Supplementary information

Experimental section

Materials

All preparation steps were carried out in a purified argon atmosphere passing through successive columns of BTS-catalyst and potassium hydroxide by means of standard Schlenk manipulations and vacuum/argon-line techniques. Schlenks were dried at 120 °C overnight before pumping under vacuum and filling them with argon. Manipulation of polymer samples were made inside an argon-filled glove box (Jacomex BS521) dried with potassium hydroxide. PAN (polyacrylonitrile) was obtained from Sigma-Aldrich, average Mw = 150,000. DMF (N,N-Dimethylformamide) was obtained from Sigma-Aldrich (extra-dry, water < 50 ppm). PAN and DMF were used without further purification.

Characterization

Thermogravimetric analysis (TGA) of the polymer-to-ceramic conversion was recorded on a Setaram TGA 92 16.18. Experiments were performed in ammonia atmosphere at 0.8 °C/min from 25 to 1000 °C (dwelling time of 2 h) using silica crucibles (sample weight of ~ 40 mg) at ambient atmospheric pressure. Chemical analyses of the poly[B-(methylamino)borazine] were made at the *Service Central de Microanalyse du CNRS* (Vernaison, France). The Fourier transform infrared spectrum (FT-IR) of the poly[B-(methylamino)borazine] was obtained from a Nicolet Magna 550 Fourier transform-infrared spectrometer in a KBr matrix (dried at 120 °C in air). In contrast, infrared spectroscopy of fibers pyrolyzed at 1000 °C and those prepared at 1800 °C was taken with a Nicolet 380 FT-IR spectrometer coupled with the Attenuated Total Reflectance (ATR) accessory. Scanning electron microscopy (SEM, Hitachi S-4800 operating at 15 kV) was used to observe at room temperature the morphology green fibers, fibers pyrolyzed at 1000 °C and those prepared at 1800 °C. Fibers were mounted on stainless pads and, due to the insulating properties of samples, the samples were sputtered with ~10 Å of a Pd/Au mixture to prevent charging during observation. Fibers prepared at 1800 °C were analyzed by Energy-Dispersive X-ray (EDX). An EDX system EDAX Genesis 4000 coupled with a SEM (Hitachi S-4800) was used to quantify boron, nitrogen, oxygen and carbon elements. Fibers prepared at 1000 °C and those obtained at 1800 °C were characterized and analyzed by a transmission electron microscopy (TEM) with a TOPCON 002B working at 200 kV.

Polymer solution preparation

The operating procedure to prepared the poly[B-(methylamino)borazine] was previously reported in our paper [*See ref 16 in the paper*].

IR data (KBr pellets, cm^{-1}): 3434 (m); 2958 (w) 2928 (w), 2898 (w), 2820 (m); 1597 (s); 1515 (s); 1460 (s); 1411 (s); 1178 (s); 1095 (m), 707 (w). ^{11}B NMR (96.29 MHz, C_6D_6, ppm): 25.7 (br); ^{1}H NMR (300 MHz, CD_2Cl_2, ppm): 1.86 br (-N(H)CH$_3$); 2.47 vbr (-N(H)CH_3); 2.56 vbr (Bridging -N(CH_3)-); 2.70-4.10 br (N(H) borazine). ^{13}C NMR (75 MHz, CD_2Cl_2, ppm) 27.6, 27.9 (-N(H)CH$_3$); 31.2 (Bridging -N(CH$_3$)-).

PAN was first dissolved at 70°C for 12 hours under a vigorous stirring in DMF to obtain a solution with PAN concentration in the range 8-12 wt%.

The poly[B-(methylamino)borazine] was also dissolved in DMF and then filtered to give a clear solution. The DMF was then evaporated from this solution to lead to a dry solid Poly[B-(methylamino)borazine], soluble in DMF.

Solid Poly[B-(methylamino)borazine] was finally added, at room temperature (RT) under flowing argon, to a PAN-DMF solution respecting a Poly[B-(methylamino)borazine]:PAN weight ratio varying from 0.1 to 0.8.

Electrospinning process

A clean and air-purged 5-mL Luer-Lock Tip syringe was equipped with a 21-gauge needle and loaded with the suitable Poly[B-(methylamino)borazine]-PAN-DMF solution. As described on Figure S1, the high voltage power was directly applied between the stainless-steel needle (positive electrode) and the metallic target (grounded electrode). The polymer flow rate is controlled using a syringe-pump (KDS 100) and set at 1 mL h^{-1}. The working distance of 10 cm was measured between the needle tip and the metallic target. It must be mentioned that the electrospinning experiments were performed in special nitrogen-filled box to prevent from polymer hydrolysis (water < 0.1 %).

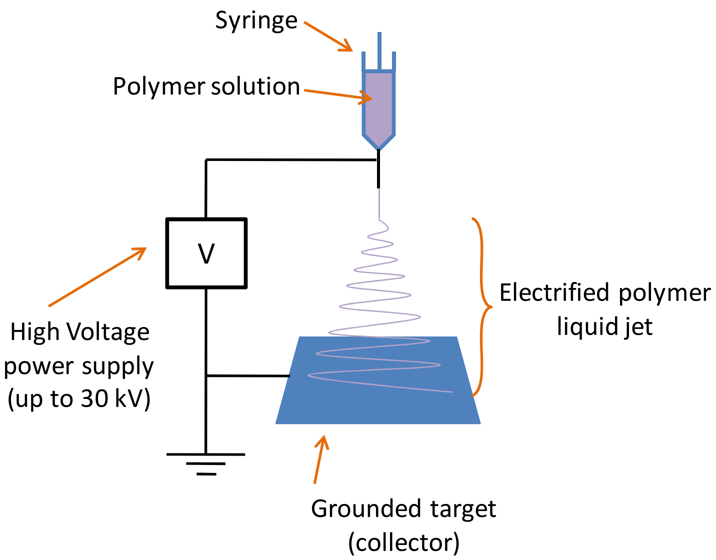

Figure S1. Scheme of the electrospinning set-up.

Polymer-to-ceramic conversion.

The targets supporting as-electrospun fibers were transferred into a silica tube inserted in a horizontal tube furnace (Gero) connected to a glove-box avoiding contamination of the samples with air and moisture. The tube was pumped under vacuum and refilled with ammonia (H_20 < 1 ppm, O_2 and Ar < 1 ppm). Subsequently, samples were subjected to a cycle of ramping of 0.8 °C min^{-1} to 1000 °C, dwelling there for 2 h, and then cooling down to RT at 5 °C min^{-1} under nitrogen. A constant flow (90 mL min^{-1}) of ammonia was passed through the tube. Then, ammonia-treated samples were introduced in a graphitic furnace (Gero Model HTK 8) which was subsequently pumped then refilled with nitrogen to be heated through a cycle of ramping of 5 °C min^{-1} to 1800 °C, dwelling there for 2 h, and then cooling down to RT at 10 °C min^{-1}. A constant flow (200 mL min^{-1}) of nitrogen was passed through the furnace.

EDX experiments

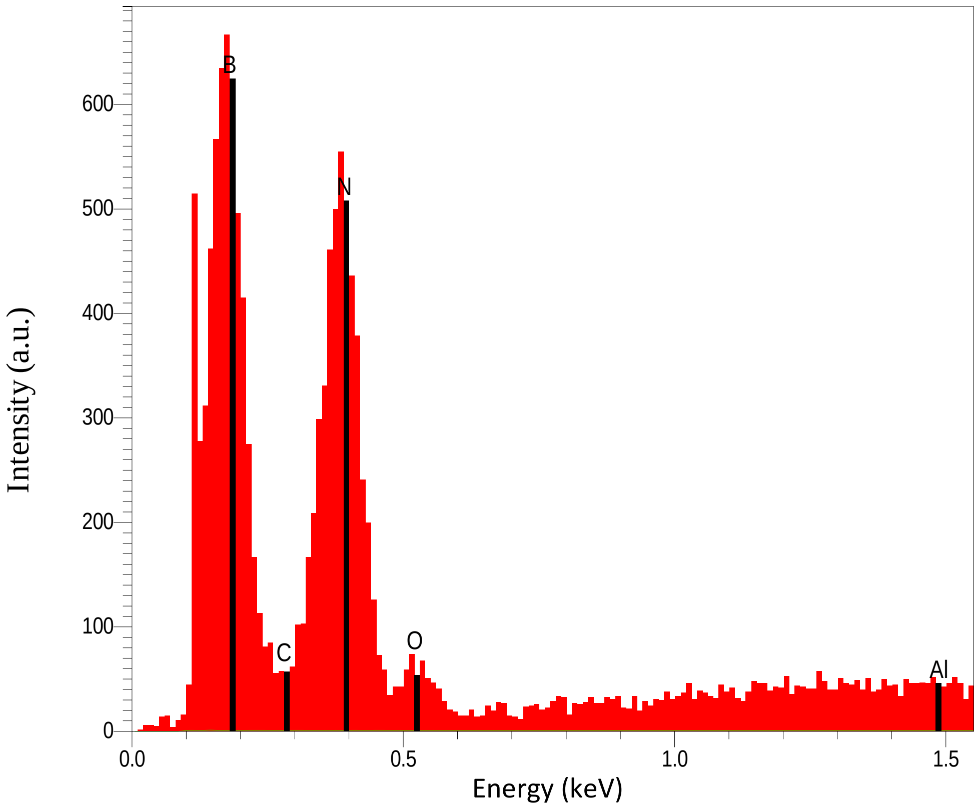

Figure S2. Electron Dispersive X-ray Analysis performed on fibers after annealing at 1800 °C under N_2.