Supporting Information

Preparation of porous nanocarbons with tunable morphology and pore size from copolymer templated precursors

Mingjiang Zhong,[a] Chuanbing Tang,*[b] Eun Kyung Kim,[a,c] Michal Kruk,[a,d] Ewa B. Celer,[e] Mietek Jaroniec,[e] Krzysztof Matyjaszewski,*[a] and Tomasz Kowalewski*[a]

[a] *Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213, United States*

[b] *Department of Chemistry and Biochemistry, University of South Carolina, Columbia, 631 Sumter Street, Columbia, South Carolina 29208, United States*

[c] *Current address: Battery R&D, AMD PJT, LG Chem Research Park, LG Chem, 104-1, Moonji-dong, Yuseong-gu, Daejeon, 305-738, Korea*

[d] *Current address: Department of Chemistry, College of Staten Island and Graduate Center, City University of New York, 2800 Victory Boulevard, Building 6S-241, Staten Island, New York 10314, United States*

[e] *Department of Chemistry, Kent State University, Kent, Ohio 44242, United States*

*To which all correspondences should be addressed: tang4@mailbox.sc.edu, km3b@andrew.cmu.edu, tomek@andrew.cmu.edu

Experimental Materials and Methods

Materials: Acrylonitrile (AN), *n*-butyl acrylate (BA), methyl 2-bromopropionate (MBP), *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA), 2,2′-bipyridine (bpy), CuBr, CuCl, $CuBr_2$, anisole, dimethylformamide (DMF), dimethylsulfoxide (DMSO), tetrahydrofuran (THF), and methanol were all obtained from Sigma-Aldrich. CuCl and CuBr were purified by stirring in glacial acetic acid followed by washing with ether and dried overnight under vacuum. Monomers were passed through a basic alumina column prior to use. All other chemicals were used as received.

Synthesis and film preparation: The majority of diblock copolymers employed in the present research were prepared by ATRP with halogen exchange, as described in our earlier studies.[1] Monofunctional bromine-terminated poly(*n*-butyl acrylate) (PBA) homopolymer was synthesized as a macroinitiator to be chain-extended with polyacrylonitrile (PAN) and thus to yield the desired PAN-*b*-PBA diblock copolymer. Thin film samples of block copolymers were prepared by drop-casting copolymer solutions (10 mg/mL) in dimethylformamide onto cleaned silicon wafer substrates (*n*-type, Silicon Quest, Inc.). The films were thoroughly dried in a vacuum chamber at room temperature and then annealed at 160 °C. Typical film thickness ranged from several hundred nanometers to few micrometers, as measured by AFM. The PAN-*b*-PBA copolymers (for both thin films and bulk materials) were converted into carbonaceous materials through heating under air to 280 °C at a rate of 20 °C/min and maintaining at 280 °C for 1 h; subsequent heating under nitrogen to target temperature (600 °C) at a rate of 10 °C/min and keeping at this target temperature for certain time and finally naturally cooling to room temperature.

Characterization: Tapping mode atomic force microscopy (TMAFM) studies were carried out with the aid of a NanoScope III-M system (Digital Instruments, Santa Barbara, CA), equipped with a J-type vertical engage scanner. The AFM observations were performed at room temperature under air using silicon cantilevers with spring constant of 20 - 80 N/m and nominal resonance frequency of 230-410 kHz (TappingMode Etched Silicon Probes). Morphologies of carbon powders and thin films obtained through the stabilization and carbonization of PAN-*b*-PBA copolymers were studied with the aid of transmission electron microscopy (TEM) (JEOL JEM-2000 EX II with acceleration voltage 200 kV). Nitrogen adsorption measurements were carried out at -196°C on a Micrometritics ASAP 2010 volumetric gas adsorption analyzer. Prior to measurements, samples were degassed at 300 °C under vacuum overnight. Brunauer–Emmett–Teller (BET) surface areas were determined from N_2 adsorption isotherms at 77 K. Multipoint BET measurements were performed at relative pressures (P/P_0) in the range of 0.05 - 0.2. The mesopore size distribution was obtained from Barett-Joyner-Halenda (BJH) method from the desorption branch.

Table S1. Morphologies of thin films of PAN-*b*-PBA diblock copolymers determined from TMAFM image.

Sample Code	Composition (DP_{BA}/DP_{AN})	M_w/M_n (from GPC)	wt%(AN)	Morphology of PAN Domains
P1	202/17	1.17	3.4	*No phase contrast*
P2	240/36	1.23	5.8	*Spherical*
P3	90/22	1.12	9.2	*Spherical*
P4	240/104	1.23	15.2	*Cylindrical*
P5	240/124	1.22	17.6	*Cylindrical*
P6	202/106	1.30	17.8	*Cylindrical*
P7	90/59	1.22	21.2	*Cylindrical/ Lamellar*
P8	90/84	1.20	27.9	*Cylindrical/ Lamellar*
P9	40/67	1.10	40.9	*Branched*
P10	70/99	1.25	36.9	*Branched*
P11	78/114	1.20	37.7	*Branched*
P12	90/128	1.36	37.1	*Branched*
P13	90/159	1.25	42.2	*Branched*
P14	117/180	1.30	38.9	*Branched*
P15	141/245	1.28	41.8	*Branched*
P16	173/305	1.35	42.2	*Branched*

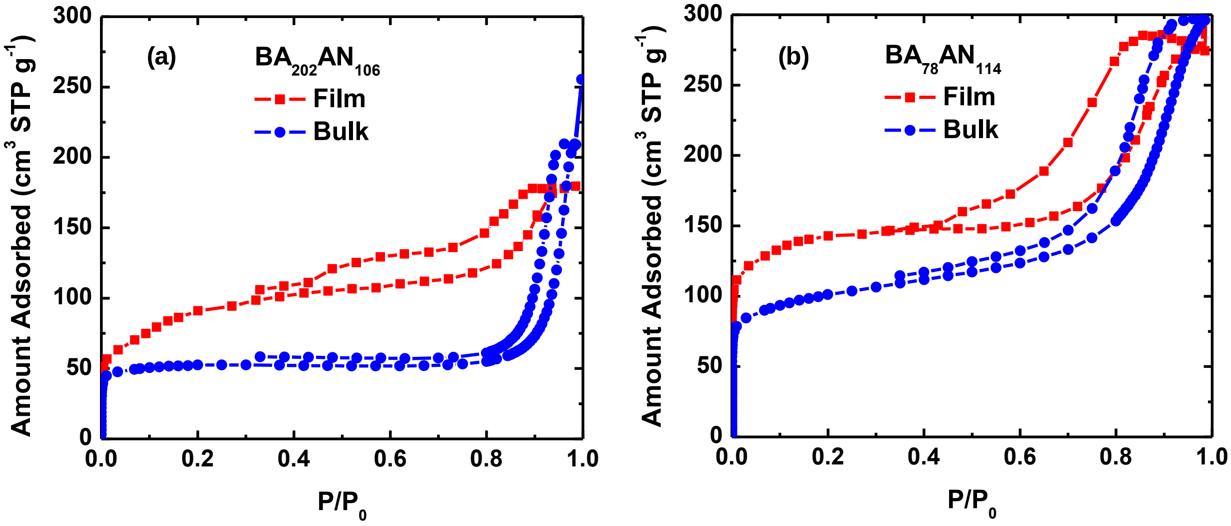

Fig. S1 N_2 adsorption/desorption isotherms at -196 °C thin film and bulk CTNCs from (a) $BA_{202}AN_{106}$; (b) $BA_{78}AN_{114}$.

References

1. (a) C. Tang, T. Kowalewski and K. Matyjaszewski, *Macromolecules*, 2003, **36**, 1465; (b) C. Tang, T. Kowalewski and K. Matyjaszewski, *Macromolecules*, 2003, **36**, 8587.