Supporting Information

An Inorganic-Organic Diblock Copolymer Photoresist for Direct Mesoporous SiCN Ceramic Patterns via Photolithography †

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Experimental

Materials. All of the reactions were carried out in a purified argon atmosphere using standard Schlenk techniques. All glassware was stored in a drying oven for several hours at 120 °C. The methylmethacrylate (MMA) monomer was obtained from Aldrich Co. Ltd. and purified by distillation under reduced pressure over CaH_2. The 2,2'-azo-bis(isobutyronitrile) (AIBN) was purchased from ACROS Organics Co., Vinylcyclicsilazane (KiON VL20, KiON Corp.), 2-isocyanatoethyl methylacrylate (IEM, Hesita Laboratories INC), and anhydrous toluene (99.99%, Aldrich) were used as received.

Synthesis of PVSZ-b-PMMA diblock copolymer photoresist. Inorganic-organic diblock copolymer Poly(vinyl)silazane-*block*-polymethylmethacrylate (PVSZ-*b*-PMMA) was synthesized via RAFT process with the presence of dithiocarbamate derivatives as RAFT agents and AIBN as a thermal initiator. In a typical synthesis (Scheme S1), a stock solution containing 5 g (16.7 mmol) of vinylcyclicsilazane (VSZ), 93 mg (0.57 mmol) of 2,2'-azo-bis(isobutyronitrile)

(AIBN), 462 mg (1.63 mmol) of pyrrole-1-carbodithioic acid benzyl ester (BPCD) as a RAFT agent, and 3 mL of anhydrous toluene were added to a Schlenk tube. The solution was degassed with three freeze-evacuate-thaw cycles and then sealed. The tube was heated at 90 ^{o}C in an oil bath for 48 h. A solution containing 4.2 g (43.0 mmol) of methylmethacrylate (MMA) and 31 mg (0.18 mmol) of AIBN was then added. The resulting solution was stirred at 90 ^{o}C for an additional 8 h. The volatiles were removed under reduced pressure to give a product poly(vinyl)silazane-*block*-polymethylmethacrylate (PVSZ-*b*-PMMA). The resulting polymer was diluted in THF, and precipitated by adding *n*-hexane. The purified PVSZ-*b*-PMMA (6.8 g, 71.6 % conversion, M_n = 19,760 g.mol^{-1}, and PDI = 1.21) was filtered out, followed by drying in vacuum.

The photoresistable inorganic-organic diblock copolymer was synthesized by modifications of as-synthesized PVSZ-*b*-PMMA diblock copolymer in an anhydrous toluene solvent by adding 2-isocyanatoethyl methacrylate (IEM). In a typical reaction, 0.3 mL (0.25 g) of IEM was slowly dropped into 1 g of as-synthesized PVSZ-*b*-PMMA solution dissolved in 3 mL toluene. The mixture was heated in an oil bath at 50 ^{o}C for 20 h. Finally, the solvent and unreacted precursor was removed by vacuum. All the processes were carried out in an inert gas atmosphere to avoid exposure to moisture.

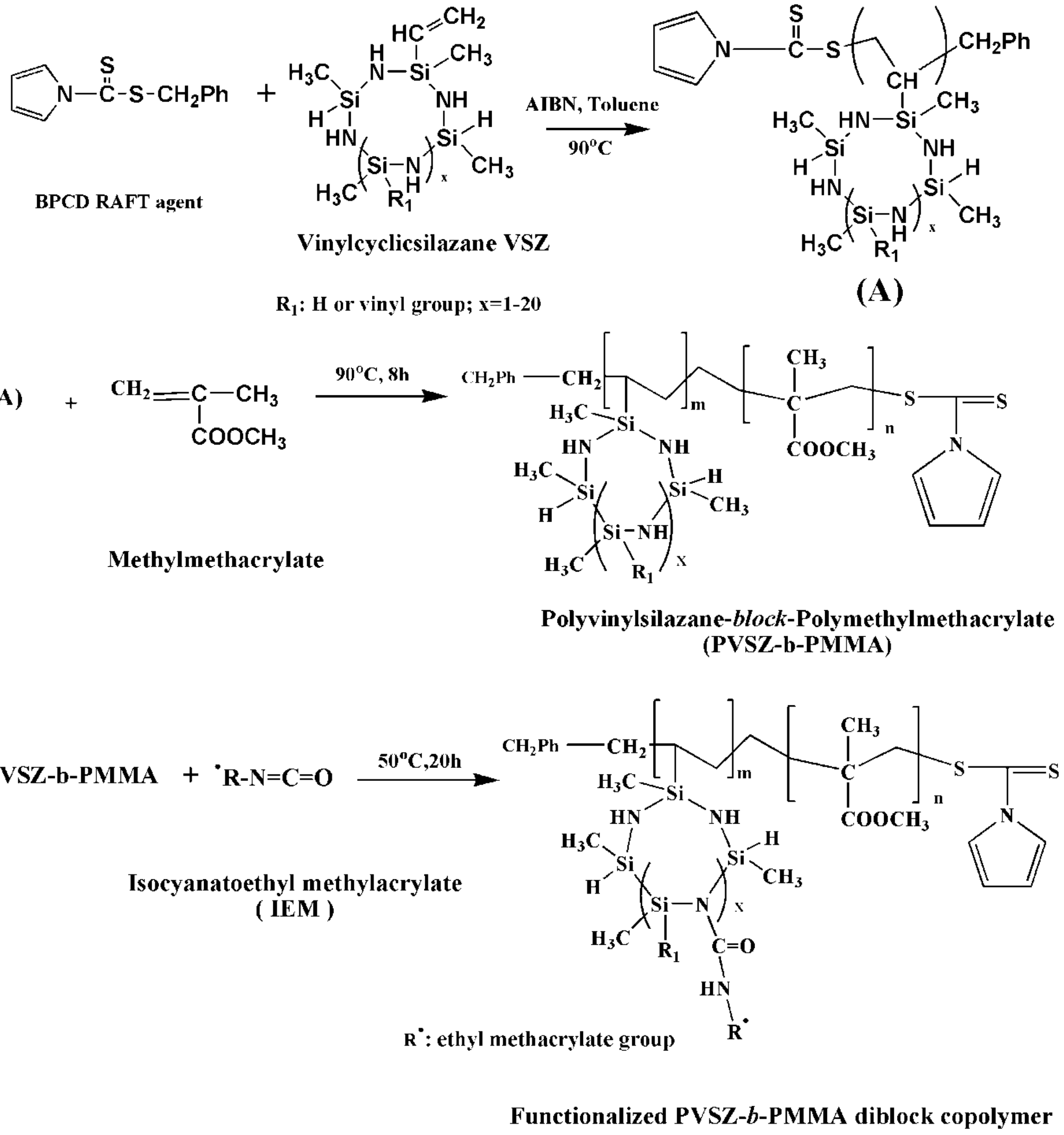
Well-ordered mesoporous SiCN ceramic microstructure. To investigate the microphase segregation of the bulk phase of mesoporous SiCN ceramic material, photoresistable PVSZ-*b*-PMMA films of approximately 0.5 mm thickness were cast over 3-4 days from a 1 to 5 wt% solution in tetrahydrofuran (THF) solvent in a 100 mm-diameter Teflon disk. The thick cast films were self-assembled by thermal annealing method without thermal initiator under Ar atmosphere at 180 °C for 20 h, and then pyrolyzed at temperatures up to 1200 °C at a heating rate of 1 °C.min^{-1} in an Ar atmosphere to convert into ceramic bulk powder type of product.

Fabrication of mesoporous SiCN ceramic patterns. Thin film type of mesoporous PVSZ-*b*-PMMA pattern was fabricated by solvent annealing method with THF and subsequent photolithography process. For self-assembly by annealed solvent, 1 wt% photoresistable diblock copolymer solution dissolved in THF (anhydrous 99.9 %) was mixed with 3 wt% (to the diblock copolymer) of Irgacure 369 photoinitiator. After stirring, for uniform coating of the layers any dust or particle or/and bubble was removed by using 0.2 μm filters. The thin films with thickness ~100 nm were prepared by spin-coating the photosensitive diblock copolymer mixture on the silicon wafer at 2000 rpm for 30 s. Subsequently, the thin film was annealed under THF solvent in a closed jar for 12 h at 30 °C to form the self-assembled PVSZ-*b*-PMMA photoresist. For line pattern by photolithography, the self-assembled PVSZ-*b*-PMMA photoresist was irradiated by conventional photomask (line pattern of 3 μm width) under a 30 mW/cm^2 UV irradiation with a mask aligner (MA6 aligner, Karlsuss) for 5 min. The UV-irradiated pattern became insoluble, while the non-irradiated parts were still soluble to be developed by rinsing with ethanol several times. At this stage, prolonged UV irradiation of the developed pattern for 10 h was applied to strengthen the inorganic network and to decompose the PMMA block, after which it was rinsed with glacial acetic acid and deionized water repeatedly. Finally, the obtained mesoporous PVSZ pattern was pyrolyzed at the same conditions as prepared for the bulk ceramic powder sample. In this work, to generate the self-assembled pores perpendicular to the surface, the surface of the silicon substrate was neutralized so as to balance the interfacial interaction of PMMA and PVSZ blocks by anchoring the random PMMA-*r*-PS copolymer (40 % of PS, Aldrich Co. Ltd.) layer. The 0.5 wt% random copolymer solution in toluene (anhydrous, 99.99%) was spin-coated on the native silicon wafer and annealed in a vacuum at 180 °C for 24 h, followed by rinsing away the excess copolymer with toluene.

Characterization Technique. The ^{1}H-, ^{13}C-, ^{29}Si- nuclear magnetic resonance (NMR) spectra were performed in $CDCl_3$ with a Bruker DMX600. The solid-state ^{29}Si NMR spectra were performed using an FT Wide Bore (600MHz) Unityl NOVA600 under cross polarization magic angle spinning (CP-MAS) conditions. The thermal properties of the polymer samples were examined by thermogravimetric analysis (TGA) (TA Instrument 2050) from room temperature up to 1000 °C in a nitrogen atmosphere at $10^{o}C.min^{-1}$. The molecular weight distribution of the synthesized polymers was investigated using gel permeation chromatography (GPC) using a Waters 515 HPLC isocratic pump equipped with a Waters 2414 Refractive Index detector and Waters styragel columns (HR 1, 2, 3, 4, 5E). For universal calibration, THF (flow rate of 1.0 mL/min) was used as a solvent, and polystyrene (Shodex standard) as a standard. The small-angle X-ray diffraction patterns were recorded on an MX Labo powder diffractometer using CuKα radiation (40 kV, 20 mA) at a scan rate of $1.0°.min^{-1}$ over the range $0.5 - 7.0^{o}$ (2θ). The pyrolyzed samples were crushed into fine particles and dispersed onto a thin holey-carbon support film, and the high-resolution transmission electron microscopy (HR-TEM) images were obtained using a JEM 2100F, JEOL, Japan, operating at 200 kV. The scanning electron microscopy (SEM) was performed using a JSM-7000F, JEOL, Japan, and Atomic Force Microscopy (AFM, XE-100, PSIA, Korea) was used to characterize the morphologies of the films. The surface area and N_2 adsorption–desorption isotherms were measured at 77 K on a Micromeritics (ASAP 2010, U.S.A.) according to the Brunaurer-Emmett-Teller (BET) method. The differential photocalorimeter (photo-DSC) experiments were analyzed using a Perkin Elmer

DSC7 device equipped with a 532 nm diode laser. Samples with 2 wt% photoinitiator (Irgacure 369) were placed in uncovered aluminum pans and cured at a laser intensity of 1.5 mW/cm^2.

Scheme S1. Synthetic route of photoresistable PVSZ-*b*-PMMA diblock copolymer



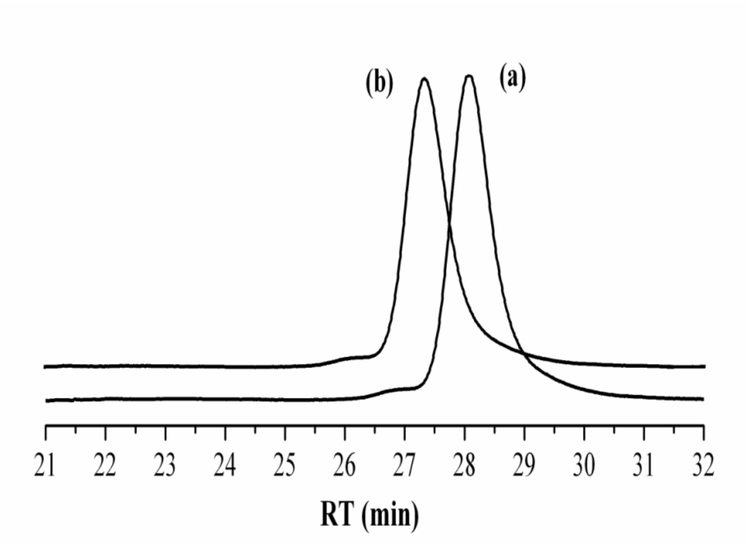


Fig. S1. GPC spectra of (a) PVSZ-*b*-PMMA (M_n = 19,760 g.mol^{-1}, PDI = 1.21) and (b) functionalized $PVSZ_{30}$-*b*-$PMMA_{109}$ (M_n =20,180 g.mol^{-1}, PDI=1.20).

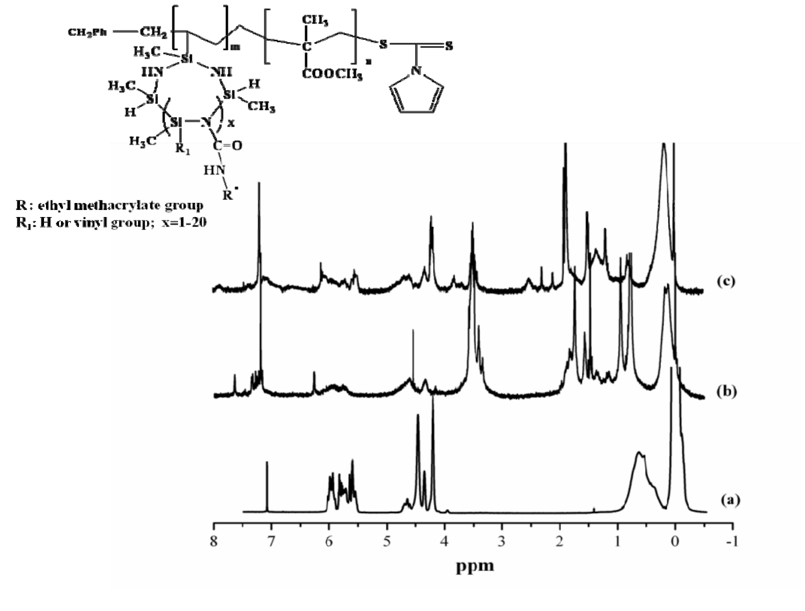


Fig. S2. ^{1}H-NMR spectra of (a) the initial vinylcyclicsilazane, (b) PVSZ-*b*-PMMA, and (c) functionalized $PVSZ_{30}$-*b*-$PMMA_{109}$ in $CDCl_3$.

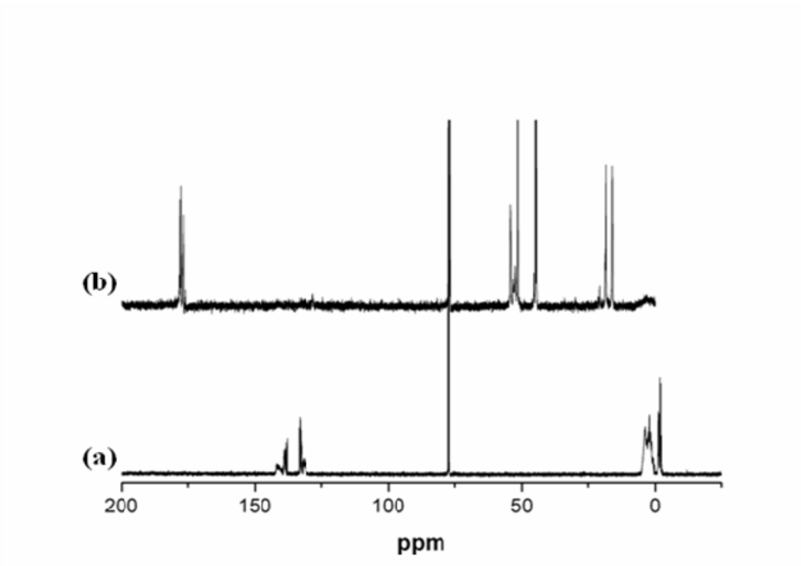


Fig. S3. ^{13}C-NMR spectra of the polymer in $CDCl_3$; (a) the initial vinylcyclicsilazane, and (b) functionalized PVSZ$_{30}$-*b*-PMMA$_{109}$.

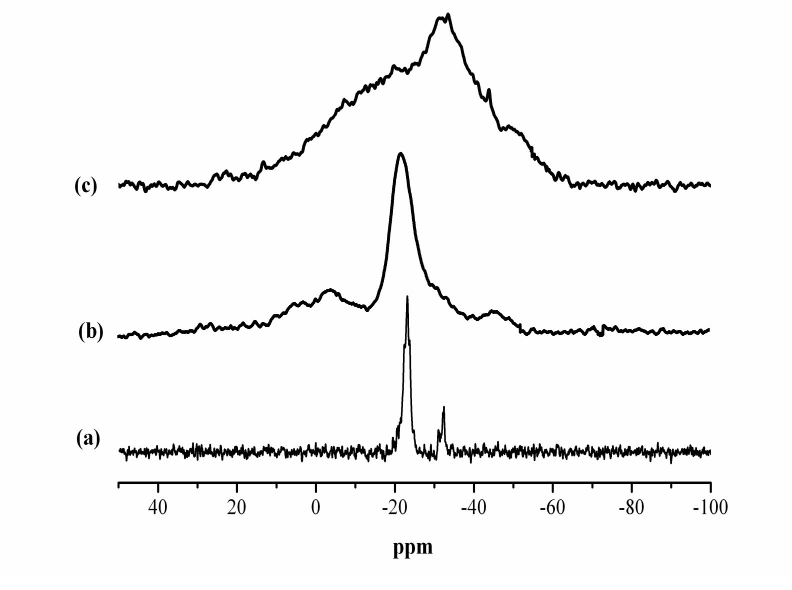


Fig. S4. ^{29}Si-NMR spectra of the polymer in $CDCl_3$; (a) initial vinylcyclicsilazane, (b) functionalized PVSZ$_{30}$-*b*-PMMA$_{109}$ and (c) functionalized PVSZ$_{30}$-*b*-PMMA$_{109}$ annealed at 1200 ^{o}C under Ar atmosphere.

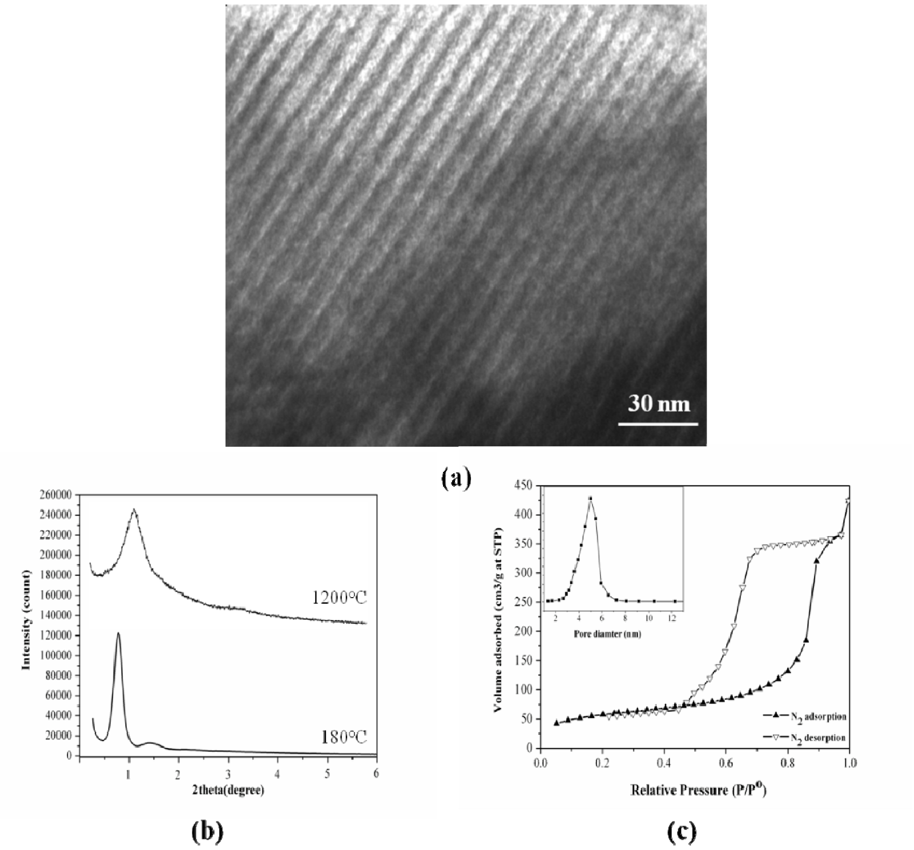


Fig. S5. Characterization of mesoporous SiCN ceramic from functionalized PVSZ$_{30}$-*b*-PMMA$_{109}$ by annealing at 1200 ^{o}C under Ar atmosphere: (a) TEM images, (b) Small-angle XRD pattern, and (c) N$_2$ adsorption-desorption isotherm and pore size distribution (inset).

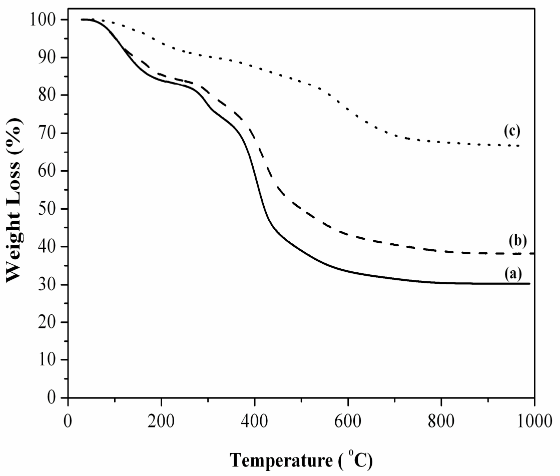


Fig. S6. Thermal properties of self-assembled PVSZ$_{30}$-b-PMMA$_{109}$ photoresist films by solvent annealing; (a) before, (b) after UV irradiation for 5 min and (c) after prolonged extra-UV exposure for 10 h and rinsed.