

Well-Defined Poly(ethylene oxide)–Polyacrylonitrile Diblock Copolymers as Templates for Mesoporous Silicas and Precursors for Mesoporous Carbons

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Poly(ethylene oxide)–polyacrylonitrile (PEO-*b*-PAN) diblock copolymers were synthesized and used as supramolecular templates for mesoporous silicas and precursors for mesoporous carbons. The copolymers were prepared from poly(ethylene oxide) homopolymers through chain extension with polyacrylonitrile (PAN) via atom transfer radical polymerization and had a low polydispersity index (~ 1.1), a degree of polymerization of PAN from 16 to 208, and a PAN content of 20–70 wt %. The copolymers were used as supramolecular templates for the formation of silica from tetraethyl orthosilicate in aqueous HCl solution. The obtained silica/PEO-*b*-PAN composites were calcined to obtain mesoporous silicas or heat-treated to convert PAN into carbon, the latter being isolated through the dissolution of silica. The silicas had specific surface areas of $\sim 550 \text{ m}^2 \text{ g}^{-1}$, total pore volumes of $0.6\text{--}1.2 \text{ cm}^3 \text{ g}^{-1}$, and uniform mesopores of diameter $\sim 10 \text{ nm}$, which appeared to be cylindrical with short-range ordering. The carbons had broad pore size distributions, yet some of them exhibited a certain degree of nanoscale ordering. Their surface areas were $\sim 900 \text{ m}^2 \text{ g}^{-1}$, and the total pore volumes were $0.9\text{--}1.9 \text{ cm}^3 \text{ g}^{-1}$. The carbons exhibited some degree of ordering of graphene sheets in their frameworks. A clear similarity between the silica pore shape and the carbon nanostructure shape was observed for samples from the silica/EO₄₅AN₄₃ composite.

Introduction

Mesoporous carbons, that is, carbons with pores of diameter in the range from 2 to 50 nm, have recently attracted a lot of attention.^{1–11} The interest in the mesoporous carbons largely stems from their prospective applications as adsorbents for large molecules and biomolecules;^{12–14} catalyst supports;¹⁵ components of electrochemical double-layer capacitors,^{2,16–19} fuel cells^{3,20} and Li-ion batteries;²¹ chromatographic packings;²² and templates for the synthesis of

inorganic nanostructures.^{23–27} An additional range of prospective applications, including those in photovoltaic cells, can now be pursued with the development of methods for the synthesis of nanoporous carbons in thin film form.^{3,28,29}

The synthesis of mesoporous carbons through inverse replication of mesoporous silica templates³⁰ has been actively pursued over the last several years,^{1–3,7,8,16,31–36} especially after the successful synthesis of ordered mesoporous carbons (OMCs)^{1,2} using ordered mesoporous silica (OMS)^{37,38}

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templates. This strategy typically involves (i) the synthesis of the silica template, (ii) its infiltration with the carbon precursor (or carbon), and (iii) carbonization of the precursor (if needed), followed by the removal of the silica template. The silica templates are often prepared using organic molecules as supramolecular templates,^{37,38} so attempts were made to directly convert these soft templates to carbon,^{39,40} thus eliminating the need for the removal of the organic template and subsequent infiltration of the silica framework with the carbon precursor. In particular, nanostructured silicas with cyclodextrin templates were directly converted to disordered microporous carbons,³⁹ and OMSs templated by poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) triblock copolymers were used to prepare OMCs.⁴⁰ The possibility of the synthesis of OMCs via templating of polymeric precursors (resorcinol–formaldehyde resin) with block copolymers was also recently demonstrated.^{28,41}

We recently showed that carbon nanoobjects and nanostructured films can be synthesized directly from phase-separated block copolymers.^{29,42,43} In such copolymers, one block (e.g., polyacrylonitrile, PAN) serves as a carbon precursor, whereas the other block (e.g., poly(butyl acrylate), PBA), which is immiscible with the first one, induces self-assembly of the block copolymer into a variety of nanostructures and is sacrificed upon pyrolysis.^{29,42} It should be noted that PAN, which is the preferred carbon source in this strategy, is known as an excellent carbon precursor for the carbon fiber synthesis⁴⁴ and also was recently used by us and others in the synthesis of OMCs^{36,45} and disordered mesoporous carbons.⁵ Our block-copolymer-based approach was successfully demonstrated by converting PBA-*b*-PAN diblock copolymers to thin carbon films consisting of isolated carbon protrusions⁴² and long-range-ordered lamellae.²⁹ The required PBA-*b*-PAN copolymers can be synthesized using a variety of controlled radical polymerization methods,^{42,46,47} including atom transfer radical polymerization (ATRP).^{48,49}

In the case of organic sacrificial blocks, which are volatilized before the completion of the carbonization of the carbon precursor blocks, the surface morphology of carbon precursor domains was typically preserved upon conversion to carbon.^{29,42} However, for thin films, this preservation may be at least partially facilitated by the presence of the underlying surface, and upon lifting off the surface, the films can undergo a structural rearrangement.²⁹ Consequently, the conversion of these copolymers to nanoporous carbon particles, monoliths, or thick films with preservation of the original morphology is a challenging task. In fact, the conversion of the bulk block copolymers into nanoporous materials is one of the present challenges in polymer science.⁵⁰ To overcome this difficulty, we have designed a new system in which the sacrificial block of the copolymer is water-soluble and the copolymer is co-assembled with silica species, which leads to the formation of the thermally stable siliceous phase. Thus formed silica acts as a scaffold supporting the formation of the carbon phase during the pyrolysis and is subsequently etched away, leaving behind the mesoporous carbon. This mesoporous carbon synthesis strategy can be regarded as a combination of the synthesis of carbons from phase-separated block copolymers⁴² and the synthesis of mesoporous carbons through inverse replication of mesoporous silica templates.³⁰ Our approach resembles the recently reported method for the synthesis of carbons from silica/poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (EO_{*m*}PO_{*n*}EO_{*m*}) composites,⁴⁰ which does not involve the use of designed copolymers.

The synthesis of well-defined poly(ethylene oxide)–polyacrylonitrile (PEO-*b*-PAN) block copolymers was accomplished using ATRP.^{48,49,51–56} The PEO-*b*-PAN copolymers were used as templates for mesoporous silicas and as precursors for mesoporous carbons (see Scheme 1). The diblock copolymers were designed to feature (i) hydrophilic PEO blocks, which can favorably interact with silica species, and (ii) hydrophobic PAN blocks that are suitable for templating the mesoporosity in silica nanostructures and can be converted into carbon through a suitable thermal treatment. The development of methods for the controlled polymerization of PAN via ATRP^{46,57,58} provided a convenient and robust avenue for the synthesis of well-defined PAN-containing precursors. As a first step, we demonstrated that these new PEO-*b*-PAN copolymers can indeed be used to synthesize silicas with short-range-ordered uniform mesopores. More importantly, the synthesis of mesoporous

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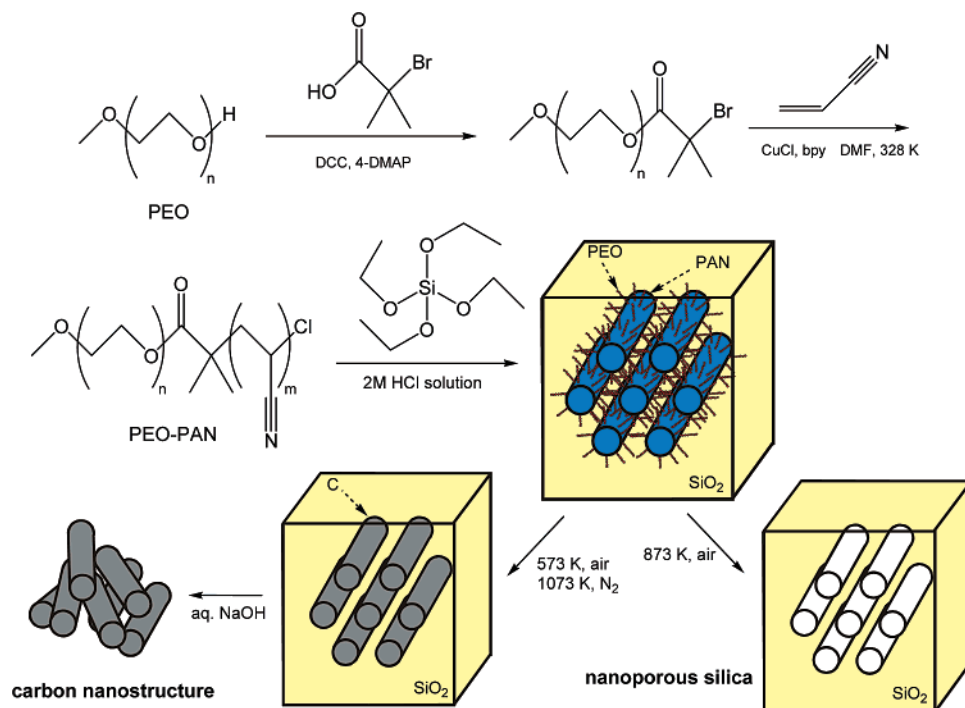
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Scheme 1. Approach for the Synthesis of Nanostructured Silica/Carbon Composites, Nanoporous Silicas, and Carbons on the Basis of the Supramolecular Templating of Silicas with PEO-*b*-PAN Copolymers

carbons from silica/PEO-*b*-PAN composites was also successful, although the latter exhibited broader pore size distributions (PSDs) and a lower degree of structural ordering.

Experimental Section

Reagents. CuCl was purified according to the procedure described by Keller and Wycoff.⁵⁹ Acrylonitrile (AN), which was purchased from Aldrich, was distilled over calcium hydride before use. Monohydroxy-terminated PEO ($M_n = 2000$ and 5000 g mol^{-1}), 2-bromoisobutyric acid, dicyclohexylcarbodiimide (DCC), 4-(*N,N*-dimethylamino)pyridine (4-DMAP), 2,2'-dipyridyl (bpy), *N,N*-dimethylformamide (DMF), dichloromethane, and diethyl ether were used as received from Aldrich. Tetraethyl orthosilicate (TEOS) was acquired from Fluka, and hydrochloric acid was purchased from Fisher Scientific.

Materials. PEO functionalized at one end with the 2-bromoisobutyrate (BiB) group was prepared via a reaction of monohydroxy-terminated PEO with 2-bromoisobutyric acid, as described elsewhere.⁶⁰ The chain extension of the functionalized PEO with PAN was carried out as illustrated below. In a typical polymerization of AN, which yielded EO₄₅AN₇₇ copolymer, 1 g of BiB-functionalized PEO (obtained from PEO with $M_n = 2000 \text{ g mol}^{-1}$, 0.5 mmol) and 31.2 mg of bpy (0.2 mmol) were dissolved in 10 mL of deoxygenated AN (0.15 mmol) and 20 mL of deoxygenated DMF. 9.9 mg of CuCl (0.1 mmol) was then added under nitrogen flow, and the reaction mixture was heated at 328 K for 27 h. The reaction mixture was then diluted with DMF, the catalyst was removed by passing the mixture through a neutral alumina column, the solvent was evaporated, and the PEO-*b*-PAN copolymer was dried under vacuum until constant weight was reached.

In a typical synthesis of a silica/PEO-*b*-PAN composite, 0.5 g of the copolymer was dissolved in 2–3 mL of DMF to obtain a

clear solution. Subsequently, water (10–20 mL) was slowly added. The resulting solution was placed in a dialysis bag and dialyzed against water for several hours to remove DMF. After the dialysis, the solution of the copolymer in water was added to an aqueous solution of HCl, whose concentration was such that the resulting copolymer solution had an HCl concentration of 2 M and a volume of 120 mL. Two other ways to prepare the copolymer solution were also employed. One of them was the addition of PEO-*b*-PAN to an aqueous 2 M HCl solution (0.5 g of copolymer per 120 mL of 2 M HCl), but even after 2 days of stirring at room temperature, the copolymer was not fully dissolved (except for the EO₄₅AN₂₀ copolymer). The other way was the dissolution of the copolymer in DMF and slow addition of 2 M HCl solution. After the solution of PEO-*b*-PAN in aqueous HCl had been prepared via one of these three ways, TEOS was added under vigorous stirring. The molar ratio of TEOS to EO units of the copolymer was 1 to 0.6 (for instance, 1 mol TEOS per 0.0133 mol of EO₄₅AN₄₃ copolymer, which corresponds to 1.78 g (1.91 mL) TEOS per 0.5 g of EO₄₅-AN₄₃). The mixture was stirred at room temperature for 24 h in a closed round-bottom flask and then heated at 368 K for 2 days in a flask with a reflux condenser attached to it to avoid the loss of water during the heating. Subsequently, the solid product (silica/PEO-*b*-PAN composite) was filtered on a Buchner funnel, washed with deionized water, and dried. To obtain nanoporous silica, the silica/PEO-*b*-PAN composite was calcined under air at 873 K for 3 h using a heating rate of 5 K min^{-1} . To convert the silica/PEO-*b*-PAN composite into a silica/carbon composite, PAN was first stabilized by heating under air to 573 K with a heating rate of 2 K min^{-1} .⁴⁴ After reaching 573 K, the air was switched to nitrogen, and after 1 h, the heating was continued at a rate of 5 K min^{-1} to reach 1073 K; this temperature was maintained for 3 h. The carbon was isolated from the silica matrix through dissolution in 3 M aqueous NaOH solution at 348 K for 1 day. The alkaline solution was changed four times during the dissolution. Finally, the carbon sample was washed with water and dried. In some cases, the carbon and silica materials will be denoted C and SiO₂, but one should keep in mind that carbons from PAN carbonized at 1073 K contain

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Table 1. PEO-*b*-PAN Block Copolymers^a

PEO macroinitiator	composition of reaction mixture AN:EO _m BiB:CuCl:bpy	conditions (temp, time)	wt % PAN	composition (NMR)	PDI
EO ₄₅ -BiB	150:1:0.2:0.4	328 K, 2 h	34	EO ₄₅ AN ₂₀	1.13
EO ₄₅ -BiB	150:1:0.2:0.4	328 K, 4.3 h	43	EO ₄₅ AN ₃₀	1.08
EO ₄₅ -BiB	200:1:0.2:0.4	328 K, 6 h	52	EO ₄₅ AN ₄₃	1.08
EO ₄₅ -BiB	300:1:0.2:0.4	328 K, 8.5 h	56	EO ₄₅ AN ₅₁	1.08
EO ₄₅ -BiB	300:1:0.2:0.4	328 K, 27 h	66	EO ₄₅ AN ₇₇	1.12
EO ₁₁₃ -BiB	300:1:0.2:0.4	328 K, 20 h	20	EO ₁₁₃ AN ₂₄	1.17
EO ₁₁₃ -BiB	600:1:0.2:0.4	318 K, 2 d	48	EO ₁₁₃ AN ₈₇	1.14
EO ₁₁₃ -BiB	1000:1:0.2:0.4	328 K, 7 d	68	EO ₁₁₃ AN ₂₀₈	1.14

^a Notation: EO_mBiB, EO_n functionalized with BiB group (macroinitiator); PDI, polydispersity of the copolymer; time: h, hours; d, days.

a significant amount of nitrogen³⁶ and that silica is a hydroxylated silicon dioxide.

Measurements. The conversion of the AN monomer was measured using a Shimadzu GC14-A gas chromatograph with an flame ionization detector equipped with a J&W scientific 30m DB WAX Megabore column. Molecular weights were measured on a GPC system consisting of a Waters 510 HPLC pump, three Waters Ultrastayragel columns (50, 10², and 10⁴ nm) and a Waters DRI detector, using DMF as the eluent with a flow rate of 1.0 mL min⁻¹. Polystyrene standards were used for the molecular weight calibration. The composition of block copolymers was determined on the basis of ¹H NMR spectra recorded on a Bruker spectrometer (300 MHz). Weight change curves were recorded under air on a TA Instruments TGA 2950 thermogravimetric analyzer in a high-resolution mode with a maximum heating rate of 5 or 10 K min⁻¹. Nitrogen adsorption measurements at 77 K were performed on ASAP 2010 volumetric adsorption analyzers (Micromeritics, Norcross, GA). Before adsorption measurements, the samples were outgassed under vacuum at 473 K for 2 h. Small-angle X-ray scattering (SAXS) data were collected at CHESS D station at the synchrotron radiation source at Cornell University. Powder X-ray diffraction (XRD) patterns were measured at wide angles on a Rigaku Geigerflex diffractometer using Cu K α radiation. Transmission electron microscopy (TEM) images were recorded on a JEOL 200EX instrument operated at 200 kV. For TEM imaging, samples were dispersed in ethanol and deposited on carbon-coated copper grids.

Calculations. The specific surface area was calculated from nitrogen adsorption data in the relative pressure range from 0.04 to 0.2 using the BET method.⁶¹ The total pore volume was estimated from the amount adsorbed at a relative pressure of 0.99.⁶¹ The PSD was calculated from adsorption branches of isotherms using the Barrett-Joyner-Halenda algorithm,⁶² the corrected form of the Kelvin equation (calibrated for siliceous cylindrical pores of diameter from 2 to 6.5 nm),⁶³ and the calibrated statistical film thickness curve for silicas.^{63,64}

Results and Discussion

Synthesis of PEO-*b*-PAN Block Copolymers. The method for the synthesis of PEO-*b*-PAN block copolymers is shown in Scheme 1 and is similar to that used by others in the preparation of PEO-containing diblock copolymer templates for the nanoporous silica synthesis.⁶⁵⁻⁶⁸ PEO terminated with

a methoxy group at one end and with a hydroxyl group at the other end was reacted with 2-bromoisobutyric acid in the presence of DCC and 4-DMAP to introduce the ATRP initiator group (BiB) at one end of the PEO chain. The completion of the esterification reaction was evident from ¹H NMR in dimethylsulfoxide (DMSO)-*d*₆, which showed the disappearance of the signal of the proton from the hydroxyl endgroup (4.56 ppm). Subsequently, ATRP of AN was carried out using a copper(I) complex with bpy as a catalyst and DMF as a solvent, to obtain the PEO-*b*-PAN block copolymer. To improve the blocking efficiency through the increase of the polymerization initiation rate with respect to the propagation rate, the halogen exchange method was employed, which involves the use of the bromine-terminated (macro)initiator and copper(I) chloride as a component of the catalyst complex.⁶⁹ The reaction conditions, compositions, and polydispersity of the PEO-*b*-PAN block copolymers are listed in Table 1. The composition was determined using ¹H NMR in DMSO-*d*₆, by integration of the peaks around 3.5 ppm (protons of the -O-CH₂- group in PEO) and around 2.1 ppm (protons of the -CH₂- group of the PAN main chain). Diblock copolymers with low polydispersities (below 1.20) were obtained. When an expression reported by Fukuda was used,⁷⁰ the polydispersity of the PAN block was estimated to be 1.2-1.4 for most of the PEO-*b*-PAN copolymers, although the polydispersity of PAN was much higher for copolymers with low PAN content (20 and 34 wt %). As expected, the degree of polymerization of the PAN block increased with time of polymerization, which allowed us to obtain PEO-*b*-PAN copolymers with different relative proportions of the blocks.

Synthesis of Silica/PEO-*b*-PAN Composites. Preparing silica/PEO-*b*-PAN composites was first attempted following a procedure typically used to synthesize copolymer-templated silicas.^{38,65} Namely, PEO-*b*-PAN copolymers was dispersed in a 2 M HCl solution under stirring, and later the silica source (TEOS) was added. The resulting mixture was stirred at room temperature for 1 day and subsequently heated at ~90 °C, typically for 2 days. As inferred from TGA, the

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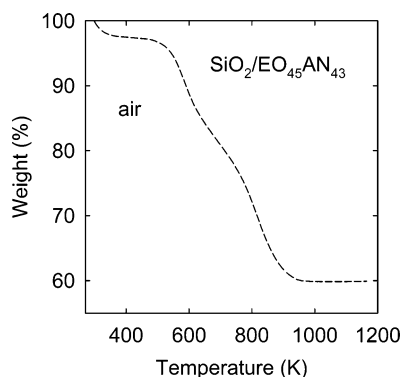


Figure 1. Weight change pattern recorded under air for silica/EO₄₅AN₄₃ composite synthesized using the method wherein the copolymer micellar solution was prepared with the aid of dialysis.

obtained precipitate had a silica/PEO-*b*-PAN ratio similar to that expected on the basis of the composition of the reaction mixture (illustrative TGA data for a silica/PEO-*b*-PAN composite are shown in Figure 1). The calcination under air afforded silicas with mesopores of diameter ~ 10 nm, but PSDs were not particularly narrow. Moreover, the increase in the PAN block length for EO₄₅AN_{*n*} copolymers from $n = 20$ to $n = 51$ did not lead to the increase in the pore diameter, which is in contrast with a typical templating behavior of block copolymers, where the increase in the hydrophobic block length results in the increase in pore diameter of templated silicas.⁷¹ In the case of this synthesis procedure, even after 2 days of stirring at room temperature, the PEO-*b*-PAN block copolymers did not fully dissolve, except for EO₄₅AN₂₀ with the shortest PAN block. It was expected that the lack of the homogeneity of the polymer solution might be the reason for the broadening of PSD for silicas and inability to control the pore diameter through the change in the hydrophobic block (PAN) length. Therefore, two other ways were employed, which allowed us to prepare homogeneous solutions of PEO-*b*-PAN copolymers. The starting point of both of them was the dissolution of the copolymer in DMF, which is a good solvent for PAN. In one case, this step was followed by a gradual addition of water and/or an aqueous solution of HCl. Although this procedure did not improve the pore size uniformity of the silicas, it was beneficial for the synthesis of carbon through the stabilization and carbonization of PAN blocks (as discussed later). In another procedure, the dissolution of the copolymer in DMF was followed by the addition of water and dialysis against water to remove DMF, followed by the addition of HCl solution. This approach afforded silicas with the most uniform mesopore sizes, and the samples prepared this way will be discussed herein, unless otherwise noted.

The XRD pattern for the bulk EO₄₅AN₄₃ copolymer (Figure 2) featured three narrow peaks at 2θ angles of 17.1, 19.3, and 23.5°, whereas the pattern for the silica/EO₄₅AN₄₃ featured a peak at 17.2°, which emerged from a broad peak centered at $\sim 23^\circ$. The peaks at 19.3 and 23.5° are due to the partially crystalline structure of PEO,⁷² whereas the peak at 17.2° is due to the partially crystalline structure of PAN.⁷³ The broad peak at $\sim 23^\circ$ is likely to arise from amorphous

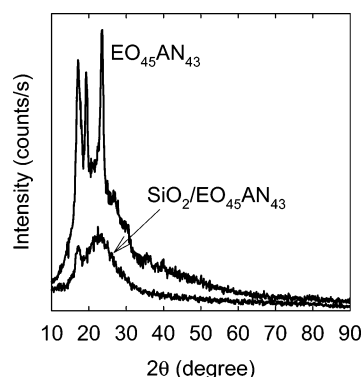


Figure 2. XRD patterns recorded for the EO₄₅AN₄₃ copolymer and silica/EO₄₅AN₄₃ composite.

silica. The partial crystallinity of PAN and PEO domains in the bulk copolymer provides a strong indication of nanoscale phase separation between PAN and PEO. After the formation of the silica/EO₄₅AN₄₃ composite, only a peak at $\sim 17^\circ$ persisted, which indicates that PAN still exhibited some crystallinity, while PEO did not form crystalline domains. Earlier studies of silicas templated with copolymers with PEO blocks and hydrophobic blocks (poly(propylene oxide) or polyisoprene) showed that PEO was occluded in the silica matrix.^{74,75} Thus, it was expected that PEO blocks of PEO-*b*-PAN copolymers in silica/PEO-*b*-PAN composites would be occluded in the silica framework, whereas the PAN blocks would form separate domains. The lack of detectable crystallinity of the PEO domains and some degree of crystallinity of the PAN domains in the silica/PEO-*b*-PAN composite are consistent with this expectation. The intensity of the PAN peak at $\sim 17^\circ$ in the silica/PEO-*b*-PAN composite was much lower than that in the bulk copolymer, which suggests that the crystallinity of the PAN block in the silica/PEO-*b*-PAN composite was lower than that in the bulk PEO-*b*-PAN copolymer. Perhaps the occlusion of PEO blocks in the silica framework disrupts to some extent the packing of PAN blocks, which are covalently linked to PEO.

Silicas Obtained from Silica/PEO-*b*-PAN Composites.

Silicas templated by EO₄₅AN₃₀, EO₄₅AN₄₃, and EO₄₅AN₅₁ copolymers were analyzed by SAXS. The SAXS pattern for the silica templated with EO₄₅AN₃₀ copolymer (Figure 3) featured a strong peak, whose position corresponded to the interplanar spacing of 12.6 nm. In addition, a weaker peak (interplanar spacing of ~ 6.3 nm) was also observed. Likewise, the SAXS pattern for silica templated with EO₄₅-AN₅₁ copolymer exhibited peaks whose positions corresponded to the interplanar spacings of 11.4 and 5.6 nm. The SAXS pattern for the silica templated with EO₄₅AN₄₃ copolymer featured a shoulder, whose position corresponded to the interplanar spacing of ~ 12 nm. A representative TEM image for the silica obtained from the SiO₂/EO₄₅AN₄₃ composite is shown in Figure 4 (top). The material appears

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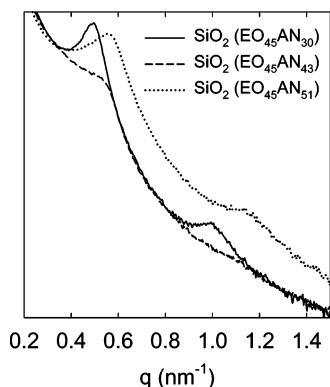


Figure 3. SAXS patterns for silicas templated by PEO-*b*-PAN copolymers.

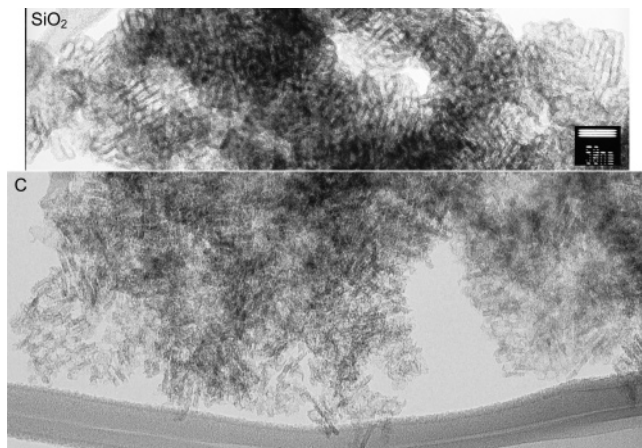


Figure 4. TEM image of silica (top) and carbon (bottom) obtained from the SiO₂/EO₄₅AN₄₃ composite.

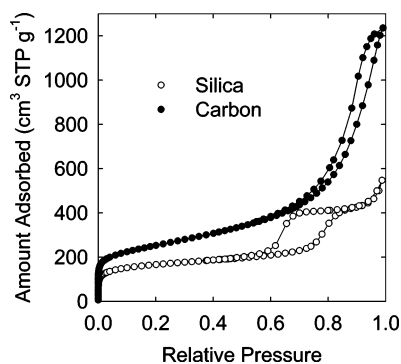


Figure 5. Nitrogen adsorption isotherms for mesoporous silica and carbon obtained from the SiO₂/EO₄₅AN₄₃ composite.

to consist of a large number of relatively small domains of short mesopores (most likely cylindrical) of uniform diameter, arranged parallel to one another. Similar structural features, although somewhat less clear, were observed for the silica obtained from the SiO₂/EO₄₅AN₅₁ composite. For the silica templated by EO₄₅AN₃₀ copolymer, the preliminary examination of TEM images also indicated some extent of local structural ordering (see Supporting Information, Figure S1). Nitrogen adsorption isotherms for all these silicas exhibited rather sharp capillary condensation steps at relative pressures of ~0.80 (see Figure 5 and Supporting Information, Figure S2). Consequently, PSDs were narrow and centered at ~10 nm (see Table 2, Figure 6, and Supporting Information, Figure S3). On the basis of TEM and PSD data, the lack of any pronounced peaks on the SAXS pattern for the

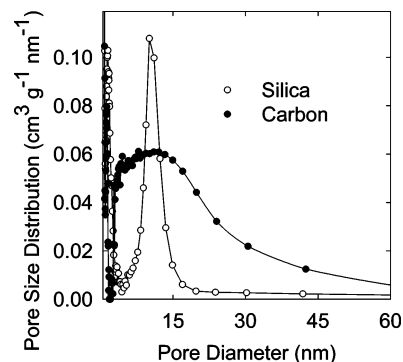


Figure 6. PSDs for mesoporous silica and carbon obtained from the SiO₂/EO₄₅AN₄₃ composite.

Table 2. Structural Properties of Mesoporous Silicas and Carbons Determined from N₂ Adsorption Data

sample	BET specific surface area (m ² g ⁻¹)	total pore volume (cm ³ g ⁻¹)	mesopore diameter (nm)
SiO ₂ (EO ₄₅ AN ₃₀)	540	0.63	10.4
SiO ₂ (EO ₄₅ AN ₄₃)	580	0.85	10.5
SiO ₂ (EO ₄₅ AN ₅₁)	600	1.16	9.7
C (EO ₄₅ AN ₃₀)	900	0.86	~6 (broad PSD)
C (EO ₄₅ AN ₄₃)	900	1.91	(broad PSD)
C (EO ₄₅ AN ₅₁)	850	1.61	(broad PSD)

silica templated by EO₄₅AN₄₃ copolymer appears to arise from the small size of ordered domains with uniform mesopores. As seen from the width of the hysteresis loops on the adsorption isotherms (Supporting Information, Figure S2),⁷⁶ the mesopores of silicas templated by EO₄₅AN₃₀ and some samples templated by EO₄₅AN₄₃ exhibited constrictions. The silicas had the BET specific surface areas of 540–600 m² g⁻¹ and the total pore volumes of 0.6–1.2 cm³ g⁻¹ (see Table 2).

In the case of the synthesis of OMSs using EO_{*m*}PO_{*n*}EO_{*m*} and poly(ethylene oxide)–poly(butylene oxide)–poly(ethylene oxide) (EO_{*m*}BO_{*n*}EO_{*m*}) copolymers as templates, the pore diameter of silica can be increased by heating the synthesis mixture with preformed silica/copolymer composite obtained at low temperature (e.g., room temperature) to a higher temperature (e.g., ~373 K).^{38,76} The pore diameter also increases as the heating is prolonged.^{38,76} The same behavior was observed for silicas templated by PEO-*b*-PAN copolymers. For instance, silica synthesized at room temperature using EO₄₅AN₂₀ copolymer as a template had a pore diameter of 6 nm, which was enlarged to 8 and 12 nm, in cases where the reaction mixture was additionally heated at 368 K for 6 h and 2 days, respectively (see Supporting Information, Figures S4 and S5). It should be noted that the above synthesis involved the direct dissolution of the copolymer in 2 M HCl (EO₄₅AN₂₀ fully dissolved under these conditions), but a similar sequence of pore size changes upon heating of the reaction mixture was also observed for samples templated by other copolymers, which were initially dissolved in DMF, with subsequent addition of water and removal of DMF via dialysis. It is clear that, for particular PEO-*b*-PAN templates, the silica pore diameter can be

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adjusted through the hydrothermal treatment. This pore size tailoring opportunity was explained as an effect of weakening of interactions between the PEO blocks and the silica as temperature is increased, which causes the increase in the hydrophobic domain volume and, thus, the pore diameter enlargement.^{38,77} An additional possible factor may be the reduction of shrinkage upon calcination for samples synthesized at higher temperatures or with longer heating times at particular temperatures. These are universal factors contributing to the pore size enlargement for silicas synthesized at different temperatures using block copolymer templates with PEO blocks. On the other hand, the control of the pore diameter of silicas templated by PEO-*b*-PAN copolymers by changing the length of the PAN block still remains elusive. The lack of any significant dependence of the pore diameter on the length of the hydrophobic PAN block of the copolymer template may arise from strong interactions between PAN blocks, as seen from the tendency of PAN to crystallize. It can be envisioned that the size of PAN domains may correspond to the smallest domain size for which the crystallization of PAN blocks would be favorable and, thus, may not depend on the PAN block length. In other words, the tendency of PAN to crystallize would lead to formation of micelles with nonequilibrium structures, and their rearrangement to micellar structures whose dimensions would be dictated by the length of the hydrophobic block, as it is observed for other block copolymer templates, would be hindered.

Carbons Isolated from Silica/Carbon Composites. In the case of carbon from the SiO₂/EO₄₅AN₄₃ composite, TEM imaging revealed a quite well-defined, although weakly ordered, structure. The sample appeared to consist of short rods, which were locally aligned parallel to one another and whose diameter and arrangement were similar to those of the mesopores in the corresponding silica (see Figure 4). Because of the fact that PEO blocks do not carbonize under the conditions employed in the present carbon synthesis, these results show that the uniform mesopores in the silica were templated by PAN domains, which were then converted to carbon. It should be noted that PAN, which is a hydrophobic block in the PEO-*b*-PAN copolymer, is expected to constitute cores of the micelles of PEO-*b*-PAN copolymer in water. The observed alignment of separate carbon rods suggests some extent of connectivity between the rods and, thus, between the pores of the silica. It would be interesting to clarify this point in the future, either by closer inspection of TEM images or by additional studies. These TEM data confirm our expectations that silica/PEO-PAN composites can be converted to silica/carbon composites, in which silica and carbon are inverse replicas of one another, and that this relation can be maintained after the removal of either carbon or silica. However, in the case of the carbon from the silica/EO₄₅AN₄₃ composite, the broadness of the PSD (Figure 6) and the featureless appearance of the SAXS pattern suggest that there was some degree of collapse of the structure upon the silica removal (which may be caused by the weakness of the structure or the lack of

three-dimensional connectivity between some of its parts). Nonetheless, this carbon exhibited a very high adsorption capacity (see Figure 5; the total pore volume was 1.91 cm³ g⁻¹) and quite high specific surface area of 900 m² g⁻¹. The isolated carbon was largely free from the silica residue (3 wt % by TGA).

A mesoporous carbon was prepared in the same way from the silica/EO₄₅AN₃₀ composite. TEM images of one of the areas of this carbon indicated an appreciable degree of local ordering (see Supporting Information, Figure S6), but other areas did not seem to be ordered, thus suggesting that the ordered structure was a minority phase in this sample. The short-range ordering observed in the corresponding silica sample suggests that the remaining part of considered carbon structure collapsed during the silica removal. Anyway, the formation of an ordered carbon structure suggests that the synthesis of OMCs from silica/PEO-*b*-PAN composites is feasible, although it may require a careful selection of the copolymer and synthesis conditions. The carbon from the silica/EO₄₅AN₃₀ composite exhibited a specific surface area of 900 m² g⁻¹, the total pore volume of 0.86 cm³ g⁻¹, and a broad PSD centered at 6 nm (see Supporting Information, Figure S3). A mesoporous carbon obtained from the silica/EO₄₅AN₅₁ composite exhibited a nitrogen adsorption isotherm similar to that of the carbon from the SiO₂/EO₄₅AN₄₃ composite (see Supporting Information, Figure S2). Its total pore volume was 1.61 cm³ g⁻¹, and the specific surface area was 850 m² g⁻¹.

A mesoporous carbon was also obtained in a similar way from the EO₁₁₃AN₂₀₈ copolymer. Its total pore volume was as high as 2.84 cm³ g⁻¹, and the BET specific surface area was 930 m² g⁻¹ (see adsorption isotherm in Supporting Information, Figure S7). The carbon had a PSD with distinct peaks at about 6 and 40 nm (see Supporting Information, Figure S8). As seen from TEM, this carbon had a very open structure, which is consistent with adsorption results that indicated the porosity of 85% (that is, the structure with carbon framework occupying just 15% of the volume of material, the rest being void space). The TEM image featured numerous stripes of constant thickness arranged in a disordered way. Thus, the carbon structure appeared to be composed of rods arranged in a disordered manner, but similar striped features on TEM images might also have been produced by side views of lamellar structures, so a definite identification of the structure of this carbon would require further studies.

To investigate the extent of graphitic ordering in the carbons derived from the composites of silica with EO₄₅-AN₃₀, EO₄₅AN₄₃, and EO₄₅AN₅₁ copolymers, wide-angle XRD data were acquired (see Figure 7). A pronounced peak at ~25° 2θ, as well as a peak at ~44°, and an increase in intensity at 80° were observed. The main peak at ~25°, which corresponds to the interplanar spacing of ~0.36 nm, can be identified as a (002) peak, whereas the peak at ~44° can be regarded as a (101) or (100) peak of a graphitic carbon structure.³⁰ The broad feature at ~80° coincides with the (110) reflection of graphite. The widths of (002) peaks for the present carbons were slightly smaller than those for OMCs from PAN, which were reported earlier.³⁶ The

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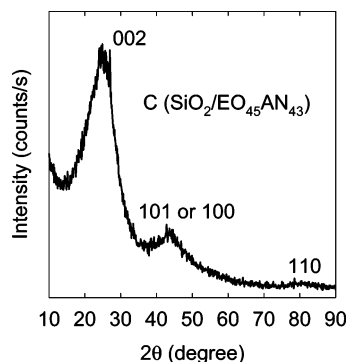


Figure 7. Powder XRD pattern for the carbon obtained from the EO₄₅-AN₄₃ copolymer.

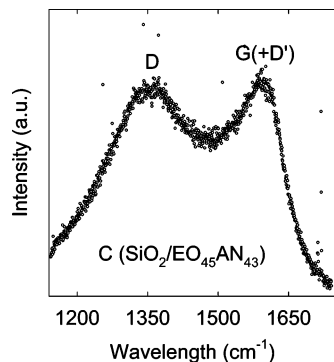


Figure 8. Raman spectrum for the carbon obtained from the EO₄₅AN₄₃ copolymer.

comparison of the present XRD data with the literature data^{78–83} for porous carbons prepared via heat treatment at about 1073 K (which was used herein) leads to a conclusion that atomic-scale ordering in the frameworks of the present PAN-derived carbons is much better than that for carbons from sucrose but not as good as for carbons derived from acenaphthene⁷⁸ or synthesized via chemical vapor deposition using acetonitrile as the precursor.⁸³ The Raman spectra for the carbons (Figure 8) featured a broad G band (most likely with a contribution from D' band)⁸⁴ at $\sim 1600\text{ cm}^{-1}$ and a D band at $\sim 1350\text{ cm}^{-1}$. The intensities of the G band (or more likely that of the combined G and D' bands) were comparable to the intensity of the D band. Because of the fact that the G band is related to the graphitic sp^2 carbon structures and the D band is related to defective graphitic sp^2 structures,^{84–86} we can conclude that the samples have some degree of atomic-scale ordering, although it is still rather low.

Mesoporous carbons were also synthesized from silica/EO₄₅AN₇₇ composites prepared simply by (i) dissolving the copolymer in DMF, (ii) adding water and aqueous HCl

solution, and finally (iii) adding TEOS. The carbons had specific surface areas of $\sim 750\text{ m}^2\text{ g}^{-1}$, total pore volumes of $\sim 0.75\text{ cm}^3\text{ g}^{-1}$, and PSDs with maxima at $\sim 4.5\text{ nm}$ (see adsorption isotherms and PSDs in Supporting Information Figures S9 and S10). Similar structures were obtained, when different carbonization conditions were employed (including heating under nitrogen to 1073 K, as well as heating under air to 493 or 573 K to stabilize PAN, and subsequently under nitrogen to 1073 or 1173 K). This synthesis procedure gave a high yield of carbon from PAN and also was found to be quite well reproducible (as verified using EO₄₅AN₈₁ block copolymer, which was synthesized under the same conditions as EO₄₅AN₇₇).

Conclusions

ATRP opened an avenue to the synthesis of PEO-*b*-PAN block copolymers with narrow molecular weight distributions via the extension of the PEO blocks with PAN, whose content is controlled by selecting the polymerization time. The obtained bulk PEO-*b*-PAN copolymers exhibit partial crystallinity of both PEO and PAN domains, which suggests the occurrence of nanoscale phase separation between PEO and PAN. PEO-*b*-PAN copolymers can serve a dual role as templates for the synthesis of nanoporous silicas and precursors for the synthesis of nanostructured carbons. In particular, these copolymers template silicas with narrow PSD centered at about 10 nm and with short-range structural ordering. The pore diameter can be adjusted by controlling the synthesis temperature and time. PAN domains of silica/PEO-*b*-PAN composites can be converted to carbon via stabilization of PAN under air and carbonization under nitrogen. The obtained carbons have surface areas of $\sim 900\text{ m}^2\text{ g}^{-1}$ and pore volumes up to as high as $2.8\text{ cm}^3\text{ g}^{-1}$. Some of these carbons exhibit short-range ordering in their structures, but they tend to have broad PSDs. The carbons derived from PAN blocks of PEO-*b*-PAN copolymers exhibit some degree of ordering of graphene sheets in their frameworks. A strong resemblance between the pore structure of the silica and the framework structure of the carbon, both derived from a single silica/PEO-PAN composite, indicates that PAN domains are primarily responsible for templating of the uniformly sized mesopores of the silica.

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Supporting Information Available: Two TEM images for silica and carbon derived from the EO₄₅AN₃₀ composite, four figures with experimental nitrogen adsorption data, and four figures with PSDs derived from nitrogen adsorption data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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