

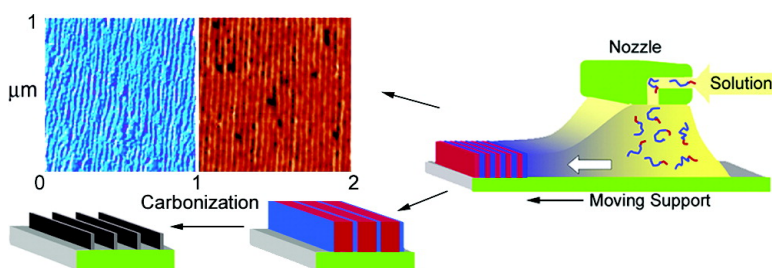
Communication

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Long-Range Ordered Thin Films of Block Copolymers Prepared by Zone-Casting and Their Thermal Conversion into Ordered Nanostructured Carbon

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One of the main challenges in the utilization of self-assembly of block copolymers to fabricate well-defined periodic nanostructures of technological relevance (e.g., for magnetic data storage^{1a,b} or for lithography^{1c}) is the achievement of long-range ordered structures. Some recently developed strategies toward this goal typically involve the use of external stimuli, such as electric field^{2a} or shear (e.g., roll casting),^{2b} or employ such phenomena as eutectic solidification,^{2c} orientation during solvent evaporation,^{2d} graphoepitaxy,^{2e} and alignment on lithographically patterned substrates.^{2f} In the present work, the technique of directional casting, also referred to as “zone-casting”, which had been originally developed to facilitate the oriented growth of molecular crystals,³ has been used to achieve large-scale alignment of nanoscale domains of a phase-separated diblock copolymer. Oriented block copolymer films were then converted into carbon films with well-defined, long-range ordered texture by applying the recently developed approach to the synthesis of nanostructured carbon.⁴ This approach is based on the use of block copolymers containing polyacrylonitrile (PAN), which serves as a carbon precursor and a sacrificial block, immiscible with PAN (e.g., poly(*n*-butyl acrylate), PBA). Nanoscale PAN domains are first stabilized by heating under air to 200–300 °C and are then carbonized through heating to about 800 °C under nitrogen, with concomitant volatilization of the sacrificial block.

The current study was carried out with PBA-*b*-PAN diblock copolymers described by the structural formula (BA)₂₄₀(AN)₁₂₄.⁵ Zone-casting was performed by depositing the copolymer solution in *N,N*-dimethylformamide (DMF) onto a moving substrate with the aid of a syringe equipped with a flat nozzle (Figure 1a). The syringe plunger and the substrate were displaced at 6 μm/s using two separate computer-controlled stepper motors. To achieve the desirable solvent evaporation rate, the temperatures of the copolymer solution and of the substrate were maintained at 90 °C. Adjustment of the solution concentration under constant solution supply rate and constant rate of substrate withdrawal made it possible to vary the film thickness in the range from 100 nm to 1 μm (c.f. Supporting Information).

The surface morphology of thin films of PBA-*b*-PAN block copolymers was visualized using tapping mode atomic force microscopy (TMAFM). Phase contrast images of films prepared by zone-casting exhibited characteristic long-range ordered striped morphology with elongated rigid PAN domains appearing as brighter stripes alternating with more compliant and mechanically lossy PBA phase (Figure 1b, left half). The periodicity (domain spacing) of this oriented texture was determined by 2-D Fourier

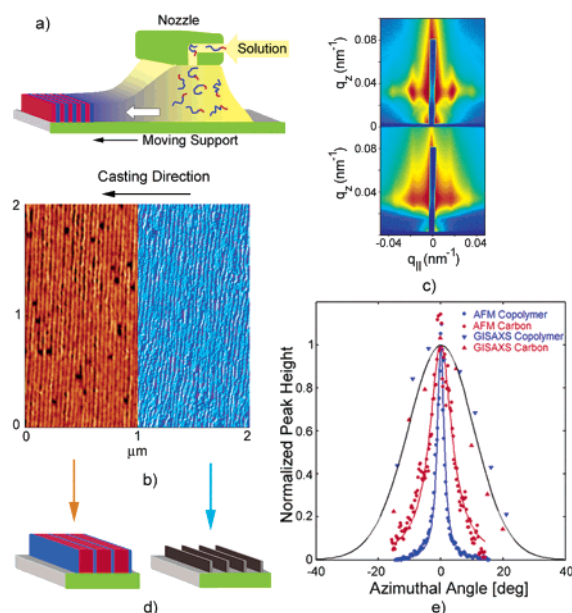


Figure 1. Long-range order in thin films of PBA-*b*-PAN block copolymers prepared by zone-casting (a) and in nanostructured carbons prepared by subsequent pyrolysis. (b) AFM phase images (left, copolymer; right, carbon); (c) GISAXS patterns acquired at 90° to casting direction (top, copolymer; bottom, carbon); (d) schematic illustration of lamellar order (left, copolymer; right, carbon); (e) azimuthal profiles of maxima in 2-D Fourier transforms of AFM images and maxima in GISAXS patterns corresponding to the lamellar period.

transform (FT) of AFM images and was equal to 37 nm. The high degree of orientation was reflected by the shape of azimuthal profiles of the FT magnitude maximum corresponding to this periodicity; the azimuthal profiles could be well fitted by a Lorentzian with a half-width at half-height, $\Delta\phi = 1.4^\circ$ (Figure 1e). Imaging of adjacent $3 \times 3 \mu\text{m}$ areas revealed that the orientation was almost perfectly preserved over the distances of tens of micrometers, as shown in the accompanying animation, constructed from overlaid images covering the range of over 30 μm in two directions: parallel and perpendicular to the orientation direction (movie, Supporting Information). Random inspection of other regions revealed that the orientation persisted over the entire sample area (3 cm × 5 cm).

Grazing incidence small-angle X-ray scattering (GISAXS) patterns of the copolymer sample prepared by zone-casting (Figure 1c, top) were consistent with the lamellar structure with lamellae perpendicular to the surface and oriented perpendicular to the casting direction (see scheme in Figure 1d, left). The periodicity determined from the position of the first maximum in the GISAXS

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pattern was equal to 36 nm, in very good agreement with AFM data. The GISAXS pattern shown in Figure 1c (top) was acquired with the incident beam aligned at an angle $\phi_0 = 90^\circ$ with respect to the casting direction. The degree of orientation with respect to casting direction was ascertained by acquiring GISAXS patterns at $\phi = \phi_0 \pm 20^\circ$. Partial azimuthal profile of the scattering maximum corresponding to the 36 nm periodicity is shown in Figure 1e. This time, the resulting peak was better fitted with a Gaussian line shape rather than with a Lorentzian, and its half-width at half-height was equal to $\Delta\phi = 12.6^\circ$. Gaussian shape of the peak and its broadening in comparison with the FT intensity peak obtained from the AFM data indicate that, over the large area sampled by GISAXS, the axis of “sharp” local orientation fluctuated by about $\pm 10^\circ$.

The orientation of lamellar domains in the direction perpendicular to the zone-casting direction might appear unexpected, especially if it were to be viewed as resulting from the anisotropic flow associated with the zone-casting process. (Numerous examples of flow-induced orientation of block copolymer domains predominantly point to the orientation *along* the flow direction.^{2b,d}) Our results suggest that in zone-casting, the orientation of block copolymer domains is governed by the attempt to align along the solvent evaporation front (phase separation zone), rather than by the anisotropic flow toward the front.

Copolymer films prepared by zone-casting were then subjected to thermal stabilization and pyrolysis at 800 °C. Remarkably, the long-range ordering of lamellar structure was retained following this treatment, yielding materials with well-defined, highly ordered nanostructure. The AFM images of resulting nanostructured carbon still revealed the presence of unidirectional, striped surface morphology (Figure 1b, right half of the image). Whereas the texture periodicity remained nearly unchanged in comparison with that of the block copolymer precursor (36 vs 37 nm, Figure S3, Supporting Information), the azimuthal profiles of the relevant peak in the 2-D FT, while still Lorentzian, were somewhat broadened ($\Delta\phi = 4.3^\circ$, Figure 1e).

Ordered lamellar structure was also clearly evident in GISAXS patterns (Figure 1c, bottom), indicating that PAN lamellae were converted into carbon sheets (see Figure 1d, right), preserving their spacing (38 nm based on the position of the first maximum in the GISAXS pattern; Figure S3, Supporting Information) and orientation normal to the substrate. Orientation of lamellae in the direction perpendicular to casting direction was also very well preserved, as indicated by the partial azimuthal profile of the relevant scattering maximum (Figure 1e), which was essentially unchanged in comparison with its block copolymer counterpart. Such nearly perfect preservation of lamellar periodicity and alignment is quite striking, given the fact that upon pyrolysis, a very substantial fraction of material was removed through the volatilization of sacrificial PBA phase and through partial dehydrogenation and denitrogenation of PAN. Transmission electron microscopy (TEM) of carbon films lifted from the substrate by HF etching (Figure S4, Supporting Information) provided strong indication that this outstanding stability of nanostructure was facilitated by the interaction with the underlying substrate. Whereas TEM images also revealed the presence of elongated (carbon) domains parallel to each other and perpendicular to casting direction, their periodicity ranged only from 12.5 to 15.7 nm, pointing to the collapse of carbon sheets onto each other upon lifting from the substrate. The thickness of carbon sheets observed in TEM images ranged from 7.5 to 9.2 nm and

was close to the thickness of PAN lamellae estimated from the lamellar period and copolymer composition. The implied limited shrinkage in the direction perpendicular to the lamellar surface upon pyrolysis could be explained by the orientation of PAN chains in this direction in apparent analogy with carbon fibers.⁶ Additional evidence of an anisotropic shrinkage of PAN lamellae upon pyrolysis comes from the broadening of the Bragg rods in the GISAXS pattern in q_z direction after pyrolysis, which is indicative of a significant decrease of the height of lamellae above the substrate surface.

In conclusion, the large-scale, long-range ordering of lamellae in thin films of PBA-*b*-PAN block copolymers was achieved by using a simple and versatile zone-casting technique. Ordered copolymer films were then successfully converted into ordered nanostructured carbons which retained the oriented morphology of the PAN precursor. Materials pyrolyzed in the temperature range from 500 to 900 °C were electrically conductive, exhibiting conductivities ranging from 10 to 10³ S/cm. Ordered anisotropic films prepared in this study are currently used as a model system in the ongoing study aimed at the elucidation of electrical transport properties in nanostructured carbons. They also show promise as field emission electrodes. The applicability of zone-casting to the control of the nanoscale morphology of other block copolymer systems is currently under investigation.

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Supporting Information Available: Experimental conditions and detailed characterization results, including TMAFM, TEM, Raman, FTIR, and GISAXS. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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