Tunable Polyacrylonitrile-Based Micellar Aggregates as a Potential Tool for the Fabrication of Carbon Nanofibers

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Since the discovery of carbon filaments,[1] buckminsterfullerene,[2] and carbon nanotubes,[3] nanostructured carbons have become the focus of a great deal of research activity, turning from a fascinating academic subject into a potential inimitable tool for the development of materials for a wide range of applications such as hydrogen storage,[4] field-emission displays,[5] and advanced fillers for nanocomposites,[6] to cite just a few. Most of the strategies proposed so far for the fabrication of these discrete carbon molecules and nanoobjects may be schematically classified under two different main approaches: (a) deposition of carbon from the vapor phase by chemical or physical techniques through complex equipment and very precise but relatively expensive methods and (b) preparation from organic precursors, often synthetic polymers, by conventional carbonization treatments such as those industrially used to produce carbon fibers, the dimensional control and tunability of the pyrolizable nanostructured materials being the key point for their industrial scale-up. On the other hand, a particular class of polymers belonging to the wider family known as soft materials, the block copolymers, has proved to be a versatile instrument for fabricating diverse polymeric and hybrid nanostructures,[7] mostly by template methods. The frequently unfavorable mixing enthalpy among the two or more covalently bonded homopolymeric blocks drives a self-assembly process into well-defined nanostructures, such as spherical, cylindrical, and lamellar periodic morphologies in bulk or spherical, cylindrical, and tubular micelles in block-selective solvents,[8] depending in both structural and dimensional terms on block incompatibility, polymer composition, and molecular weight. In this context, the combination of such self-organizing properties[9] with the last achievements on polymer synthesis has allowed phase-separated block copolymers containing polyacrylonitrile (PAN), an excellent carbon precursor, and a second easily decomposable component,[10] whose controlled pyrolysis already permitted the fabrication of mesoporous carbons[10c] and carbon nanoparticles, to be delivered.[11] Recent works have also investigated the formation of porous carbon nanotubes via template wetting with PAN containing block copolymers[12] and porous structures from the partial pyrolysis of templates of cross-linked phenolic resins and a block copolymer.[13]

Herewith we describe a facile and low-cost method for the preparation of carbon nanofibers from tunable worm-like micellar aggregates of PAN-based block copolymers/PAN blends, whose main steps are illustrated in Scheme 1. The dimensional control of the micellar PAN core enabled what seems to be a difficult length scale, that is, the mesoscale, to be covered with the fabrication of carbon precursors with diameters between a few tens and hundreds of nanometers.[14] PAN peculiar polarity and crystallinity not only induce commercially important properties, including compatibility with polar substances and low gas permeability, but also have a strong influence at the nanoscopic level, for example, on the phase behavior of the corresponding block copolymers. Moreover, the high incompatibility of PAN in block copolymers with less polar polymers facilitates the phase-separation in bulk[10] and the micellization in block-selective solvents. As an example, polyacrylonitrile-*block*-polystyrene (PAN-*b*-PS) and polyacrylonitrile-*block*-poly(methyl methacrylate) (PAN-*b*-PMMA) micelles can be easily prepared by direct dissolution in a selective solvent for the second block.[15]

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Scheme 1. Fabrication Steps for Tunable Carbon Nanofibers

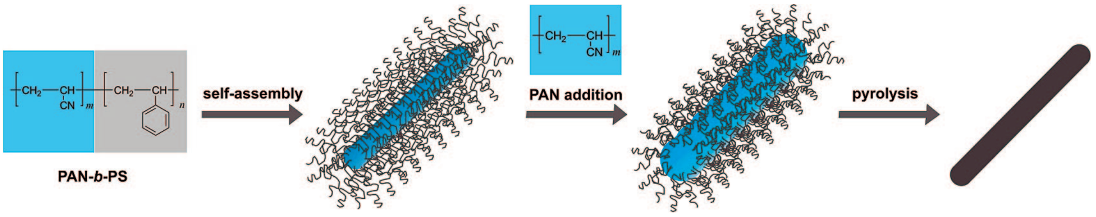

Table 1. Molecular Characteristics of the PAN-Based Block Copolymers and Hydrodynamic Radius for Their Micelles

polymer	M_n[a] (g/mol)	M_w/M_n[a]	PAN cnt.[b] (wt %/vol %)	R_H[c] (nm)	R_{PAN}[d] (nm)
PAN_{20}-*b*-PS_{61}	7200	1.50	16/14	10	4
PAN_{20}-*b*-PS_{177}	19300	1.32	5.9/5.3	15	3
PAN_{20}-*b*-PS_{210}	26300	1.54	5.1/4.6	17	4
PAN_{20}-*b*-$PMMA_{260}$	27200	1.36	3.8/3.9	20	4

[a] Determined by size exclusion chromatography, based on PS standards. M_w/M_n of the PAN block = 1.03, determined by MALDI. [b] Weight percentage from ^{1}H NMR. Volume percentage calculated taking densities of PAN, PS, and PMMA to be 1.17, 1.05, and 1.19 g/cm^3. [c] Hydrodynamic radius from DLS measurements at 25 °C and polymer concentration of 1 mg/mL. [d] Core radius estimated from volume ratio.

Micellization of a series of copolymers with identical PAN block lengths was carried out in chloroform, and their micellar morphologies in solution and in the solid state were characterized by dynamic light scattering (DLS), and atomic force microscopy (AFM), and transmission electron microscopy (TEM), respectively. Molecular characteristics of the block copolymers are presented in Table 1. The absence of PAN peaks in the ^{1}H NMR spectra of the copolymers in deuterated chloroform indicated that the micellar core was very compact and possibly glassy,[16] with a swollen corona constituted by the second block, suggesting at the same time that the micelles are frozen, and did not exchange any unimers after their formation. DLS correlation functions were measured at different scattering angles and in a wide range of concentrations, between 0.2 and 2.0 mg/mL. Corresponding CONTIN analysis[17] indicated a unimodal size distribution for all the samples, such as that illustrated in Figure 1a, with hydrodynamic radii (R_H's; Table 1) that remain constant for the whole investigated range of concentrations. Angular dependence of the DLS data is examined in the Supporting Information. Size clearly depends on the length of coronal chains, that is, R_H increases from around 10 to 17 nm for a PS block changing from 6000 to 25 000 g/mol.

Figure 1b–f presents TEM and AFM images of samples prepared by evaporation of dilute solutions onto carbon coated copper grids. Notwithstanding most diblock copolymers self-assemble in selective solvents to form spherical micelles,[18] a cylindrical morphology was observed for all the copolymers, possibly as a consequence of the crystalline nature of the PAN core.[19] Micelles appear to be flexible and seem to exhibit a wide range of contour length, from around 1 μm to several micrometers. The diameters are rather uniform and ranged from 35 to 50 nm, depending on the block copolymer. In the case of slight flexible worm-like micelles from other semicrystalline block copolymers, the absence of a clear contribution of the rotational mode in the CONTIN plot, which for rod-like rigid structures would be evident as a second peak, was ascribed to very slow rotational motions.[19c,d] Similarly, given the observation in our system of translational diffusion constants in the order of 10^{-11} m^2 s^{-1} and the estimation of very small rotational coefficients (see Supporting Information), we do not expect to be able to separate the rotational contribution from that of the translational diffusion.

The calculation of the volume ratios of the copolymers also led to the estimation of the micellar inner structures and especially of the core radius, R_{PAN}, by considering a cylindrical geometry, as reported in Table 1. The constancy of such a value, ~4 nm, in the whole series supports the hypothesis of a stable and uniform packing of PAN chains independently on the length and the interactions of the swollen corona with the solvent. Although the core diameter is potentially modulable by varying the length of the PAN block, that is, its molecular weight, we focused our efforts on alternative and more practical methods that do not involve further tailored copolymer synthesis and especially on those involving a direct and efficient introduction of PAN into the micelles. The effect of homopolymer as an additive to diblock copolymer micelles was only partially explored and essentially consists of a change of morphology and/or an increase of average micellar size.[20] Homopolymer addition to aggregates with a semicrystalline core was never investigated before and, at least for the specific case of PAN block copolymers, seems to not involve any morphological transition.[15] Premixed blends of PAN_{20}-*b*-PS_{210} (herewith considered as representative of all the series) with PAN_{20} were directly dissolved in chloroform, while micellar size changes corresponding to increasing amounts of homopolymer were monitorated by DLS. Solutions present a main size distribution with a narrow profile, as the one in Figure 2a (a more detailed discussion is reported in the Supporting Information).

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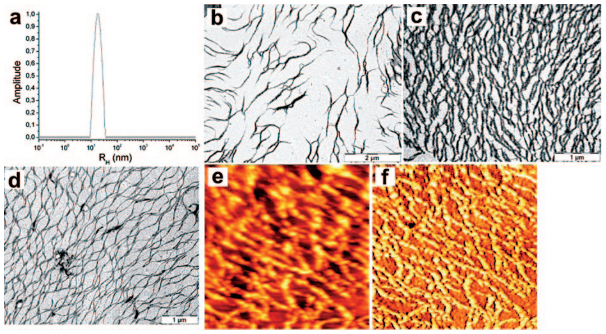

Figure 1. Typical CONTIN analysis from the right-angle DLS correlation functions of micelles in chloroform (a, PAN_{20}-*b*-PS_{210}) and various TEM and AFM images of micellar aggregates deposited onto carbon-coated copper grids from chloroform solutions at different concentrations. TEMs show regions where micelles are isolated (b, PAN_{20}-*b*-PS_{210}, 0.2 mg/mL) and regions with different levels of packing (c, PAN_{20}-*b*-PS_{210}, 1.0 mg/mL; d, PAN_{20}-*b*-PS_{177}, 1.0 mg/mL). Tapping mode AFM phase and topography 2 × 2 μm images (e, f, PAN_{20}-*b*-$PMMA_{260}$, 1.0 mg/mL).

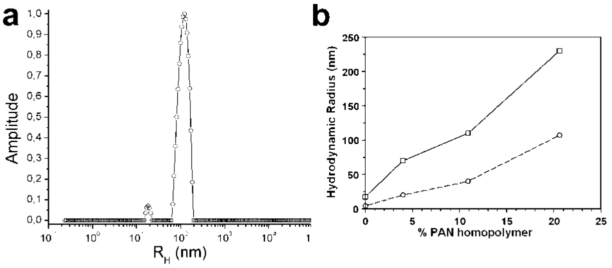

Figure 2. CONTIN analysis from the right-angle DLS correlation functions of PAN_{20}-*b*-PS_{210} with 4% PAN_{20} in chloroform (a) and influence of added PAN on micelle hydrodynamic radius (b). Dashed line indicates the diameter of the PAN core, estimated on the basis of the PAN/PS volume ratio.

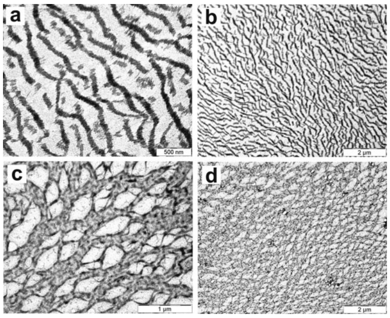

Figure 3. TEM images of PAN_{20}-*b*-PS_{210}/PAN_{20} micellar aggregates deposited onto carbon-coated copper grids from 1.0 mg/mL chloroform solutions. From a mixture with 4% PAN (a, b) and 20% PAN (c, d).

The results presented in Figure 2b show that the micelles are linearly increasing in size with the addition of PAN, clearly indicating that such molecules are incorporated into the core. An increase greater than expected might be accounted for by a ribbonlike model of the aggregation of the micelles in solution.[19c] The effect was drastic and enabled the diameters ($2R_H$) to be controlled in a wide range of dimensions, between 40 and around 400 nm. Giant wormlike micelles were visualized by TEM and AFM (Figure 3a–d), often observing a preferential orientation of aggregates, which was associated with conventional motion during solvent evaporation. The diameters measured by TEM were smaller than those obtained by DLS, for example, around 100 nm against 140 nm for the solution with 4% PAN added. We assumed that the difference is due to the different expansion of the corona. In solution, PS chains are swollen by the interaction with the solvent, while the dried micelles were laid down on a solid support, with the coronal chains collapsed onto the rigid backbone and the surface.

The last step of the novel route we have developed for the fabrication of carbon fibers (Scheme 1) simply relies on the conversion of the well-defined PAN-containing nanostructures into the corresponding carbonaceous structures through a commonly used procedure of pyrolysis. Dried aggregates are suitable for carbonization with retention of the original morphology of PAN domains. As a matter of fact the typical processing, consisting of a pretreatment in air at 200–250 °C to stabilize PAN by cyclization and increase the carbon yield followed by controlled pyrolysis up to 600–1000 °C,[11b,21] results in a complete removal of the sacrificial block (see characteristic thermogravimetric analysis in Supporting Information) and a PAN to carbon yield of ~50%. By considering the diameter of the pyrolyzable core estimated as explained above on the basis of the total PAN/PS volume ratio (see dashed line in Figure 2b), the fabricated nanofibers will have a diameter shrunk to half the precursor diameter.[22] Some of the resulting fibers are visible in the micrographs in the Supporting Information. It is worth noticing, as expected, that the original nanostructuring, that is, the fiber-like aspect, upon processing is retained only in the case of samples subjected to the stabilizing pretreatment in air, whereas it is completely lost upon a direct pyrolysis. Their Raman spectra were very similar to those obtained for carbon fibers from a PAN precursor by conventional pyrolysis techniques,[14b] attesting to the coexistence of disordered and graphitic carbons.

In summary, we described a scalable method for the fabrication of carbon nanofibers based on conventional pyrolysis of novel cylindrical precursors with modulable diameter. Dimensionally stable worm-like micellar aggregates with a compact PAN core could be prepared for the first time, with a precursor diameter tunable by controlling the relative amounts of PAN-based block copolymer to PAN homopolymer to be dissolved in a selective solvent.

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Supporting Information Available: Detailed experimental methods, DLS experiments, thermogravimetric analysis, and TEM images (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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