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Direct Preparation of High Surface Area Mesoporous SiC-Based Ceramic by Pyrolysis of a Self-Assembled Polycarbosilane-*block*-Polystyrene Diblock Copolymer

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Direct pyrolysis of a self-assembled inorganic−organic block copolymer can be a promising route for fabricating the ordered ceramic nanostructures based on the achievements of organic−organic block copolymers. Here we report the synthesis of a novel polycarbosilane-*block*-polystyrene diblock copolymer by ring-opening living anionic polymerization in a THF and *n*-hexane solvent system at −48 °C. The resulting block copolymer revealed phase-separation behavior in the nanoscale to form a self-assembled nanostructure that was converted to a mesoporous ceramic phase after heating at 800 °C. The pyrolyzed ceramic product exhibited well-ordered mesoporous SiC-based ceramic structures with a high BET surface area of 1325 $m^2\ g^{-1}$ and an average mesopore size of 7.8 nm containing a large amount of micropores.

Introduction

Silicon carbide (SiC) materials exhibit unique properties such as high thermal conductivity, excellent thermal stability, resistance toward oxidation, high mechanical strength, and chemical inertness. These properties make them attractive for generation of high-temperature semiconducting devices,[1] as hydrogen storage materials,[2] and as catalyst supports.[3] Well-ordered mesoporous SiC materials are essential for a number of these applications. Various mesoporous SiC materials have previously been synthesized using the sacrificial template and chemical vapor infiltration (CVI) methods.[4] For example, mesoporous SiC materials were prepared via a carbothermal reduction reaction using mesoporous silica MCM-48,[5] and mesoporous silica SBA-15 as a solid template.[6,7] However, these methodologies are not suitable for industrial production of powder materials due to engineering difficulties and require a harmful etching step, most commonly with strong acid, which limits the coating applications to substrates. Therefore, use of self-assembled block copolymers is an attractive area with substantial attention on creation of well-ordered nanostructured materials at a large scale and facile processibility.[8–13] To date, most of the block copolymers used in self-assembly studies and applications have focused on organic−organic diblock copolymers. They have been used as self-assembly templates for the synthesis of inorganic materials such as oxide ceramics with periodic order at the nanoscale.[14–16] There are few reports on the synthesis of mesoporous ceramics using inorganic−organic diblock copolymers.[17] Malenfant et al. recently reported the synthesis of nanostructures BCN and mesoporous BN ceramics based on hybrid organic−inorganic block copolymer.[18] In addition, we also reported the application of poly(vinyl)silazane-*block*-polystyrene diblock copolymer as a ceramic precursor of a mesoporous SiCN

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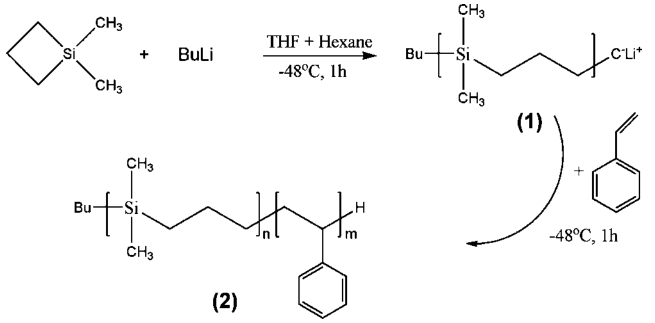
Scheme 1. Synthetic Route of Polycarbosilane-*block*-polystyrene Diblock Copolymer



ceramic.[19] However, to the best of our best knowledge, there is no report on the fabrication of mesoporous SiC ceramic through direct pyrolysis of self-assembled block copolymers.

In this study, for the first time, well-ordered mesoporous SiC ceramic with high surface area was synthesized through direct pyrolysis of self-assembled polycarbosilane-*block*-polystyrene (PCS-*b*-PS) diblock copolymer, which was synthesized by ring-opening living anionic polymerization. Moreover, the composition of ordered ceramic nanostructures can be controlled by changing the gaseous atmosphere.

Experimental Section

All reactions were carried out in a purified argon atmosphere using standard Schlenk techniques. All glassware utilized was stored in a drying oven for several hours at 120 °C. *n*-Butyllithium (1.6 M in hexane, Aldrich Co. Ltd.) was used as purchased. Tetrahydrofuran (THF, anhydrous 99.9%) and *n*-hexane (95%) solvents were dried with a sodium−benzophenone mixture under reflux and then distilled over CaH_2 under reduced pressured. 1,1-Methylsiletane and styrene monomers (Aldrich Co. Ltd.) were purified by distillation under reduced pressure over CaH_2.

In a typical synthesis, a 100 mL round-bottom flask with a Teflon cover magnetic stirring bar and a rubber septum were placed with THF (10 mL) and *n*-hexane (10 mL) under an argon atmosphere. The solution was cooled to −48 °C using a dry ice and acetonitrile solution. A *n*-butyllithium solution (1.6 M, 0.25 mL, 0.4 mmol) was added followed by 1,1-methylsiletane (2 g, 2.574 mL, 19.95 mmol). The reaction mixture was stirred at −48 °C for 1 h to afford the living polycarbosilane (**1**). Styrene (2 g, 2.2 mL, 19.2 mmol) was slowly added and stirred for a further 1 h, as shown in Scheme 1. A 0.5 mL amount of methanol was then added to terminate polymerization. The resulting product was precipitated in excess methanol, filtered, and dried to give 3.82 g of polycarbosilane-*block*-polystyrene (PCS-*b*-PS) diblock copolymer with a synthetic yield of 95.5%. In order to investigate the microsegregation and formation of mesoporous SiC ceramic, approximately 0.5 mm thick PCS-*b*-PS films were prepared by casting a toluene solution dissolved with 1−5 wt % of polymer on a 100 mm diameter of Teflon disk, standing for over 3−4 days. The film was then annealed in a nitrogen atmosphere at 180 °C for 3 h. The cast film was peeled off the Teflon disk and pyrolyzed at temperatures up to 800 °C at a heating rate of 1 °C min^{-1} in a nitrogen atmosphere and held for 3 h to allow complete conversion of the films to ceramic materials ($C-SiC-N_2$). Then nitrogen gas was replaced by air for 3 h to obtain free carbon SiC ceramic materials (SiC−Air).

Table 1. Molecular Weight and Volume Fraction of Polycarbosilane-*block*-polystyrene Diblock Copolymers

sample	$M_{n(PCS)}$[a] (g mol^{-1})	$M_{n(PS)}$[b] (g mol^{-1})	$M_{n(Total)}$[c] (g mol^{-1})	PDI	PCS_m-*b*-PS_n (*m*:*n*)	f_{PCS}[d]
1	2800	1800	4600	1.16	28:18	0.62
2	4500	4200	8600	1.12	45:40	0.55
3	20 700	8200	28 300	1.19	205:79	0.71

[a] Calculated from ^1H NMR. [b] Calculated from GPC. [c] Calculated from GPC. [d] Calculated from $N_n^* = N^*_{n,PCS} + N^*_{n,PS} = N^*_{n,PCS}(\rho^*_S/\rho^*_{CS})^{1/2} + N^*_{n,PS}(\rho^*_{cs}/\rho^*_S)^{1/2}$ and $f_{PCS} = N^*_{n,\ PCS}(N^*_{n,PCS} + N^*_{n,PS})$ where $N_{n,i}$ are the degree of polymerization of each block and ρ^*_i are the molar densities. For the density, we used the values 1.102 and 1.047 g cm^{-3} for PCS and PS, respectively.

^1H and ^{29}Si nuclear magnetic resonance (NMR) spectroscopy was performed in $CDCl_3$ with a Bruker DMX600. ^{29}Si magic angle spinning (MAS) NMR experiments were performed on an FT Wide Bore (600 MHz) UnitylNOVA600. Tetramethylsilane (TMS) was used as the internal standard. The molecular weight distribution of the synthesized polymers was examined 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). THF (flow rate of 1.0 mL min^{-1}) and polystyrene (Shodex standard) were used as the solvent and standard for universal calibration, respectively. The thermal properties of the polymer samples were examined by thermogravimetric analysis (TGA) (TA Instrument 2050) from room temperature to 1000 °C in a nitrogen atmosphere at 10 °C min^{-1}. Small-angle X-ray diffraction patterns were recorded on a small-angle X-ray diffractometer (SA-XRD, D/MAX-2500(SWXD), Rigaku, Japan) using Cu Kα radiation (40 kV, 20 mA) at a scan rate of 1.0° min^{-1} over the range 0.25−6.0° (2θ). Wide-angle X-ray diffraction patterns were performed by powder X-ray diffraction (XRD, D/MAX-IIIC (3 kW), Rigaku, Japan) using Cu Kα radiation. The pyrolyzed samples were crushed into fine particles and dispersed onto a thin holey-carbon support film. In addition, the high-resolution transmission electron microscopy (HRTEM) images were obtained using a JEM 2100F, JEOL, Japan, operating at 200 kV. The high-resolution SEM images of polymeric samples were performed using a field emission scanning electron microscope (FE-SEM, S-4800, Hitachi, Japan). Energy-dispersive X-ray spectroscopy (EDS) was performed at 5 KeV, 30° tilt by field-emission scanning electron microscopy (FE-SEM; Philips XL30SFEG, Eindhoven, The Netherlands). The surface area and N_2 adsorption−desorption isotherms were measured at 77 K on a Micromeritics (ASAP 2010) after outgassing at 350 °C for 10 h according to the Brunauer−Emmett−Teller (BET) method. The desorption isotherm was used to estimate the distribution of pore size.

Results and Discussion

The synthesis of polycarbosilane-*block*-polystyrene (PCS-*b*-PS) diblock copolymer was proceeded in accordance with the living anionic mechanism in THF−hexane (1:1) at −48 °C. Formation of the block copolymer was confirmed by GPC measurement (for details see Supporting Information, Figure S1) and ^1H NMR spectra.

A range of block copolymers with a controlled molecular weight of block copolymer and narrow polydispersity (<1.2) is listed in Table 1. These results demonstrate an excellent degree of control achievable with ring-opening living anionic polymerization to obtain the desired block copolymers. The block copolymer sharply shifted to a higher molecular weight region with a narrow molecular weight distribution, which

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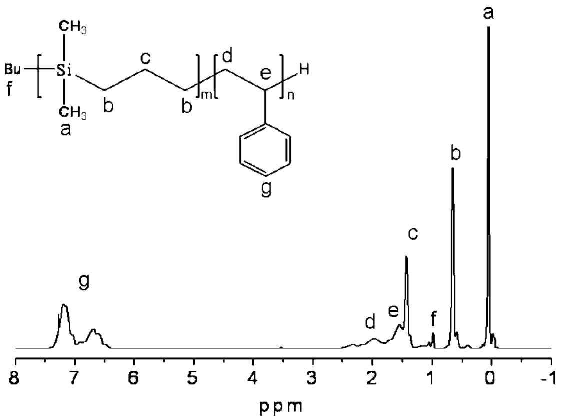

Figure 1. ^1H NMR spectrum of PCS_{205}-*b*-PS_{79} diblock copolymer in $CDCl_3$.

is typical evidence for formation of PCS-*b*-PS polymer.[20] The number-average molecular weight (M_n) and composition of the obtained diblock polymers (*n:m*) were determined by ^1H NMR integral ratios of signals corresponding to the initiation end group and each polymer segments. The molecular weight of obtained block polymers (sample 2, $M_n = 8600$ g mol^{-1}; sample 3, $M_n = 28\,300$ g mol^{-1}) measured by GPC was in good agreement with M_n (sample 2, $M_n = 8000$ g mol^{-1}; sample 3, $M_n = 26\,000$ g mol^{-1}) calculated from the initial concentration ratio of *n*-butyllithium and the sum of two monomers. Moreover, the composition (*n:m*) of the obtained block copolymers were also in good agreement with the ratio of the initial concentration of each monomer. The detailed chemical structure of PCS-*b*-PS polymer ($M_n = 28\,300$ g mol^{-1}; PDI = 1.19) was confirmed by ^1H NMR spectroscopy, as shown in Figure 1. The signals at $\delta = 0.12$, 0.76, and 1.43 ppm were assigned to Si$-CH_3$, Si$-CH_2$, and $-CH_2$ groups, respectively, and are characteristic of the polycarbosilane block. From the polystyrene block, the signals corresponding to the C_6H_5, CH_2, and CH protons were observed at $\delta = 6.5-7.3$ and $1.5-1.9$ ppm, respectively. In addition, formation of polycarbosilane blocks was also confirmed by ^{29}Si NMR spectra (Figure 2). The peak at 18.5 ppm disappeared, and a new peak was found at ~0.9 ppm due to the ring-opening polymerization of 1,1-methylsiletance to form polycarbosilane, from a comparison of the spectrum of Figure 2a and 2b. After being pyrolyzed at 800 °C the ^{29}Si MAS NMR spectrum of the mesoporous SiC sample showed a broadening of the peak at -17.5 ppm (Figure 2c), which was assigned to the structural components of the amorphous $Si(Csp^3)_4$ units.[21]

Thermogravimetric analysis in nitrogen indicated that the obtained block copolymer ($M_n = 28\,306$ g mol^{-1}; PDI = 1.19) began to decompose with a small mass loss of 5 wt % at 200 °C, which was attributed to the early stage of thermal curing and decomposition (see Supporting Information, Figure S3a). The second weight loss stage (~35 wt %) at the narrow temperature range of 370−420 °C corresponded to thermal decomposition of PS blocks. From 430 to 800 °C an additional mass loss of 30 wt % was observed. It was presumably due to the pyrolytic decomposition of inorganic PCS blocks for transformation into the ceramic phase.[21] Finally, the ceramic yield of 28.5 wt % at 1000 °C was obtained in the form of the final SiC ceramic nanostructured product. In comparison, the obtained block copolymer exhibited a much lower ceramic yield when compared to poly(vinyl)silazane-*block*-polystyrene diblock copolymer, as previously reported.[19] It is reasonably interpreted with the absence of cross-linkable groups such as vinyl, silane groups in backbone of PCS block, and the presence of high organic moiety (propylene) of carbosilane block. The excess carbon in the final SiC ceramic product was examined by SEM/energy-dispersive X-ray spectroscopy (EDS), which resulted in the estimation of 24.6 atom % for Si, 68.2 atom % for C, and 7.2 atom % for O, which is relatively consistent with the composition $Si_{1.0}C_{2.77}O_{0.29}$. In addition, it was observed that by simple addition of curable and compatible vinylcyclicsilazne (VSZ) to the PCS block enhances formation of a highly cross-linked network in the inorganic block.[19,22] The ceramic yield of the modified block copolymer was enhanced with no disturbed self-assembly behavior.

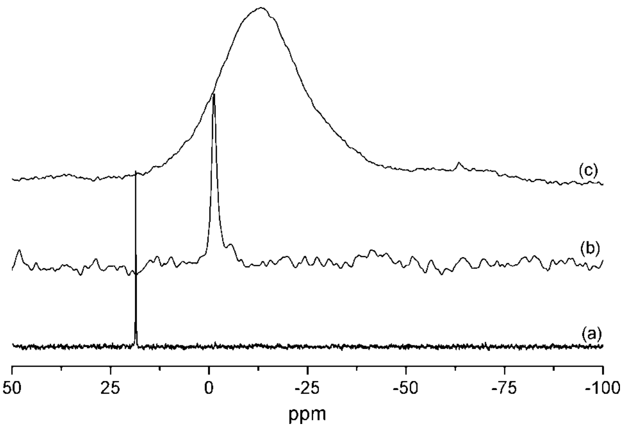

Figure 2. ^{29}Si NMR spectra of (a) 1,1-methylsiletance monomer, (b) polycarbosilane-*block*-polystyrene diblock copolymer in $CDCl_3$ solvent, and (c) mesoporous SiC ceramic pyrolyzed at 800 °C under N_2 atmosphere.

In order to produce the self-assembled ceramic film using the PCS_{205}-*b*-PS_{79} diblock copolymer ($M_n = 28\,300$ g mol^{-1}; PDI = 1.19), the polymer dissolved in toluene solvent was cast on a Teflon disk and allowed to evaporate slowly under an an Ar atmosphere at room temperature. The organic PS block was subsequently pyrolyzed at 800 °C to form pores, while the inorganic PCS block was transformed to form the ceramic wall. As shown in Figure 3, the small-angle X-ray diffraction patterns (SA-XRD) of the self-assembled polymeric film showed a sharp peak at $2\theta = 0.88°$, indicating that a hexagonally packed cylindrical morphology was formed with a *d* spacing of 9.84 nm and a cylinder diameter of ~11.4 nm. This result is in excellent agreement with the result predicted from the phase diagram of PMMA-*b*-PS, as calculated by Leibler[23] and Matsen.[24] In addition, the morphology of the top view of the polymeric film was

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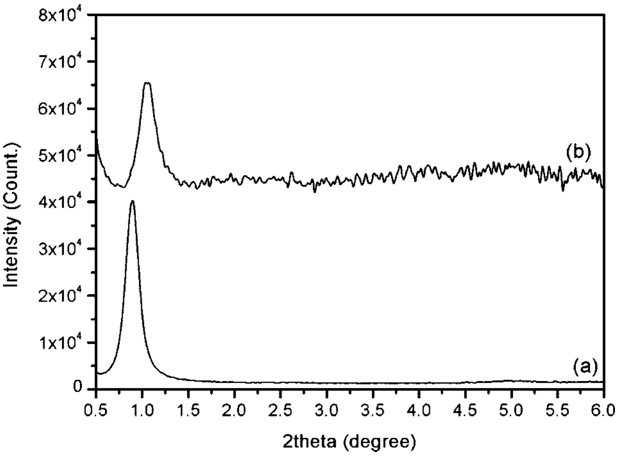

Figure 3. Small-angle X-ray diffraction patterns of PCS_{205}-*b*-PS_{79} diblock copolymer at (a) 180 and (b) 800 °C under N_2 atmosphere.

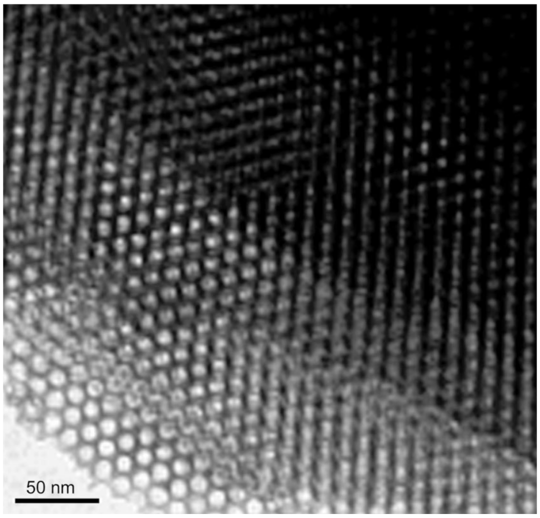

Figure 4. TEM image of self-assembled PCS_{205}-*b*-PS_{79} diblock copolymer pyrolyzed at 800 °C under N_2 atmosphere.

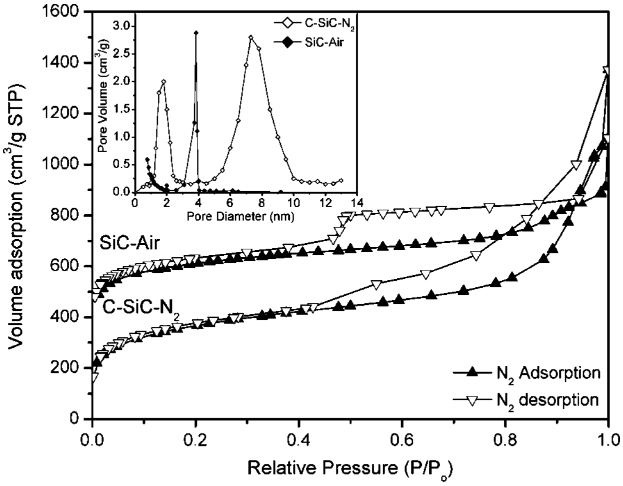

Figure 5. N_2 adsorption−desorption isotherm and pore size distribution (inset) of mesosporous SiC ceramic annealed in a different atmosphere.

Table 2. Pores Characteristic of Mesoporous SiC Ceramic after Annealing in Different Atmospheres

	surface area (m^2 g^{-1})			
samples	mesopores area	micropores area	pore volume (cm^3 g^{-1})	pore diameter (nm)
C−SiC−N_2	829	496	1.45	7.8; 2.0
SiC−Air	795		0.96	4.1

observed by FE-SEM (see Supporting Information, Figure S2), which shows the nanoscale domains with a size of ~12 nm formed by phase separation. In contrast, PCS-*b*-PS (1) and (2) (Table 1) did not show the microphase separation, presumably due to the low molecular weight of the polymers. For the pyrolyzed product at 800 °C, the single diffraction peak shifted to higher $2\theta = 1.08°$, corresponding to a smaller *d* spacing of 6.45 nm and pore diameter of ~7.45 nm. The TEM image of the sample (Figure 4) reveals the well-ordered hexagonal arrangement of cylindrical channels with consistent pores diameter of ~7.2 nm, which is similar to the structure of mesoporous silica, SBA-15.[6] The highly decreased pore size of the ceramic product, compared to that of the polymeric phase, is caused by the severe shrinkage due to the low ceramic yield of the block copolymer (ca. 30.5 wt % at 800 °C).

The porosity characteristics of the sample annealed at 800 °C under N_2 atmosphere were investigated by measuring the N_2 adsorption−desorption isotherm at −196 °C (Figure 5). The sample exhibited a type IV adsorption isotherm with an H_2 hysteresis loop. The Brunauer−Emmertt−Teller (BET) analysis of this isotherm confirmed the presence of a highly mesoporous structure with a pore volume close to 1.45 cm^3 g^{-1} with a very high specific surface area of 1325 m^2 g^{-1} and a bimodal pore size distribution of ~7.8 and ~2.0 nm, as determined by the BJH desorption pore distribution method (Figure 5, inset). These results are comparable with the surface area and pore volume of various mesoporous oxide ceramic products[25] and mesoporous carbon CMK-3.[26] It is believed that the pore structures with high surface area can be developed by rigorous evolution of gaseous byproducts during pyrolysis. In addition, it turned out that the mesopores and micropores (<2 nm diameter) accounted for more than 60% of the entire pore volume and 37% of the overall surface area, respectively (Table 2). The presence of micropores is presumably due to the excess carbon formed in mesoporous SiC during the pyrolysis process. The observed results clearly demonstrated that PCS_{205}-*b*-PS_{79} diblock copolymer could become a reliable route to prepare a cylindrical hexagonal mesoporous SiC ceramic with microporous walls. This material with hierarchical pore structure has the potential for extended applications similar to mesoporous carbon, particularly at high temperatures. In addition, after annealing at 1000 °C for 2 h under an air atmosphere, the surface area and average pore size were drastically reduced to 795 m^2 g^{-1} and 4.1 nm, respectively. The significant change in the pore characteristics must be attributed to the disappearance of micropores and volume shrinkage by burning out of the excess carbon, which is consistent with a TGA weight loss of 12% when pyrolyzed in air (see Supporting Information, Figure S3(b)). Alternatively, the energy-dispersive X-ray spectroscopy (EDS) data reveals that the mesoporous SiC−Air sample contained

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silicon, carbon, and oxygen with compositions of 40.2, 44.5, and 15.3 atom % ($Si_{1.0}C_{1.11}O_{0.38}$), respectively. Interestingly, the resulting material shows a high oxidation resistance with little increase of oxygen content of SiC−Air compared to the C−SiC−N_2 sample. Finally, the crystallization behavior of mesoporous SiC ceramic was analyzed by wide-angle X-ray diffraction (W-XRD) (see Supporting Information, Figure S4). The pattern of the C−SiC−N_2 sample showed only a broad diffraction peak with a 2θ value of 17, which can be assigned to amorphous carbon.[27] After annealing in air, the diffraction corresponding to amorphous carbon disappeared. This result is in good agreement with the TGA and EDS results. Furthermore, the PCS-*b*-PS polymer synthesized in the present report may be useful for preparation of nanostructured powders, film, and nanowires.

Conclusion

We demonstrated that polycarbosilane-*block*-polystyrene diblock copolymer was successfully synthesized using ring-opening living anionic polymerization. The resulting polymer was used for the first time as a new precursor for formation of well-ordered mesoporous SiC-based ceramic materials via self-assembly. The mesoporous SiC-based ceramics directly obtained by pyrolysis at 800 °C of self-assembled PCS-*b*-PS polymer exhibited a high BET surface area of 1325 m^2 g^{-1} with an average mesopore size of 7.8 nm containing a large amount of micropores. The novel organic−inorganic block copolymer with facile processibility has great potential to open a new field for generation of mesostructured nonoxide ceramics for a broad class of applications.

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Supporting Information Available: GPC cuvers (Figure S1), FE-SEM image of PCS-b-PS copolymer thin film (Figure S2), TGA curves of polymer and ceramics (Figure S3), XRD patterns (Figure S4), and *t*-plot micropore surface area (Figure S5) (PDF). This information is available free of charge via the Internet at http://pubs.acs.org.

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