin(\theta)/\lambda$. The film structure before and after pyrolysis was detected using X-ray diffraction (XRD) in a $\theta/2\theta$ geometry using Cu Kα source (Panalytical X'Pert PRO). The angle of incidence, θ, was varied from 0.25 to 1.5°. Grazing-incidence small-angle X-ray scattering (GISAXS) measurements were performed at Argonne's Advanced Photon Source using the 8-ID-E beamline. Two-dimensional scattering images were measured using a charge-coupled device (CCD) detector at a distance of 1.975 m and an X-ray wavelength of 0.169 nm (photon energy of 7.35 keV).

The optical properties and thickness of the films were quantified using spectroscopic ellipsometry (M-2000, J. A. Woollam). A Cauchy model with an Urbach adsorption was applied to approximate the optical properties of the as-made films and mesoporous polymer resin films after pyrolysis. Ellipsometric porosimetry (EP) was performed with the same M-2000 instrument using toluene (Aldrich) as a probe molecule in order to provide the pore size distribution and the porosity of the pyrolyzed films. The films were exposed to varied relative pressures of toluene vapor controlled by air and saturated toluene using two mass flow controllers (MKS). The change in refractive index of films during the pore filling/empting provides vapor adsorption/desorption isotherms as a function of toluene partial pressure.[35] As the films are predominately polymeric, they were swollen by exposure to toluene; however, the change in film thickness was less than 10% for all films examined. The effect of thickness change on the calculated film porosity was negligible for these films based upon previous studies of porous polyphenylene films.[36] Therefore, by assuming all of the pores were filled with liquid toluene and neglecting the minor thickness change from swelling, the porosity of the film was calculated using the Bruggeman effective medium approximation. To estimate the pore size distribution (PSD), adsorption and desorption curves were fit to an arbitrary function based upon a series of Gaussian and sigmodial functions as described previously.[37] To quantify the PSD, the radius of the pore, r_p, was calculated using the

Kelvin equation with a correction for the adsorbed layer as $r_p = r_k + t$, where r_k is the Kelvin radius and t is the thickness of the absorbed layer on the pore wall before capillary condensation occurs in the mesopore; t is defined by the BET equation, based upon the adsorption of the same molecule on a nonporous surface.[14,35]

Transmission electron microscopy (TEM) was performed on the mesoporous films using a JEOL 2010F microscope operating at 200 kV. TEM cross-session samples were prepared by first grinding, dimpling, and then ion-milling the film to obtain a thin region for TEM imaging.

Acknowledgment. The authors acknowledge financial support from the State of Arizona. Facilities supported by the Center for Solid State Science were used for the characterization of materials. This work is partially supported by the National Science Foundation under Grant No. CBET-0746664. D.F. and D.Y.Z. thank NSF of China for financial support. K.G.Y. acknowledges the support of NSERC Canada in the form of a postdoctoral fellowship. N.J.F. is supported by a NIST-NRC postdoctoral fellowship program. This work was funded in part by the NIST Office of Microelectronics Programs. We acknowledge J. Strzalka for help with X-ray scattering measurements. Additionally, the authors thank M. Tate and H. Hillhouse for providing the NANOCELL code (http://www.ecn.purdue.edu/~hugh). Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

Supporting Information Available: XRD patterns of the mesoporous polymer films templated by F127 with F127/phenol molar ratio of 0.01/1 and 0.008/1 for the as-made films, and films pyrolyzed at 350 °C, adsorption/desorption isotherms and pore size distributions of mesoporous polymer-resin films with P123/phenol ratios in the hexagonal mesopore range of 0.008−0.013 using toluene vapor as a probe. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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