

## Supplementary information- Experimental details

Materials and processing: Polysilazane (Ceraset, Kion Corp., NY), with molecular weight and polydispersity index of 3 Kg/mol and 3.71, respectively, was used as received without further purification. The polybutadiene-block-polyethylene oxide copolymer (PB-*b*-PEO) was purchased from Polymer Sources Inc., Dorval, Canada.

***Templated assembly of PSZ in PB-PEO.*** Dicumyl peroxide initiator (2wt% of polysilazane) was first dissolved into PSZ. This PSZ and PB-*b*-PEO were then dissolved separately in a 1:1 (vol.) mixture of tetrahydrofuran and chloroform to obtain 5wt% solutions. Subsequently the solutions of precursor and block copolymer were mixed according to the designed proportion. These homogenous solution mixtures were then cast into Teflon dishes and allowed to dry at room temperature for 6-12 hours. All mixing and drying was conducted in a glove box under nitrogen. The dried polymer blends were transferred into a vacuum oven pre-set to 70°C to eliminate any residual solvent, then annealed at 100°C for 12 hours to allow for self-assembly of PB-*b*-PEO and PSZ. Films of about 0.5 mm in thickness were then peeled from the Teflon dishes and transferred into a tube furnace with flowing nitrogen. The samples were heated to 400°C for one hour in order to induce cross-linking. Pyrolysis experiments were conducted by further heating the cross-linked samples at a constant rate of 0.5°-20°C/min to final temperatures of 700° to 1500°C, the dwell time at the final pyrolysis temperature was 2-4 hours.

***Transmission electron microscopy.*** Polymeric samples were microtomed either at room temperature (after being embedded in an epoxy matrix) or at -150°C. Fully pyrolyzed samples were crushed into fine particles and dispersed onto a thin holey-carbon support film. All samples

were characterized in the absence of contrast-enhancing agents. Chemical microanalysis was performed on a 200 keV field emission TEM (FEI Tecnai F20) equipped with EDS and EELS capabilities. EELS line profiles were performed in STEM mode with reference to dark-field images acquired from an off-axis detector. Drift-correction software was employed during line profile acquisition to mitigate the effects of specimen drift from thermal and mechanical sources. EELS spectra were acquired with an energy resolution of 1.0 eV using an energy dispersion of 0.5 eV and a 3.0 mm spectrometer entrance aperture. Elemental counts were extracted from individual energy-loss spectra after background removal from each core edge (Si L<sub>2,3</sub>, C K and O K) to yield qualitative chemical line profiles.

***Small angle X-ray diffraction and scattering.*** X-ray diffraction experiments were performed at the Department of Polymer Science, UMass-Amherst using a Molecular Metrology Small Angle X-ray Scattering Instrument (Molmet.com, USA). A monochromatic incident X-ray beam ( $\lambda = 0.1518$  nm) was used and the diffraction data were collected using a 2-D multi-wire detector coupled to a computer monitor so that the emerging diffraction and scattering patterns can be followed in real time. The diffraction patterns were recorded from the samples in the real d-spacing range of 100–10 nm.

***NMR Spectroscopy.*** <sup>13</sup>C and <sup>29</sup>Si NMR spectra were acquired on a Bruker Avance 500 spectrometer operating at 125.8 MHz for <sup>13</sup>C and 99.4 MHz for <sup>29</sup>Si. The polymers were dissolved in 3.5mL of chloroform-d and run overnight. <sup>13</sup>C experimental parameters included a spectral width of 24.5kHz, acquisition time of 1.34s, 32K data points, and 5s total recycle time. The <sup>29</sup>Si acquisition parameters included a 24.8kHz spectral width, 1.32s acquisition time, 32K

data points, and a total of 5s recycle time.  $\text{Cr}(\text{acac})_3$  was added to these solutions to shorten the  $T_1$ 's, and gated decoupling was used.

***Porosity analysis.*** Brunauer-Emmett-Teller (BET) adsorption-desorption isotherms of  $\text{N}_2$  were obtained at  $-196^\circ\text{C}$  with a Micromeritics ASAP 2020 instrument. Before the BET tests, samples were outgassed at  $250^\circ\text{C}$  for more than 5 hours. The desorption isotherm was used to estimate the distribution of pore-size. Relative density was estimated according to the cumulative pore volume obtained by BET and the nominal theoretical density of amorphous silicon carbonitride,  $2.3\text{g}/\text{cm}^3$ .