

Publication I

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Functional Carbon Nanoflakes with High Aspect Ratio by Pyrolysis of Cured Templates of Block Copolymer and Phenolic Resin

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Selective separation of gases such as O₂/N₂ or CO₂/CH₄ through membranes is a rapidly growing field in industrial gas production.¹ Additionally the oxygen separation process is central, for example, in packaging requirements for pharmaceutical, food, and cosmetics applications, where diffusion of oxygen has to be hindered. The majority of today's gas separation membranes are based on polymeric hollow-fiber modules.¹ Efficient materials permitting good selectivity and high permeation to be achieved have been proposed, such as microporous zeolites or carbon based materials.^{2–7} Microporous carbon materials^{8,9} have uniform pore sizes of several angstroms and have particularly interesting gas separation properties. To limit their high processing cost and inherent brittleness, these materials are often combined with polymer matrices to yield polymeric membranes with efficient selective separation performance.^{10–14} Enhanced O₂/N₂ or CO₂/CH₄ selectivity has been achieved by using spherical microporous carbon particles with diameter from submicrometer to a few micrometers¹² or using high aspect ratio planar flakes made of aluminophosphate.¹³ Recent efforts toward suitable design of carbon nano-

objects^{15–17} possibly serving as sieves have focused on the design of spherical^{15,16} and cylindrical¹⁷ structures and other mesoporous carbon matrix materials including gyroid structures.^{18–22} Yet, to obtain high gas permeation rates the thickness of the selective separation layer has to be very thin¹ (<0.5 μm) which makes of utmost importance the design of the shape and aspect ratio of zeolites, carbon, or ceramic molecular sieve materials. When using flakes, in particular, the planar shape of the sieves allows, in principle, aligning the flakes parallel to the membrane surface, enabling very thin membranes.

A general procedure to design ceramic nano-objects with tunable shape, which includes planar flakes, has been reported using polyisoprene–polyethyleneoxide block copolymer templates.^{23–25} Yet, no work has been reported up to date on carbon nanoflakes, which, as a result of their high selectivity, would have even larger relevance for polymer based membranes.

Here we report a strategy to design microporous carbon nanoflakes, by combining the self-assembly of block copolymer templates, selective swelling of a specific mesophase by phenolics low molecular weight compounds, and controlled chemical pyrolysis at moderate temperature. A schematic representation of the procedure followed is reported in Figure 1.

Low polydispersity index (PI = 1.09) polystyrene-*block*-poly(4-vinylpyridine) (PS-P4VP; number average total molecular weight, M_n = 45 600 g/mol, 12% P4VP) was selected as block copolymer template (Polymer Source, Inc.). This block copolymer alone formed P4VP spheres in a continuous PS matrix; see Supporting Information Figure S1. When mixed with phenolic resin (Vulkadur RB, Bayer, Ltd.) and hexamethylenetetramine (HMTA) as the curing agent (phenolic resin/HMTA ratio of 88:12) a selective swelling of the P4VP phase was achieved owing to hydrogen-bonding complexation between the phenolic and P4VP. By using a

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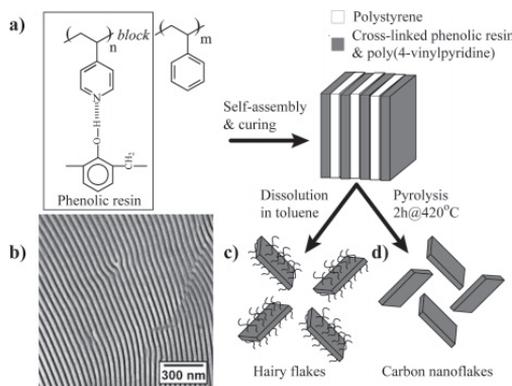


Figure 1. Schematics for the preparation of "hairy" flakes and pyrolyzed carbon flakes by using lamellar block copolymer template. (a) Phenolic resin, PS-P4VP block copolymer, and schematics of their mutual hydrogen bonding. (b) TEM micrograph showing a highly ordered lamellar structure after the cross-linking of the phenolic resin. (c) "Hairy" flakes can be obtained by dissolving the polystyrene lamellar phase in toluene. (d) Alternatively, during the selected pyrolysis conditions, block copolymer template is removed, leading to formation of carbon nanoflakes.

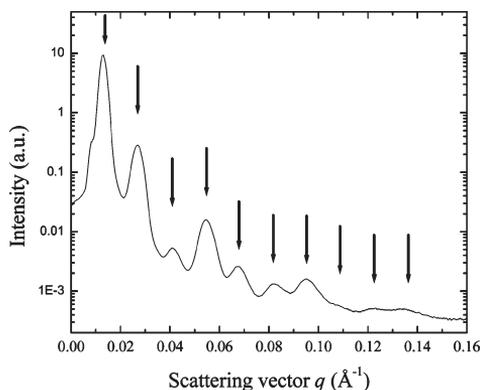


Figure 2. SAXS diffractogram showing long-range ordered lamellar phase with period of 46 nm in the cross-linked PS-P4VP block copolymer/phenolic resin blend.

total overall composition of 60 wt % PS in the blend formed by PS-P4VP/HMTA/phenolic resin, a lamellar phase was finally obtained, as revealed by transmission electron microscopy (TEM) analysis (see Figure 1). Cross-linking of the P4VP domains with the phenolic/HMTA compounds was successively achieved by curing the blend at 190 °C for 2 h. Similar concepts using PS-P4VP template and phenolics formulations have been recently used to design micro- and mesoporous materials in bulk and thin films.^{26–28}

Figure 2 shows a small-angle X-ray scattering (SAXS) diffractogram of the PS-P4VP/phenolic resin blend after the cross-linking. As many as 10 consecutive reflections, $q_1:q_2:q_3:\dots:q_{10}$ spaced as 1:2:3:...:10 reveal the presence of a lamellar phase with very long range order. The first peak,

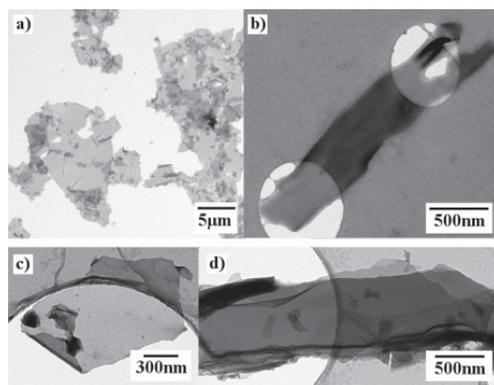


Figure 3. TEM images of nanoflakes as prepared by dispersing them onto holey carbon TEM grid from dilute solutions. (a) A low magnification image showing "hairy" nanoflakes obtained by the cross-linked but not pyrolyzed sample. (b) A higher magnification from the "hairy" nanoflake. The flake surfaces are covered with polystyrene brushes. (c) TEM micrograph showing carbon nanoflakes after the pyrolysis. (d) TEM image of an aggregate where a few flakes are stacked together.

centered at $q_1 = 0.136 \text{ nm}^{-1}$, indicates an overall period of 46 nm for the lamellar organization. Starting from these lamellar structures two different types of nanoflake materials could be obtained on the basis of different post-processing routes.

In the first case "hairy" flakes of lateral size averaging from 1 to 10 μm were obtained by dissolving the polystyrene lamellar phase in toluene. The flakes consisted of approximately 15–20 nm thick cross-linked P4VP-phenolic resin lamellae decorated on the surface by PS polymer brushes. The presence of a polymer brush on the surface of these flakes further enables dispersing the flakes within a polymeric matrix compatible with the polymer brush. By using different block copolymer templates one can thus access polymeric membranes on the basis of a vast class of homopolymers.

In the second case, carbon flakes with high aspect ratio were obtained by a controlled pyrolysis process. Cross-linked lamellar phases were maintained at 420 °C for 2 h in air. Previous work demonstrated that using these conditions both the PS lamellae and the P4VP polymer chains within the phenolic matrix are removed, leading to microporous carbon materials with an average micropore diameter of 5.4 Å, as measured by positron annihilation lifetime spectroscopy (PALS).²⁸ Figure 3a shows the wide field TEM image of the hairy flakes obtained as described above and schematically illustrated in Figure 1c.

Figure 3b,c illustrates and compares at higher magnification TEM micrographs of "hairy" flakes and carbon flakes, respectively. In the case of Figure 3c, the edges of the carbon flakes appeared to be well defined and sharper than in the case of "hairy" flakes (Figure 3b). This is to be attributed to the presence of the PS brush decorating the surface of the "hairy" flakes, which diffuse the contrast in electron microscopy imaging. "Hairy" flakes could be easily dispersed in toluene solution whereas in the case of pyrolyzed carbon flakes ultrasonication was required to disperse them in organic solvents such as ethanol. Furthermore, in the case of carbon nanoflakes, a greater tendency to form small

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aggregates was observed compared to hairy flakes, as shown in Figure 3d, where a few-flakes aggregate is shown.

In conclusion we have presented a procedure to design carbon nanoflakes based on the self-assembly of block copolymer templates into long-range ordered lamellar morphologies, the selective swelling of one lamellar domain by phenolic resins, the cross-linking of this domain, and the controlled pyrolysis of the resulting material. The carbon flakes obtained with this procedure present a high aspect ratio (lateral size up to several micrometers and thickness of ~ 20 nm), large surface area per unit volume, and microporosity, which is essential for selective separation applications. We anticipate that the procedure described here can potentially

lead to microporous carbon materials for polymer separation membranes with enhanced and tunable properties.

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Supporting Information Available: Sample preparation data and details on experimental TEM and SAXS procedures (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Supporting Information

Materials, sample preparation data, and details on experimental TEM and SAXS procedures.

Materials: Poly(4-vinylpyridine)-*block*-poly(styrene) (P4VP-*b*-PS) diblock copolymer ($M_{n,P4VP} = 5,600$ g/mol, $M_{n,PS} = 40,000$ g/mol, and $M_w/M_n = 1.09$) was provided by Polymer Source Ltd. and was used without further purification. Phenolic resin (Novolac) was supplied by Bayer Ltd. (Vulcadur RB). Cross-linking agent hexamethylenetetramine (HMTA) was acquired from Aldrich (99+ %) and tetrahydrofuran (THF) was provided by Riedel-de Haën (99.9 %).

Sample Preparation: In order to obtain lamellar structure, the weight percent of PS in the complexes was selected to be 60 %. The Phenolic resin/HMTA ratio in all complexes was 88:12. Phenolic resin, HMTA and P4VP-*b*-PS were dissolved in THF separately until the solutions were homogenous. The solutions were combined and the mixtures were stirred for 1 day at room temperature. THF was slowly evaporated at room temperature and thereafter the samples were vacuum dried at 30 °C for 1 day. Curing of the sample was performed using the following temperature profile: 100 °C for 2 hours, 150 °C for 2 hours, and finally 190 °C for 2 hours. Pyrolysis of cross-linked sample was performed by slowly heating from room temperature up to 420 °C using the heating rate of 1 °C/min without protective gas atmosphere and thereafter sample was isothermally kept at 420 °C 120 min. Based on our previous work, these pyrolysis conditions lead to

microporous carbon based materials, with the average pore diameter of 5.4 Å (Valkama, S.; Nykänen, A.; Kosonen, H.; Ramani, R.; Tuomisto, F.; Engelhardt, P.; ten Brinke, G.; Ikkala, O.; Ruokolainen, J., *Advanced Functional Materials* **2007**, 17, 183-190)

Transmission electron microscopy (TEM): *Sample preparation for the bulk cross-linked sample:* The sample was embedded into epoxy Eponate 12, which was cured at 60 °C for 20 hours. Sections thickness of 70 nm were cut using Leica Ultracut UCT ultramicrotome with a Diatome diamond knife and sections were collected on 600-mesh size copper grids

Sample preparation for the nanoflakes: The cross-linked sample prior to pyrolysis was dispersed in a dilute solution of toluene to yield “hairy” nanoflakes, whereas the pyrolysed material was dispersed in ethanol using ultrasonification (Brans Digital Sonifier 450-D). Thereafter a drop of solution containing either nanoflake dispersion, was casted onto holey carbon TEM grids. Bright field TEM was performed with FEI Tecnai 12 transmission electron microscope using 120 kV accelerating voltage and Gatan UltraScan 1000 CCD camera.

Small-angle X-ray Scattering (SAXS): measurements were performed with a SAXS device consisting of a Bruker MICROSTAR microfocuss rotating anode X-ray source with Montel Optics (CuK α radiation $\lambda = 1.54$ Å), where the beam was further collimated using four sets of JJ X-ray 4-blade slits. The sample to detector distances of 1.5 m was used spanning a q -range from 0.006 to 0.2 Å $^{-1}$. Scattering intensities were measured using a 2D area detector (Bruker AXS). The magnitude of the scattering vector is given by $q =$

$(4\pi/\lambda)\sin\theta$, where 2θ is the scattering angle. The q -values were calibrated using a silver behenate standard ($d = 58.4 \text{ \AA}$). Corrections for spatial distortion and detector response were made using a Fe-55 source. The SAXS patterns from the samples were absorption corrected and the background scattering was subtracted.

Transmission electron microscopy image of plain PS-P4VP block copolymer.

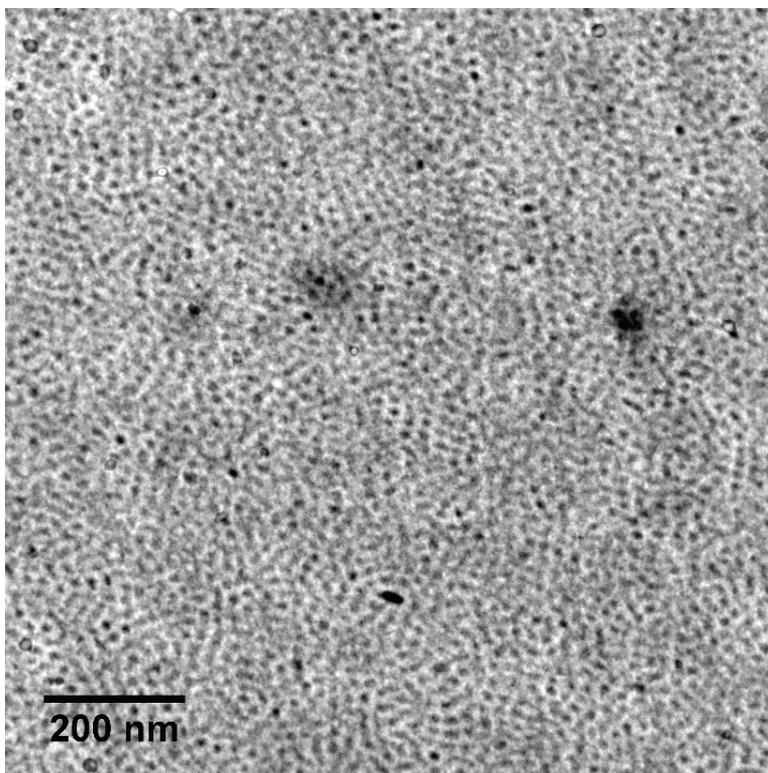


Figure S1. Transmission electron micrograph of poly(styrene)-*block*-poly(4-vinyl pyridine) (number average total molecular weight, $M_n = 45\,600 \text{ g/mol}$, 12 wt% poly(4-vinyl pyridine)).