J|A|C|S
COMMUNICATIONS

Nanostructured Carbon Arrays from Block Copolymers of Polyacrylonitrile

Tomasz Kowalewski,* Nicolay V. Tsarevsky, and Krzysztof Matyjaszewski*

Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213

Received December 28, 2001

Carbon materials prepared by pyrolysis of organic precursors play an important role in many areas of chemistry and chemical engineering, such as separation processes, electrochemistry, catalysis, energy storage/conversion devices, etc.[1] Well-defined carbon nanostructures have been receiving a tremendous amount of attention since the discovery of fullerenes[2] followed by carbon nanotubes.[3] Numerous envisioned applications of nanostructured carbons include nanocomposites,[4] gas storage media[5] (in particular hydrogen storage for fuel cells[6]), catalyst supports,[7] and proximal probes.[8] The electrical properties of carbon nanotubes point to the possibility of their use as nanoelectronic devices, such as field effect transistors[9] and field-emission electrodes for flat panel displays.[10]

In this Communication, we present a novel approach to well-organized nanostructured carbon materials, based on the carbonization of block copolymers containing polyacrylonitrile (PAN). In a certain way, it resembles the synthesis of fullerenes and carbon nanotubes, where a nanostructured carbon is obtained from decomposition products of organic precursors. The synthesis of carbon nanotubes in currently used processes such as arc discharge,[11] laser ablation,[12] and chemical vapor deposition[13] effectively proceeds from the gas phase, where control of the resulting species is still a big challenge. The distinguishing feature of the method presented here is that it relies on the use of block copolymers in which the carbon precursor (PAN) is preorganized into a well-defined nanostructure through familiar phase-separation-driven self-assembly,[14] induced by the presence of a sacrificial, immiscible block (e.g., *n*-butyl acrylate). The nanostructured precursor phase serves then as a template of the target carbon material, which is obtained by pyrolysis accompanied by volatilization of sacrificial phase. The key to success of such a strategy is the survival of the original nanostructure through pyrolysis. This might appear extremely challenging, since a high extent of graphitization typically requires heating the material to temperatures as high as 600 °C and above. Herein we demonstrate that this can be accomplished utilizing the process of thermal stabilization used in the manufacturing of carbon fibers.[15] During this step the material is heated to 200−230 °C in the presence of air, which leads to conversion of PAN into a cross-linked, ladder polymer[15] and to stabilization of the nanostructure.

Several block and gradient copolymers were prepared, but throughout this study we focused on well-defined ABA triblock copolymer of acrylonitrile (AN) and *n*-butyl acrylate (BA) with average composition $(AN)_{45}-(BA)_{530}-(AN)_{45}$ and polydispersity $M_w/M_n = 1.26$. The copolymer was prepared by atom transfer radical polymerization (ATRP).[16] The first step was the preparation of BA-based macroinitiators using the difunctional initiator dimethyl 2,6-dibromoheptanedioate and CuBr/*N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA) as the catalyst. To achieve controlled polymerization of AN using poly(BA)-based macroinitiators, it is necessary to increase the relative rate of initiation versus propagation, which was achieved using halogen exchange (i.e., CuCl/bipyridine was applied as the catalyst).[17]

Ultrathin copolymer films were prepared by spin-coating from 2 to 50 mg/mL solutions in DMF onto freshly cleaved mica or onto silicon wafer chips with a native oxide layer on the surface. Thin films (from hundreds of nanometers to micrometers) were prepared by placing a drop of solution on the substrate and allowing the solvent to evaporate freely. Prior to pyrolysis, the samples were vacuum-annealed for 1−2 h at temperatures of 200−230 °C and cooled to room temperature in order to ensure uniform starting morphologies. The surface morphology of films was studied with the aid of tapping-mode atomic force microscopy (AFM).

Visualization of phase-separated PAN domains in the PBA matrix was possible owing to compliance-based contrast[18] between the soft PBA matrix ($T_g \approx -50$ °C, as determined by differential scanning calorimetry) and rigid PAN domains ($T_g > 100$ °C). AFM images of annealed films revealed the presence of uniformly spaced globular protrusions, with an average center-to-center spacing of ∼30 nm (Figure 1a, Table 1). These regular protrusions were identified as rigid PAN domains, since they were more pronounced upon switching from "light tapping" imaging conditions (set-point $S = A/A_o \rightarrow 1$, where A_o and A denote respectively the "free" cantilever amplitude and the amplitude maintained by the feedback loop during imaging) to "hard tapping" ($S \approx 0.5-0.7$). The globular shape of PAN domains is consistent with the spherical morphology which was indeed expected, given the composition of the copolymer under study (∼6.5 wt % of PAN).[19] Following vacuum annealing, the samples were then subjected to 2 h of annealing at 200−230 °C in contact with air in order to stabilize the PAN phase, and subsequently they were pyrolyzed by heating at 20 °C/min under nitrogen gas from room temperature.

As shown in AFM images of samples heated to 600 and 1200 °C (Figure 1b,c), the samples retained the overall domain topology and spacing (Table 1).

In contrast with pristine and annealed samples, the morphology of pyrolyzed materials did not change upon switching between light tapping and hard tapping, indicating the disappearance of the soft, compressible PBA phase. Consistent with this observation, the samples exhibited a pronounced increase of overall roughness, as characterized by the rms roughness and height range (Table 1). Upon pyrolysis the materials underwent extensive graphitization, as evidenced in Raman spectra (Figure 2), which were very similar to those reported in the literature for carbon fibers,[20] with a characteristic strong, relatively narrow band around 1600 cm^{-1}, corresponding to a graphitic species (G-band) and a broader band centered around 1350 cm^{-1}, corresponding to an sp^3 carbon species (D-band).[20] In contrast, flame pyrolysis of the control samples, which were not subjected to heat stabilization, resulted in the formation of randomly scattered nanoparticulate residues (see

---

* Address correspondence to these authors. E-mail: tomek@andrew.cmu.edu.

10.1021/ja0178970 CCC: $22.00

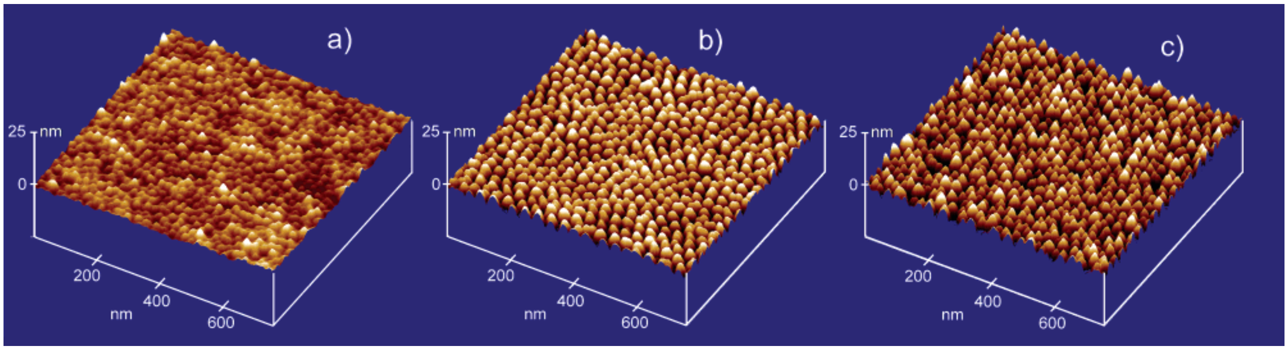

Figure 1. Tapping-mode AFM images illustrating the effect of thermal treatment on the evolution of nanoscale morphology of ultrathin (d < 50 nm) films of $(AN)_{45}-(BA)_{530}-(AN)_{45}$ block copolymer spin-coated onto a silicon wafer. (a) Sample vacuum-annealed for 2 h at 220 °C to equilibrate the morphology; (b) sample heated under nitrogen at 20 deg/min from room temperature to 600 °C and (c) to 1200 °C.

Table 1. Surface Geometry of $(AN)_{45}-(BA)_{530}-(AN)_{45}$ before and after Pyrolysis to Different Temperatures

	before	600 °C	1200 °C
domain spacing (nm)[a]	31	34	30
rms roughness (nm)	0.84	1.4	2.0
height range (nm)	6.1 ± 0.6	7.6 ± 0.3	10.5 ± 1.0

[a] Determined from 2-D Fourier transforms of images.

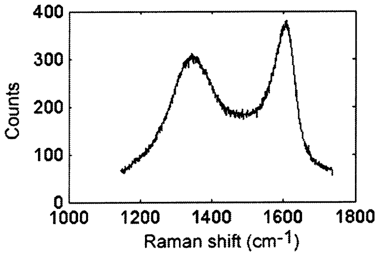

Figure 2. Raman spectrum of the sample pyrolyzed by heating under nitrogen at 20 deg/min to 900 °C.

Supporting Information). Interestingly, as shown in the Supporting Information, following heat stabilization, even relatively poorly controlled flame pyrolysis resulted in materials with well-defined nanostructure corresponding to the morphology of a block copolymer precursor. This robustness of the described route to well-defined nanostructured carbons suggests that it should be highly amenable to scale-up. Extension of this route to block copolymers with other morphologies (cylindrical, gyroid,[21] lamellar) should be relatively straightforward. The resulting nanostructured carbons are not expected to achieve the atomic-level perfection of fullerenes or carbon nanotubes. However, their well-defined nanostructure may lead to interesting electronic effects, such as a dependence of the band gap on the size and topology of carbon domains. They may also find applications in numerous areas utilizing pyrolytic carbons (e.g., supercapacitors, membranes, electrodes), where control of nanoscale morphology would be highly desirable, but so far has not been fully achieved.

Acknowledgment. The NSF (T.K., DMR 9871874; K.M., DMR 0090409), the ATRP/CRP Consortia, and the Carnegie Mellon University (T.K. start-up) are acknowledged for funding. Raman spectra were acquired by Art Hewig in Professor Tod Przybycien's laboratory (Department of Chemical Engineering).

Supporting Information Available: Details of the synthesis; AFM characterization of block copolymers (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Burchell, T. D., Ed. *Carbon materials for advanced technologies*; Pergamon: Amsterdam, Oxford, 1999.
(2) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature (London)* **1985**, *318*, 162−163.
(3) Iijima, S. *Nature (London)* **1991**, *354*, 56−58.
(4) Schadler, L. S.; Giannaris, S. C.; Ajayan, P. M. *Appl. Phys. Lett.* **1998**, *73*, 3842−3844.
(5) Gadd, G. E.; Blackford, M.; Moricca, S.; Webb, N.; Evans, P. J.; Smith, A. M.; Jacobsen, G.; Leung, S.; Day, A.; Hua, Q. *Science* **1997**, *277*, 933−936.
(6) Dillon, A. C.; Jones, K. M.; Bekkedahl, T. A.; Kiang, C. H.; Bethune, D. S.; Heben, M. J. *Nature (London)* **1997**, *386*, 377−379. Dillon, A. C.; Heben, M. J. *J. Appl. Phys. A: Mater. Sci. Process.* **2001**, *72*, 133−142.
(7) Planeix, J. M.; Coustel, N.; Coq, B.; Brotons, V.; Kumbhar, P. S.; Dutartre, R.; Geneste, P.; Bernier, P.; Ajayan, P. M. *J. Am. Chem. Soc.* **1994**, *116*, 7935−7936.
(8) Dai, H.; Hafner, J. H.; Rinzler, A. G.; Colbert, D. T.; Smalley, R. E. *Nature (London)* **1996**, *384*, 147−150.
(9) Collins, P. G.; Zettl, A.; Bando, H.; Thess, A.; Smalley, R. E. *Science (Washington, D.C.)* **1997**, *278*, 100−103.
(10) de Heer, W. A.; Chatelain, A.; Ugarte, D. *Science (Washington, D.C.)* **1995**, *270*, 1179−1180.
(11) Bethune, D. S.; Kiang, C. H.; de Vries, M. S.; Gorman, G.; Savoy, R.; Vazquez, J.; Beyers, R. *Nature (London)* **1993**, *363*, 605−607.
(12) Thess, A.; Lee, R.; Nikolaev, P.; Dai, H.; Petit, P.; Robert, J.; Xu, C.; Lee, Y. H.; Kim, S. G.; Rinzler, A. G.; Colbert, D. T.; Scuseria, G. E.; Tomanek, D.; Fischer, J. E.; Smalley, R. E. *Science* **1996**, *273*, 483−487.
(13) Jose-Yacaman, M.; Miki-Yoshida, M.; Rendon, L.; Santiesteban, J. G. *Appl. Phys. Lett.* **1993**, *62*, 657−659.
(14) Hamley, I. W. *The Physics of Block Copolymers*; Oxford University Press: Oxford, 1998.
(15) Bajaj, P.; Roopanwal, A. K. J. *Macromol. Sci., Rev. Macromol. Chem. Phys.* **1997**, *C37*, 97−147.
(16) Wang, J.-S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614−5615.
(17) Shipp, D. A.; Wang, J.-L.; Matyjaszewski, K. *Macromolecules* **1998**, *31*, 8005−8008.
(18) Magonov, S. N.; Cleveland, J.; Elings, V.; Denley, D.; Whangbo, M. H. *Surf. Sci.* **1997**, *389*, 201−211.
(19) Bates, F. S.; Fredrickson, G. H. *Annu. Rev. Phys. Chem.* **1990**, *41*, 525−557.
(20) Tuinstra, F.; Koenig, J. L. *J. Chem. Phys.* **1970**, *53*, 1126−1130.
(21) Hajduk, D. A.; Harper, P. E.; Gruner, S. M.; Honeker, C. C.; Kim, G.; Thomas, E. L.; Fetters, L. J. *Macromolecules* **1994**, *27*, 4063−4075.

JA0178970