

Well-Ordered Nanostructure SiC Ceramic Derived from Self-Assembly of Polycarbosilane-Block-Poly(methyl methacrylate) Diblock Copolymer

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The fabrication of SiC ceramic materials with an ordered nanostructure through the direct pyrolysis of a self-assembled inorganic–organic block copolymer has generally been unsuccessful even though the versatile processibility has been demonstrated with organic–organic block copolymers. Here we report the synthesis of a novel polycarbosilane-*block*-poly(methyl methacrylate) diblock copolymer through ring-opening living anionic polymerization in a THF and *n*-hexane solvent system at $-48\text{ }^{\circ}\text{C}$. The resulting block copolymer exhibited phase-separation behavior on the nanoscale to form a self-assembled nanostructure that was converted to a mesoporous ceramic after heating at $800\text{ }^{\circ}\text{C}$. The characterization of diblock copolymer is simultaneously investigated by GPC, and NMR analyses. The self-assembly of diblock copolymer is characterized by small-angle X-ray scattering (SAXS), atomic force microscopy (AFM), and scanning electron microscopy (SEM). In particular, the preparation of high-temperature-stable nanostructured silicon carbide and mesoporous silicon carbide ceramic directed from cross-linked polycarbosilane blocks with a high ceramic yield are described, which exhibits well-oriented nanostructures with the size in a range of 4–10 nm. These exciting results have a great potential to open a new field for the generation of nanostructured non-oxide ceramic or metal–ceramic materials for a broad class of applications.

Keywords: Self-Assembly, Block Copolymers, Nanostructured Ceramics, Mesoporous SiC.

1. INTRODUCTION

The self-assembly of block copolymers has attracted considerable interest for their potential as an efficient and effective route for fabricating highly ordered structures on the nanometer scale. The block length can be tuned using controlled polymerization methods. Therefore, the morphology and size of the nanoscale phase-separated domains can be varied from spheres, to hexagonally close-packed cylinders, and to lamellar structures. The potential applications for these structures include lithographic templates for nanowires, photonic crystals, and high-density magnetic storage media.¹ The key to many future applications is the long range ordering and precise placement of the phase-separated nanoscale domains.² The formation of ordered nanoscale domains in block copolymers using self-assembly is affected by several parameters including the Flory-Huggin interaction parameter χ , which reflects the incompatibility between blocks, the degree of polymerization (N) and the volume fraction (f) of the blocks.^{3,4}

Generally, self-assembly into a highly ordered morphology requires a block copolymer with a fairly narrow molecular weight distribution i.e., there should be very little variation in the degree of polymerization of the polymer chains.

Over the past decade, the thin film of block copolymer has become increasingly attractive in the area of nanotechnology.⁵ After suitable preparation, the films exhibit a laterally varying yet highly ordered distribution of different polymeric components, with microdomain sizes and characteristic distances ranging from 10 to 100 nm.⁶ To date, most block copolymers used in self-assembly studies and applications have focused on organic–organic diblock copolymers. These have been used as self-assembly templates for the synthesis of inorganic materials such as oxide ceramics with periodic order on the nanoscale.^{7–9} Li et al. reported the combination of a self-assembled block copolymer and nanoimprint lithography to fabricate nanopatterns.² However, there are few reports on metal-containing block copolymers^{10,11} and on the use of organic block copolymers as a template for non-oxide mesoporous ceramic.^{12–15} Matsumoto et al. reported the preparation

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of ceramic particles from inorganic–organic block copolymers.^{16–17} Malenfant et al. reported the synthesis of BCN nanostructures and mesoporous BN ceramics based on hybrid organic–inorganic block copolymers.³ Recently, we reported poly(vinyl)silazane-*block*-polystyrene diblock copolymer as a ceramic precursor of a mesoporous SiCN ceramic.¹⁸ However, to our best knowledge, there is no report on the fabrication of nanostructured SiC ceramic through direct pyrolysis of self-assembled block copolymers.

In this study, ring-opening living anionic polymerization was used to synthesize the polycarbosilane-*block*-poly(methyl methacrylate) (PCS-*b*-PMMA) diblock copolymer, which enables the formation of ordered ceramic nanostructures with a controllable morphology and composition. In particular, we describe the synthesis of a mesoporous silicon carbide (SiC) ceramic directly from the self-assembly of a block copolymer and pyrolysis process.

2. EXPERIMENTAL DETAILS

All 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. Butyllithium 1.6 M in hexane was used as purchased from Aldrich Co. Ltd. Tetrahydrofuran (THF, anhydrous 99.9%) and *n*-hexane (95%) solvents were dried with a sodium-benzophenone mixture under reflux, and distilled over CaH₂ under reduced pressure. 1,1-methylsiletane and methyl methacrylate monomers were purchased from Aldrich Co. Ltd., then purified by distillation over CaH₂ under reduced pressure.

In a typical synthesis, THF (10 mL) and hexane (10 mL) were placed in a 100 mL round bottom flask with a Teflon cover magnetic stirring bar and a rubber septum under an argon atmosphere. The solution was cooled to –48 °C using a dry ice and acetonitrile solution. In addition, a *n*-butyllithium solution (1.6 M, 0.25 mL, 0.4 mmol) was added, followed by 1,1-methylsiletane (2 g, 2.5 mL, 19.95 mmol). The reaction mixture was stirred at –48 °C for 1 h to afford the polycarbosilane (1). To the solution thus prepared, 1,1-diphenylethylene (0.063 mL, 0.36 mmol) was added. The solution turned dark red. After the solution was stirred for 1 h, methyl methacrylate (1.886 g, 2.0 mL, 18.83 mmol) was slowly added and stirred for a further 1 h. 0.5 mL methanol was then added to terminate the polymerization. The resulting product was precipitated in excess methanol, filtered and dried to give 3.5 g polycarbosilane-*block*-poly(methyl methacrylate) (PCS-*b*-PMMA) with a synthetic yield of 90 wt%. In order to investigate the microphase segregation and formation of mesoporous SiC ceramic, approximately 0.5 mm thick PCS-*b*-PMMA films were prepared by casting a toluene solution dissolved with 1 to 5 wt% of the polymer on a 100 mm-diameter Teflon disk, and leaving

them to stand for more than 3–4 days. The films were then annealed in an argon atmosphere at 200 °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 an argon atmosphere to allow the complete conversion of the films to ceramic materials.

¹H-NMR were performed in CDCl₃ with a Bruker DMX600. 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) and polystyrene (Shodex standard) were used as solvents, which are the standard for universal calibration, respectively. Small-angle X-ray diffraction (SA-XRD) was performed on a MX Labo powder diffractometer using CuK α radiation (40 kV, 20 mA) at a scan rate of 1.0°/min over the range 0.5–7.0° (2 θ). The morphologies of block copolymer thin film were performed by Atomic Force Microscopy (AFM, SPI3800N Probe Station, Japan) and Scanning Electron Microscopy (SEM, Hitachi S-4800, Japan).

3. RESULTS AND DISCUSSION

The synthesis of the polycarbosilane-*block*-poly(methyl methacrylate) (PCS-*b*-PMMA) diblock copolymer was proceeded in accordance with living anionic mechanism in THF-hexane (1:1) at –48 °C. The formation of the block copolymer was confirmed by GPC and ¹H-NMR. Table I lists a range of block copolymers with a controlled molecular weight and narrow polydispersity (<1.3). These results demonstrate the excellent degree of control achievable with ring-opening of the living anionic polymerization to obtain the desired block copolymers.

Table I shows the GPC results of polycarbosilane homopolymer and PCS-*b*-PMMA diblock copolymer. The block copolymer shifted to a higher molecular weight region with a narrow molecular weight distribution, which is consistent with the formation of a PCS-*b*-PMMA polymer. The number average molecular weight (M_n) and composition of the obtained diblock polymers (*n*:*m*) were determined by the ¹H-NMR integral ratios of the signals

Table I. Molecular weight data of polycarbosilane-*block*-poly(methyl methacrylate).

Sample	$M_{n, PCS}^a$ (g/mole)	$M_{n, PMMA}^b$ (g/mole)	$M_{n, PCS-b-PMMA}^c$ (g/mole)	PCS _{<i>m</i>} - <i>b</i> - PMMA _{<i>n</i>} (<i>m</i> : <i>n</i>)	PDI	Volume fraction (<i>f</i> _{PCS})
1	4,800	7,500	12,300	48:75	1.27	0.22
2	7,700	10,300	18,100	77:103	1.21	0.45
3	36,500	12,800	49,300	365:128	1.19	0.73

^a–^cCalculated by GPC data. ^bCalculated by ¹H NMR spectrum.

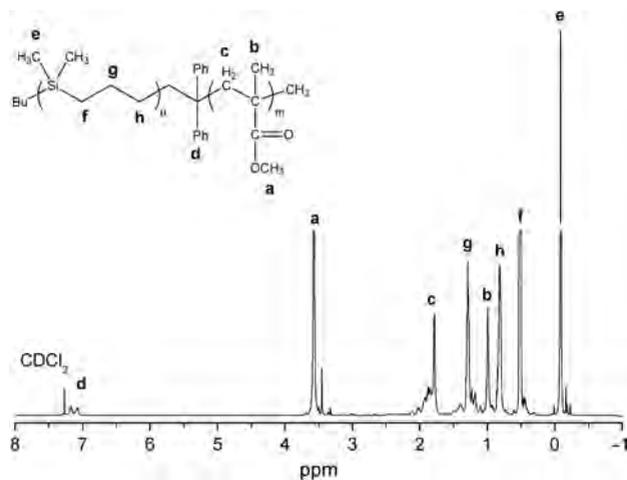


Fig. 1. ^1H NMR spectrum of polycarbosilane-*block*-poly(methyl methacrylate) in CDCl_3 solvent.

corresponding to the initiation end group and each polymer segment. For example, the molecular weight of the block polymer (sample 3: $M_n = 49,300$ g/mol) measured by GPC was in good agreement with the M_n calculated from the initial concentration ratio of *n*-butyl lithium and the sum of the two monomers ($M_n = 48,000$ g/mol). Moreover, the composition (*m:n*) 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 the PCS-*b*-PMMA polymer 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-CH₃, Si-CH₂, and -CH₂ groups, respectively, and are characteristic of the polycarbosilane block. From the poly(methyl methacrylate) block, the signals corresponding to the -OCH₃, -CH₂ and -CH₃ protons were observed at $\delta = 3.65$ ppm, 1.78 ppm, and 0.97 ppm, respectively.

Thermal gravimetric analysis in nitrogen indicated that the block copolymer obtained began to decompose with a small mass loss of 10 wt% at 200 °C, which was attributed to the early stage of thermal curing and decomposition. The second stage of weight loss (~35 wt%) occurred at the narrow temperature range 370 ~ 420 °C and corresponded to the decomposition of the PMMA blocks. From 430 °C to 800 °C, an additional mass loss of 20 wt% was observed, which was presumably due to the cross-linking and decomposition of the inorganic PCS blocks to transform to the ceramics.¹⁹ Finally, a ceramic yield of 22.5 wt% at 1000 °C was obtained as a final SiC ceramic nanostructured product. In comparison, the block copolymer obtained shows a low ceramic yield compared with the previously reported poly(vinyl)silazane-*block*-polystyrene diblock copolymer.¹⁸ The low ceramic yield of the block copolymer due to the absence of crosslinkable groups such as vinyl, silane groups in the backbone of the PCS block. Therefore, a curable and compatible compound with the PCS block can be added to enhance the ceramic yield of

PCS-*b*-PMMA for reliable ceramic application. At 30 wt% vinylcyclohexylsilazane (VSZ) (with respect to the mass of PCS blocks), a well known highly cross-linkable inorganic oligomer, as a SiCN ceramic precursor,^{18,20} was added with no disturbance in the self-assembly behavior. The ceramic yield of PCS-*b*-PMMA was improved from 22.5 to 38.5 wt% because of the cross-linked Si-CH₃, Si-CH₂ groups from the PCS blocks with vinyl and silane groups from VSZ.¹⁹

In order to investigate the self-assembly of the PCS₃₆₅-*b*-PMMA₁₂₈ diblock copolymer ($M_n = 49,300$ g/mol; PDI = 1.19), the polymer dissolved in the toluene solvent was cast onto a Teflon disk and allowed to evaporate slowly under an Ar atmosphere at room temperature. Then the PCS block was cross-linked at 200 °C for 3 h. The organic PMMA block was decomposed by UV irradiation and then rinsing with acetic acid and water. As shown in Figure 2(a), the SA-XRD of the self assembly polymeric film showed a sharp peak at $2\theta = 0.67^\circ$, indicating that a hexagonally packed cylindrical morphology was formed with a *d*-spacing of 12.84 nm and a pore diameter of ~14.8 nm. For the pyrolyzed product at 800 °C (Fig. 2(b)), after completely removing PMMA blocks and transforming the PCS blocks to ceramics, the SA-XRD pattern showed a single diffraction peak at $2\theta = 1.22^\circ$, which corresponds to a *d*-spacing of 5.45 nm. The porosity characteristics of the sample annealed at 800 °C were examined by measuring the N₂ adsorption-desorption isotherm at -196 °C. The Brunauer-Emmert-Teller (BET) analysis of this isotherm confirmed the presence of a highly mesoporous structure with a pore volume close to 0.65 cm³/g, with a high specific surface area of 525 m²/g, and a narrow pore size distribution of 5.8 nm. These results are comparable to the surface area and pore volume of various non-oxide ceramic products.²¹ These results

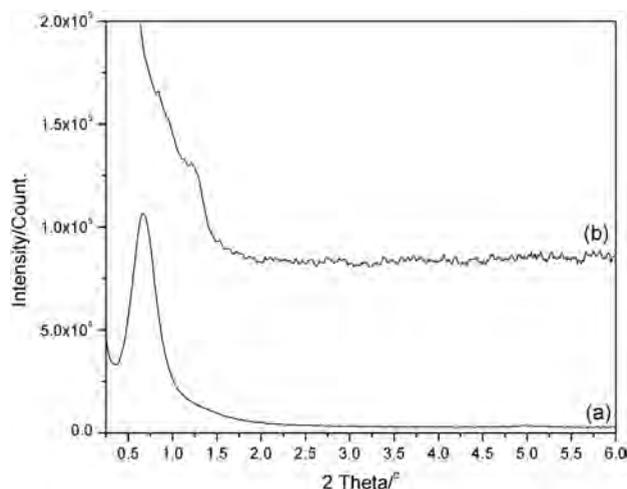


Fig. 2. Small angle X-ray diffraction pattern of self-assembled PCS₃₆₅-*b*-PMMA₁₂₈ diblock copolymer: (a) at room temperature, and (b) after pyrolysis at 800 °C under Ar atmosphere.

clearly show that the PCS-*b*-PMMA diblock copolymer can become a reliable route by enhancing the curing chemistry to prepare versatile mesoporous non-oxide ceramics with a high thermal stability.

In order to fabricate the nanostructured thin film, 0–30 wt% (with respect to the mass of PCS blocks) vinylcyclosilazane (VSZ) was added to a 2 wt% solution of a PCS₃₆₅-*b*-PMMA₁₂₈ diblock copolymer in toluene, stirred for 2 h, and then spin-coated on a neutralized Si wafer. The film thickness was controlled by the control spin-coating speed. The spin coated film was stored at 190 °C for 24 h under a vacuum atmosphere. The morphology of the film was observed by atomic force microscopy (AFM). In the polymer phase, the AFM result indicated that the PMMA cylinders were oriented normal to the surface with

a domain size of 20 nm and a periodicity of 35 nm, as shown in Figure 3(a). When a 30 wt% of VSZ was added, the orientation of the PMMA cylinders was changed to parallel to the substrate as seen in Figure 3(b). The hexagonal packing of the cylinders and the orientation of such samples were also observed by SEM images (Fig. 4). The orientation of cylinders was changed from perpendicular to parallel to substrate which can be assigned to the small change of the film thickness. In addition, the discrepancy between the periodicity of the cylinders in the cast film and that of the spin-coated film can be attributed to the sample preparation. In the case of the cast film, the mobility of the solvent swollen chains was higher, and the block copolymers could readily achieve their equilibrium structure. In the case of the spin-coated film, adhesion to the substrate coupled with rapid solvent evaporation effectively prevented polymer chain mobility. In order to avoid the influence of interfacial interactions on the orientation of the microdomains, the substrate surface was chemically modified as previous reported.² The samples were prepared on silicon wafers with neutral properties. This change had no significant effect on the microphase separation and similar relief structures were found for the films with thicknesses ranging from 30 to 200 nm.

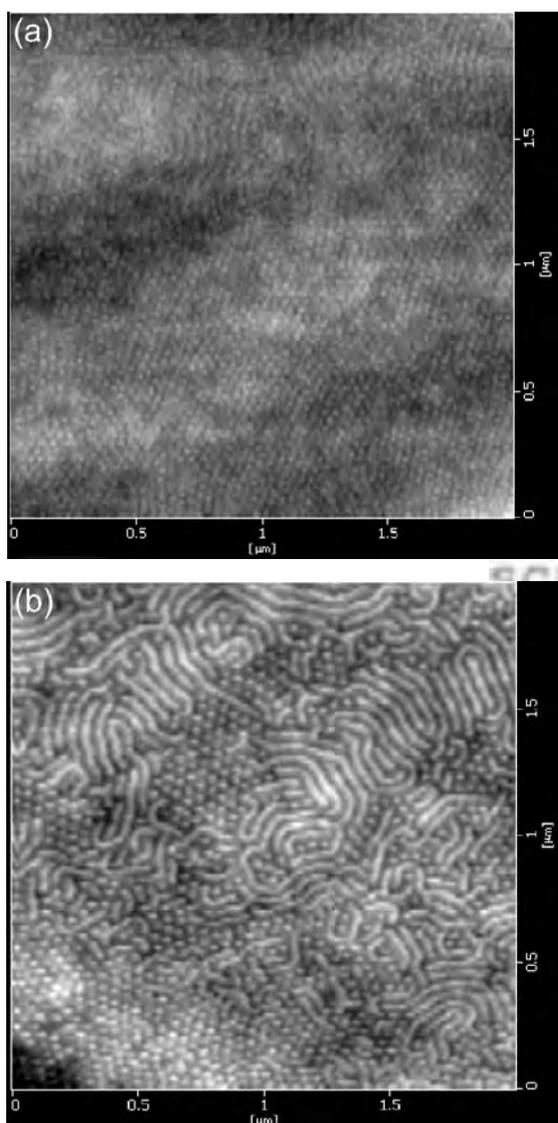


Fig. 3. AFM images of PCS₃₆₅-*b*-PMMA₁₂₈ diblock copolymer thin films containing (a) 0, and 30 wt% VSZ after annealing at 190 °C, 24 h under vacuum atmosphere.

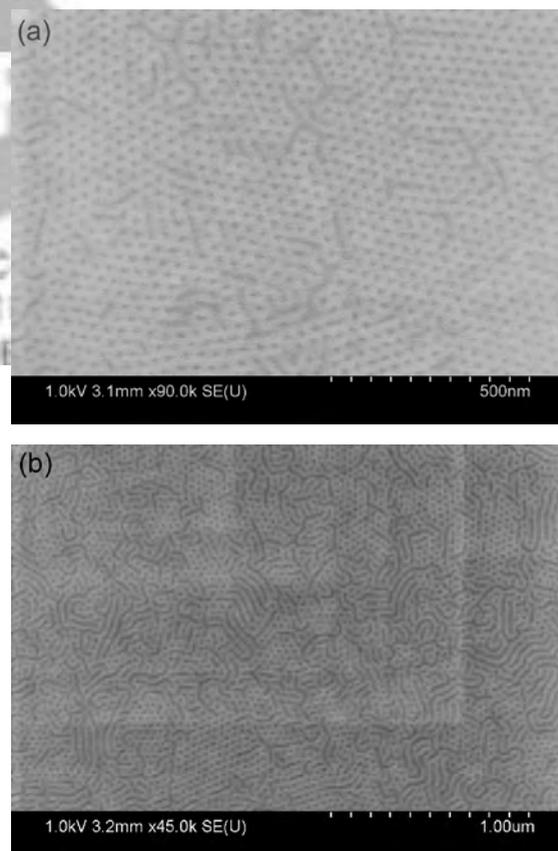


Fig. 4. SEM images of PCS₃₆₅-*b*-PMMA₁₂₈ diblock copolymer thin films containing (a) 0, and 30 wt% VSZ after annealing at 190 °C, 24 h under vacuum atmosphere.

4. CONCLUSIONS

Polycarbosilane-*block*-poly(methyl methacrylate) diblock copolymers were successfully synthesized using ring-opening living anionic polymerization. The resulting polymer was used as a new precursor for a well-ordered mesoporous SiC-based ceramic material through self-assembly. The PCS-*b*-PMMA copolymer was also self-assembled in thin film form and transformed to mesoporous SiC ceramic film by pyrolysis at 800 °C. An important feature of this study is that a mesoporous thin film can be generated very rapidly using simple spin- or dip-coating techniques. These exciting results have great potential in the generation of mesostructured non-oxide ceramics for a broad range of applications.

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