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Synthesis of Ceramic Particles by Micellization, Cross-Linking, and Pyrolysis of Carbosilane Block Copolymers

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Synthesis and pyrolysis of carbosilane block copolymer particles were investigated. Poly(1-(3-butenyl)-1-methyl-silacyclobutane)-*block*-poly(methyl methacrylate) (BMSB$_m$-*b*-MMA$_n$, (m, n) = (81, 99) and (300, 160)) was prepared by living anionic polymerization of BMSB and MMA, where m and n represent average polymerization degrees of BMSB and MMA segments. The block copolymer formed micelles in *N*, *N*-dimethylformamide. The core of the micelle was cross-linked by Pt-catalyzed hydrosilation of butenyl groups with 1,2-bis(dimethylsilyl)ethane. The hydrodynamic diameters of the core-cross-linked micelles evaluated by dynamic light scattering were 56 nm for BMSB$_{81}$-*b*-MMA$_{99}$ and 148 nm for BMSB$_{300}$-*b*-MMA$_{160}$ in tetrahydrofuran. Pyrolysis of the core-cross-linked micelles at 850 °C under nitrogen flow provided spherical ceramic particles, though pyrolysis of non-cross-linked block copolymers gave no ceramics. The particle diameters of the pyrolytic products evaluated by atomic force microscopy were in the range of 30~40 nm for BMSB$_{81}$-*b*-MMA$_{99}$ and 40~60 nm for BMSB$_{300}$-*b*-MMA$_{160}$.

Key words: micelle, cross-linking, nanoparticle, polycarbosilane, pyrolysis, silicon-containing ceramics

1. INTRODUCTION

Polycarbosilanes, which have a backbone consisting of silicon and carbon atoms, are known as silicon-containing ceramics precursors [1]. Pyrolysis of polycarbosilanes under an inert atmosphere gives silicon carbides (SiC), while pyrolysis in the presence of oxygen provides Si-C-O compounds. Many studies have been performed on this subject in the last three decades [2,3], and SiC ceramics fibers are now commercially manufactured. However, synthetic method of nanoparticles by pyrolyzing such polymers remains unknown so far [4].

On the other hand, it is well-known that block copolymers form nano-scale micelles in solvents selective for one of the blocks [5, 6]. The core of the micelle consists of an insoluble block, and the shell consists of both a soluble block and the solvent. By cross-linking the core of the micelle, we can easily obtain core-shell structured nanoparticles. In this study, we considered that by micellization and core-cross-linking of carbosilane block copolymer followed by pyrolysis of the particles, we can synthesize silicon-containing ceramics nanoparticles (SiC, or Si-C-O).

2. EXPERIMENTAL

2.1 Materials

1-(3-Butenyl)-1-methylsilacyclobutane (BMSB) was prepared by treatment of 1-chloro-1-methyl-silacyclobutane with 3-butenylmagnesium bromide in tetrahydrofuran (THF) and purified by distillation under reduced pressure over $LiAlH_4$. Methyl methacrylate (MMA) and 1,1-dipheynylethylene (DPE) were purchased from Wako Pure Chemicals and purified in a standard method. Butyllithium hexane solution (0.8 M) was prepared by dilution of commercially available butyllithium hexane solution (1.6 M) with dry hexane. Lithium chloride was dried at 130 °C (1.0 x 10^2 Pa) for 3 h. 1,2-Bis(dimethylsilyl)ethane (BSiE) was prepared by reduction of 1,2-bis(chlorodimethylsilyl)ethane (purchased from ShinEtsu Chemicals) with $LiAlH_4$ in diethyl ether. $H_2PtCl_6{\bullet}nH_2O$ was purchased from Wako and used as delivered. THF was distilled over sodium benzophenone ketyl under argon before use. *N*, *N*-Dimethylformamide (DMF) was first distilled over CaH_2 and then distilled over activated molecular 4A sieves under reduced pressure.

2.2 Polymerization

Dry lithium chloride (60 mg, 1.4 mmol), THF (14 mL), and BMSB (700 mg, 5.0 mmol) were added to a 100 mL two-necked round-bottomed flask equipped with a three-way stopcock, a rubber balloon, a rubber septum, and a magnetic stirring bar in an argon atmosphere. After the flask was cooled to -55 °C, butyllithium (0.82 mmol/L, hexane solution, 0.37 mL, 0.30 mmol) was added and the mixture was stirred for 1 h. Then DPE (0.07 mL, 0.47 mmol) was added. The color of the solution turned dark red. The mixture was stirred for 30 min, and MMA (1.49 g, 14.9 mmol) was added. The red color of the solution immediately disappeared. The mixture was stirred 1 h, and a mixture of methanol/water (5/1 v/v, 0.5 mL) was added. The mixture was poured into water, and the polymer was extracted with toluene, dried over anhydrous Na_2SO_4, and concentrated to give BMSB$_{81}$-*b*-MMA$_{99}$ (2.19 g) in a quantitative yield. BMSB$_{300}$-*b*-MMA$_{160}$ was also prepared in the same way as described above.

2.3 Core-cross-linking of the block copolymer micelle

To a two-necked 50 mL round-bottomed flask equipped with a three-way stopcock, a rubber balloon, a rubber septum, and a magnetic stirring bar, ca.20 mg of $H_2PtCl_6 \cdot nH_2O$ was added and the flask was filled with argon. A DMF (5 mL) solution of BMSB$_{81}$-*b*-MMA$_{99}$ (70 mg) and BSiE (0.03 mL, 0.16 mmol) were added to the flask, and the mixture was stirred for 24 h. The resulting solution was poured into methanol. The precipitate was filtered out, washed with methanol, and concentrated in vacuo to give core-cross-linked block copolymer micelle (CCL-BMSB$_{81}$-*b*-MMA$_{99}$) (90 mg). Here, "CCL-" is used for an abbreviation of core-cross-linked. CCL-BMSB$_{300}$-*b*-MMA$_{160}$ was also prepared in the same way as described above.

2.4 Pyrolysis of core-cross-linked block copolymer micelles

Pyrolysis of CCL-polyBMSB-*b*-polyMMA was performed by heating the sample on a quartz substrate at 5 °C/min to 850 °C and held at 850 °C for 30 min in Motoyama MS-1213 electric furnace under N_2 flow of 1.0 L/min to give pyrolyzed core-cross-linked micelles (PyCCL-BMSB$_{81}$-*b*-MMA$_{99}$). The pyrolyzed product of the core-cross-linked micelle will be referred to as "PyCCL-" hereafter. For sample preparation, dilute THF solutions (ca. 1.0 x 10^{-5} wt%) of the CCL-polyBMSB-*b*-polyMMA were spread on a quartz substrate and air-dried.

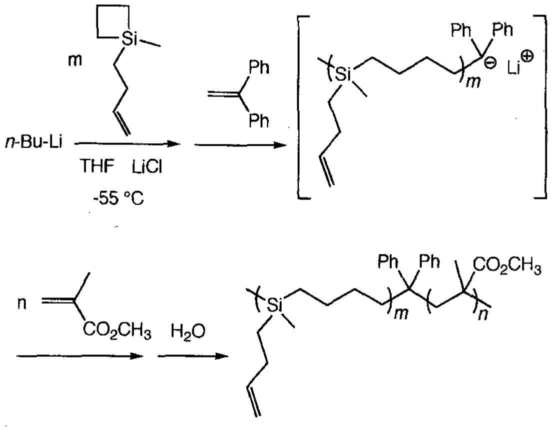
2.5 Measurements

Proton NMR spectra were recorded on a JEOL GSX-270 spectrometer. The average polymerization degrees *m* and *n* were determined by ^{1}H NMR measurement. Gel permeation chromatography was carried out in chloroform on a JASCO GPC-900 system equipped with four polystyrene gel columns (Shodex K802, K-803, K-804, and K-805). Molecular weight distributions were determined relative to polystyrene standards. DLS experiments were carried out on Otsuka Photal SLS-6000HL equipped with a correlator (Photal GC-1000) and He-Ne laser. The decay rate was evaluated by cummulant or double-exponential fitting. After the translational nature of the decay was confirmed by angler dependence, the translational diffusion coefficient was converted to the hydrodynamic diameter by using the Stokes-Einstein equation. Thermal gravimetric analysis (TGA) was performed on Mac Science TG-DTA 2000S using alumina pan under an N_2 flow of 50 mL/min at heating rate of 5 °C/min. AFM was performed on SPI3800 probe station and SPA300 unit system (Seiko Instruments) in Dynamic Force Mode (non-contact mode). The cantilever was made of silicon (Olympus, Tokyo, Japan) and its spring constant was 2 N/m.

3. RESULTS AND DISCUSSIONS

3.1 Block copolymer synthesis

To construct a polycarbosilane block copolymer, we chose BMSB as a silicon-containing monomer and MMA as a non-silicon-containing monomer, because both silacyclobutanes and MMA can be anionically polymerized in a living manner, and the 3-butenyl groups on the silicon atom can later be used for cross-linking. In addition, it seemed easy to form micelles by using this block copolymer because polyBMSB is a non-polar segment while polyMMA is a polar segment. We have already reported a practical method to prepare a block copolymer of 1,1-diethylsilacyclobutane and methacrylate esters using butyllithium as an initiator and DPE as a mediator for the methacrylate polymerization [7]. The same methodology was applied to the synthesis of the block copolymer here as shown in Scheme 1. Two block copolymer samples were prepared in this study. The molecular characteristics are listed in Table I.



Scheme 1. Synthesis of polyBMSB-*b*-polyMMA

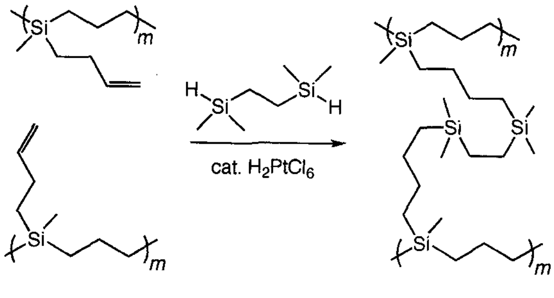
Table I. Molecular characteristics of BMSB$_m$-*b*-MMA$_n$

m^a	n^a	M_n^a	M_w/M_n^b
81	99	21300	1.13
300	160	57900	1.42

^{a}estimated by ^{1}H NMR, ^{b}determined by polystyrene-calibrated GPC

3.2 Micelle formation and core-cross-linking

The polyBMSB-*b*-polyMMA samples were dissolved in DMF, and dynamic light scattering measurement was taken for the 1wt% solutions. In both cases, slow scattering decay was observed, which indicated the existence of multi-molecular micelles. Table II summarizes the hydrodynamic diameters of the block copolymer micelles evaluated by DLS analysis. The core of the micelle consists of polyBMSB, which is insoluble in DMF, and the shell consists of swollen polyMMA, which is soluble in DMF.



Scheme 2. Hydrosilation of polyBMSB with BSiE

The core-cross-linking of the micelle was carried out by treatment of the block copolymer micelle with disilyl compound, BSiE, in the presence of platinum catalyst (Scheme 2). Figure 1 shows ^{1}H NMR spectra of the block copolymer before and after the reaction. The NMR signals became very broad and the intensity of the vinyl proton signals significantly decreased after the treatment with BSiE, indicating the occurrence of hydrosilation. The efficiency of the hydrosilation was considered to be about 80%, which was estimated from NMR signal intensity of the vinyl protons.

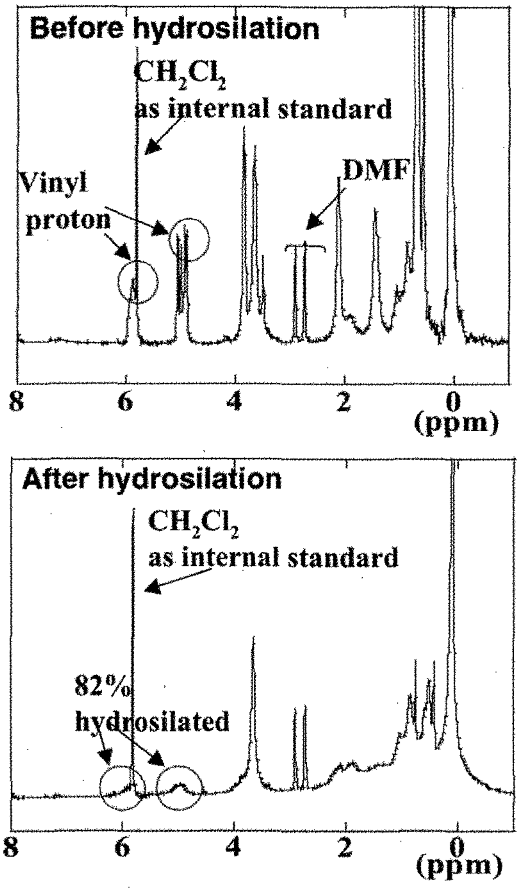


Figure 1. ^{1}H NMR spectra of BMSB$_{81}$-*b*-MMA$_{99}$ and BSiE in DMF-d$_7$ before and after hydrosilation

Table II. Particle sizes of polyBMSB-*b*-polyMMA evaluated by DLS

polymer	D_{micelle} in DMF (nm)	$D_{\text{CCL-micelle}}$ in DMF (nm)	$D_{\text{CCL-micelle}}$ in THF (nm)
BMSB$_{81}$-*b*-MMA$_{99}$	40	54	56
BMSB$_{300}$-*b*-MMA$_{160}$	142	144	148

D_{micelle}: hydrodynamic diameter of micelle
$D_{\text{CCL-micelle}}$: hydrodynamic diameter of core-cross-linked micelle

DLS analysis of the reaction mixture (in DMF) confirmed the existence of particles with almost the same sizes as those of the micelles before the hydrosilation. The hydrodynamic diameters were estimated at 54 nm for BMSB$_{81}$-*b*-MMA$_{99}$ (the increase of the diameter might be due to a little contribution of micelle-micelle cross-linking) and 144 nm for BMSB$_{300}$-*b*-MMA$_{160}$ (Table II). Additionally, DLS analysis of the hydrosilated micelles in THF, which is a good solvent for both polyBMSB and polyMMA, also gave almost the same particle sizes (Table II). These results indicated that the core cross-linking of the block copolymer micelles was effectively achieved.

3.3 Pyrolysis of core-cross-linked micelles

Figure 2 shows the TGA results of the core-cross-linked (CCL) micelle, non-cross-linked block copolymer, BMSB homopolymer, and MMA homopolymer under nitrogen. Pyrolysis of the CCL-micelle occurred in a two-step procedure. The first step began at 300 °C and was almost completed at 400 °C, and the second step began at 400 °C and ended at 500 °C. This is due to the large difference in the decomposition temperatures of polyBMSB and polyMMA. Decomposition of polyMMA occurred from 300 °C to 400 °C, while decomposition of polyBMSB occurred from 400 °C to 500 °C. This means that the shell of the CCL-micelle first decomposed, and then the core decomposed. A more interesting observation here is that pyrolysis of the core-cross-linked micelle gave a good amount of ceramics (24.4wt%), while pyrolysis of the non-cross-linked block copolymer afforded almost no ceramics (3.6wt%). This implies that cross-linking plays an important role in this synthetic process.

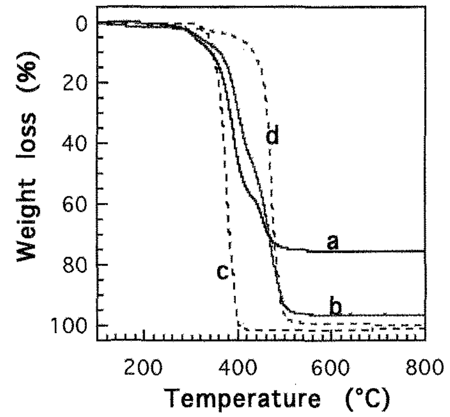


Figure 2. TGA results under N$_2$ flow. **a**: CCL-BMSB$_{81}$-*b*-MMA$_{99}$, **b**: BMSB$_{81}$-*b*-MMA$_{99}$, **c**: polyMMA, **d**: polyBMSB, Heating rate: 5 °C/min

3.4 Nanostructures of the particles

To examine the nanostructures of the CCL-micelles and their pyrolyzed products, we dried a dilute micelle solution on a quartz substrate and directly pyrolyzed it in an electric furnace. The particle on the substrate was observed by AFM before and after the pyrolysis. Figures 3 and 4 shows typical AFM images. In figure 3(a), spherical particles were observed for CCL-BMSB$_{81}$-*b*-MMA$_{99}$, whose diameters were in the range of 40~50 nm. In figure 3(b), particles with diameters in the range of 30~40 nm were observed for PyCCL-BMSB$_{81}$-*b*-MMA$_{99}$. The particles shrunk to some extent by pyrolysis, probably because the decomposition of the shell and the organic component of the core occurred. In figures 4(a) and (b), this trend is observed more clearly. The diameters of CCL-BMSB$_{300}$-*b*-MMA$_{160}$ were in the range of 100~150 nm, while those of PyCCL-$BMSB_{300}$-*b*-MMA_{160} were in the range of 40~ 60 nm.

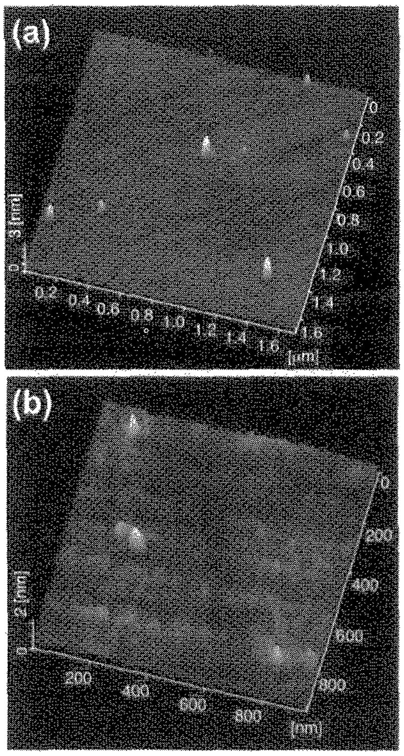


Figure 3. AFM image of (a) CCL-$BMSB_{81}$-*b*-MMA_{99} and (b) PyCCL-$BMSB_{81}$-*b*-MMA_{99} on a quartz substrate.

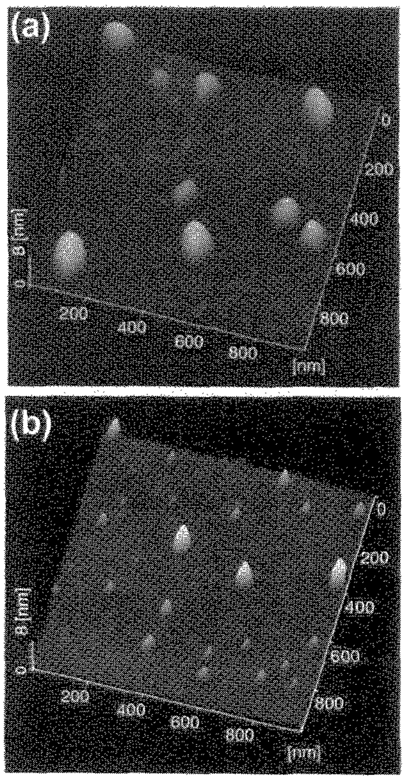


Figure 4. AFM image of (a) CCL-$BMSB_{300}$-*b*-MMA_{160} and (b) PyCCL-$BMSB_{300}$-*b*-MMA_{160} on a quartz substrate.

Although rather broad size distributions were observed in all cases, the particles of PyCCL-$BMSB_{300}$-*b*-MMA_{160} were apparently larger than those of PyCCL-$BMSB_{81}$-*b*-MMA_{99}. These results clearly indicate the nanostructures of the ceramic particles derived from the structures of the precursor micelles and the particle sizes can be controlled by the sizes of the precursor micelles.

4. CONCLUSIONS

Polycarbosilane fine particles having a polyMMA shell were synthesized by micellization of polysilacyclobutane-*b*-polyMMA in DMF and core-cross-linking by hydrosilation with disilyl cross-linking reagent. The particles could be transformed into spherical silicon-containing nanoparticles by pyrolysis in a nitrogen atmosphere. These results indicated that utilization of block copolymer self-assembly is a powerful tool for preparation of nanomaterials. Although polycarbosilanes can give SiC if pyrolyzed under a strictly inert atmosphere, the pyrolyzed product in this study may have a Si-O structure because of the oxidation with a trace amount of contaminated oxygen in the pyrolysis system. X-ray fluorescence (XRF) analysis is now in progress to confirm the chemical structure of the products. Additionally, application of this new compound to functional electronic materials is currently under investigation.

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