Supporting Information to

Magnetoceramic Nanocrystals from a Bulk Pyrolysis of Novel Hyperbranched Polyferrocenyl(boro)carbosilanes

by Jie Kong, Thomas Schmalz, Günter Motz, and Axel H. E. Müller**

Experimental Section

Materials: Hexachloro-1,3-butadiene (97%), dichlorodimethylsilane (98%), dichloromethylvinylsilane (97%), *n*-butyllithium in hexane solution (1.6M) , anhydrous diethyl ether and methanol were purchased from Sigma-Aldrich Co. All the reagents were used as received without further treatment. Anhydrous tetrahydrofuran (THF) was freshly distilled for use under reflux using sodium/benzophenone.

Synthesis of polydiacetylene(dimethyl)silanes: The linear polydiacetylene(dimethyl)silanes (PDDMS) was prepared as the following process. Under an insert argon atmosphere, a 100 mL flame-dried flask equipped with a Teflon stir bar, septum, and high-vacuum stopcock was charged with tetrahydrofuran dried at reflux over sodium/benzophenone (30 mL) and *n*-butyllithium in hexane solution (45 mL, 72 mmol). In a dry ice/acetone bath (-78^{o}C), the hexachloro-1,3-butadiene (4.82g, 18 mmol) was added through an argon-purged syringe. The mixture was allowed to room temperature and stirred for 6 h. Then dichlorodimethylsilane (2.36g, 18 mmol) was charged through an argon-purged syringe and the mixture was stirred overnight. Upon completion of the reaction, the excess reagents and solvent were removed under vacuum line. After rotary evaporation (20 mbar, 50 ^{o}C), the mixture was soluble into ethyl ether (100 mL) and filtered. After rotary evaporation (20 mbar, 25 ^{o}C), the crude product was soluble in 5 mL of diethyl ether and precipitated into 50 mL of methanol for three times. Then the product of PDDMS was obtained as brown solid (1.22 g, 64% yield). ^{1}H NMR (*1*, $CDCl_3$, ppm): 0.37-0.42 (6H, -Si(CH_3)$_2$-). ^{13}C NMR (*1*, $CDCl_3$, ppm): -2.86 (2C, -Si(CH_3)$_2$-), 82.30 (1C, -(CH_3)$_2$Si*C*≡C), 89.21 (1C, (CH_3)$_2$SiC≡*C*). ^{29}Si NMR (*1*, $CDCl_3$, ppm): -36.94 (1Si, -(CH_3)$_2$*Si*-). FT-IR (*1*, KBr, cm^{-1}): 2060 (ν -C≡C-), 1247 (ν Si-CH_3). Representative molecular weight: M_w=4,270, M_w/M_n=1.38.

Synthesis of polydiacetylene(methylvinyl)silanes (PDMVS): The synthesis procedure of linear polydiacetylene(methylvinyl)silanes (PDMVS) was similar to PDDMS, but with dichloromethylvinylsilane (2.62 g, 18 mmol) instead of dichlorodimethylsilane. The PDMVS was obtained as brown solid (1.62 g, 75% yield). ^{1}H NMR (*1*, $CDCl_3$, ppm): 0.41-0.44 (3H, -Si(CH_3)-), 6.21, 6.02 (Si-CH=CH_2), 6.06 (Si-C*H*=CH_2). ^{13}C NMR (*1*, $CDCl_3$, ppm): -2.86 (2C, -Si(CH_3)$_2$-), 82.10 (1C, -(CH_3)ViSi*C* ≡ C), 91.22 (1C, (CH_3)ViSiC ≡ *C*), 132.1 (Si-*C*H=CH_2), 137.8 (Si-CH=*C*H_2). ^{29}Si NMR (*1*, $CDCl_3$, ppm): -44.71 (1Si, -(CH_3)Vi*Si*-). FT-IR (*1*, KBr, cm^{-1}): 2060 (ν -C≡C-), 1450, 1605 (-*C*H=CH_2), 1247 (ν Si-CH_3). Representative molecular weight: M_w=1,260, M_w/M_n=1.78.

Characterization

Nuclear Magnetic Resonance (NMR) measurements were carried out on a Bruker AC–250 spectrometer (Bruker BioSpin, Switzerland) to collect the ^{1}H and ^{13}C spectra. Chemical shifts are referenced to tetramethylsilane (TMS).

Size Exclusion Chromatography (SEC) measurements were performed at room temperature on an apparatus equipped with four PSS–SDV gel columns (5 μm) with a porosity range from 10^2 to 10^5 Å (PSS, Mainz, Germany) and together with a differential refractometer and an ultraviolet detector at 254 nm. THF (1% toluene as an internal standard) was used as an eluent with a flow rate of 1.0 mL/min. Polystyrene (PS) standards with narrow molecular weight distribution (PSS, Mainz) were used for the calibration.

Fourier-transform infrared spectroscopy (FT-IR) was carried out on a Spectrum 100 FT-IR spectrometer from Perkin Elmer. For measurements, the U-ATR unit was used. The dried samples were directly placed on top of the U-ATR unit for measurements.

Results:

The synthesis route of linear silicon-diacetylene copolymers, i.e. polydiacetylene(dimethyl)silanes (PDDMS) and polydiacetylene(methylvinyl)silanes (PDMVS) is summarized in Figure 1b. The mole ratio of silane (dichlorodimethylsilane or dichloromethylvinylsilane) to hexachloro-1,3-butadiene is 1:1. The isolated copolymers are brown solids at room temperature with the M_w of 1,260-4,270 g/mol using polystyrene as standard, which were completely dissolvable in aliphatic and aromatic hydrocarbons such as tetrahydrofuran, 1,4-dioxane and toluene. Their molecular structures were confirmed by ^{13}C NMR and FTIR analyses (Figure 2). The acetylenic carbons were identified by peak resonances in 89-82 ppm region for PDDMS and in 91-81 ppm region for PDMVS, respectively. At the same time, the silylmethyl carbons and vinyl carbons were observed at -1.0 ppm, 138 ppm and 131 ppm. ^{29}Si NMR with a single peak at -37.0 ppm and -44.7 ppm confirm its silyl unit in PDDMS and PDMVS, respectively. The structures of copolymers were also identified by FTIR spectroscopy (Figure 2c), which showed strong acetylenic stretching (2070 cm^{-1}) and strong Si-CH$_3$ deformation (1270 cm^{-1}) absorptions. Compared with the splitting of the peaks in the acetylenic region of boron-silicon-diacetylene copolymers,[1, 2] the single peak for almost all the carbons in ^{13}C NMR spectra indicates the regular microstructure and low end group effects of copolymers obtained.

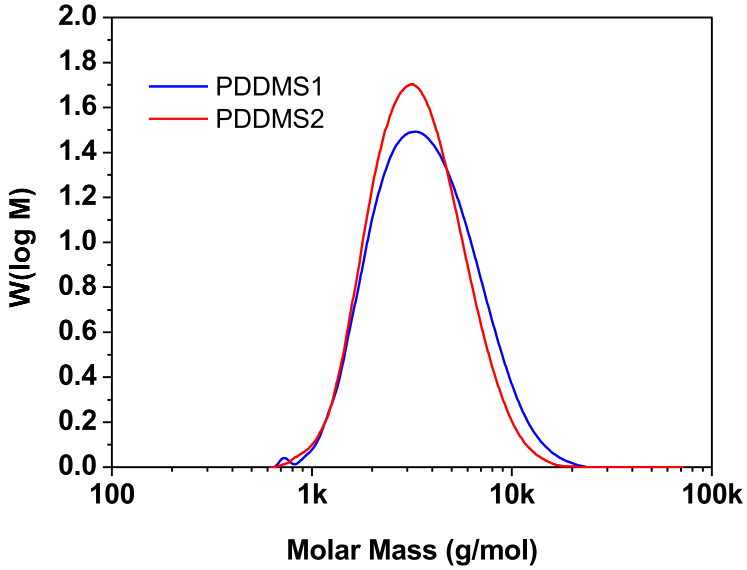

Figure S1. Molecular weight curves of PDDMS

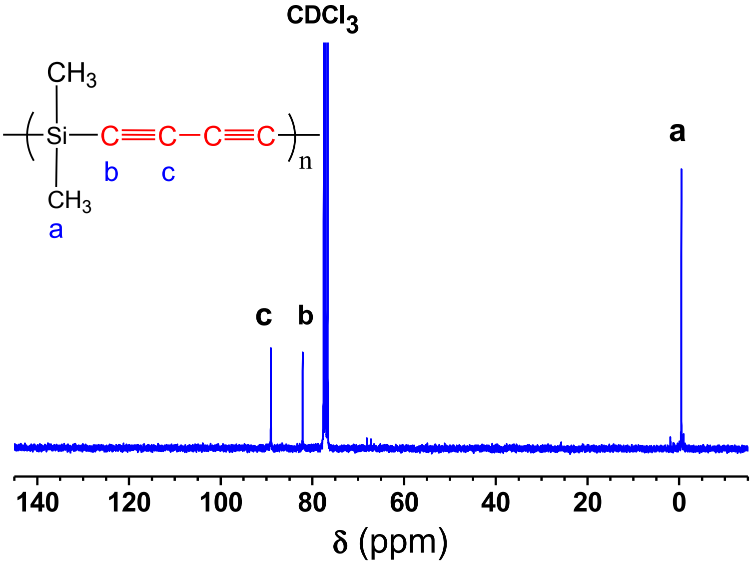

Figure S2. ^{13}C NMR spectrum of PDDMS in $CDCl_3$

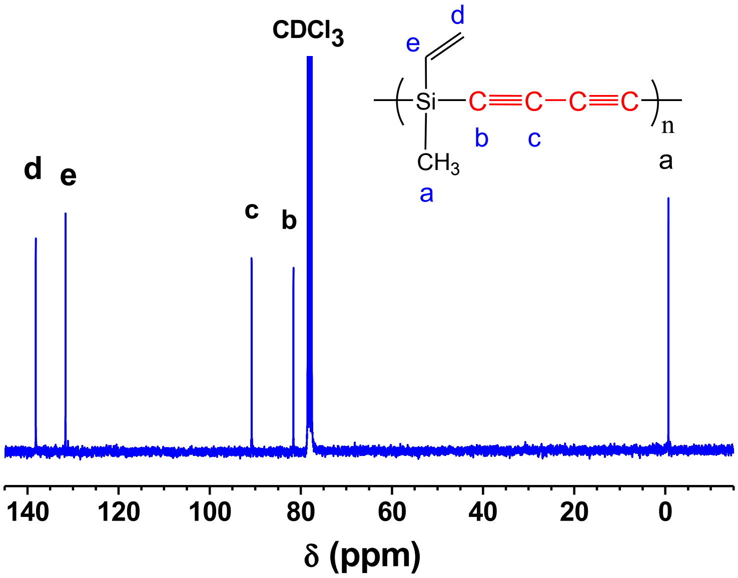

Figure S3. ^{13}C NMR spectrum of PDMVS in $CDCl_3$

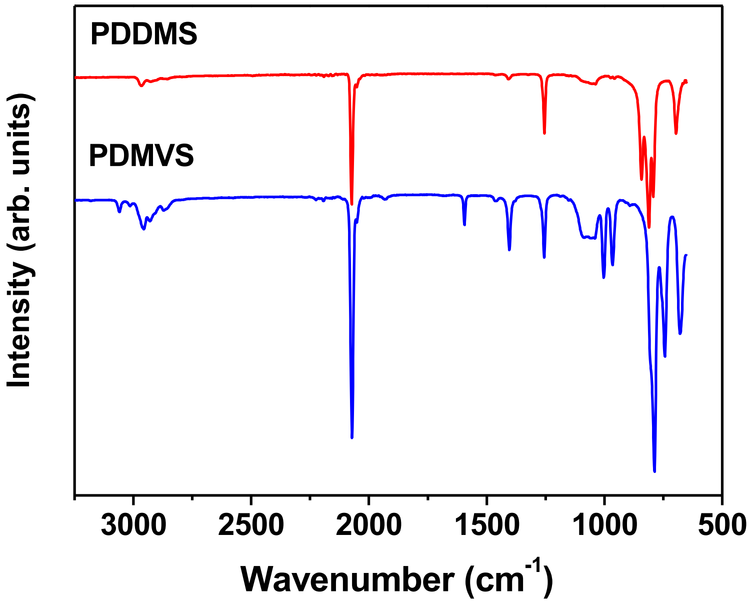

Figure S4. FT-IR spectra of silicon-diacetylene copolymers

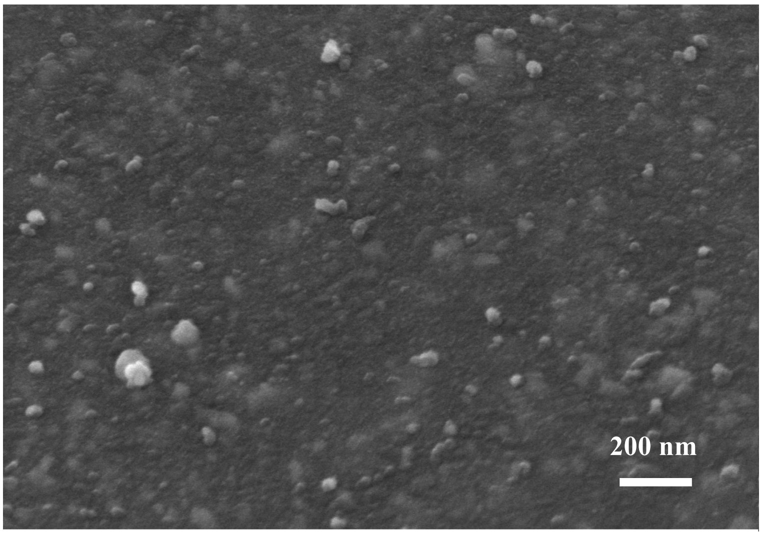

Figure S5. SEM images of C3 from pyrolysis of hyperbranched polyborocarbosilane of hb-PBCS-Vi.

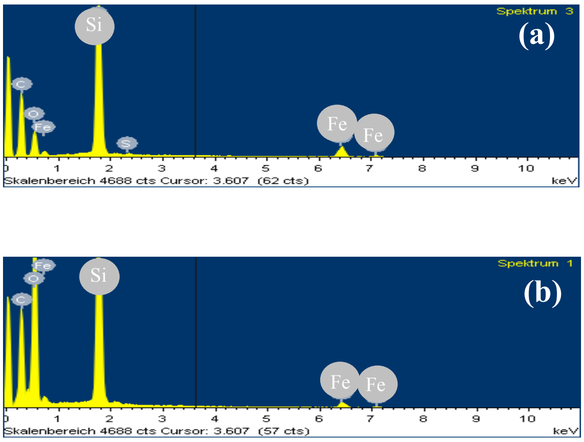

Figure S6. EDX spectrum of ceramics (C7) from pyrolysis of the mixture of hb-PCS-SiH and PDMVS with a weight ratio of 2:1 at 1100 °C in an atmosphere of nitrogen, (a) Plateau region, (b) Microsphere region.

References:

(1) Bréfort, J.L. ; Corriu, R.J.P. ; Gerbier, Ph.; Guérin, C.; Henner, B.J.L.; Jean, A.; Kuhlmann, Th.; Garnier F. ; Yassar, A. *Organometallics*, **1992**, 11, 2500.

(2) Sundar R.A.; Keller, T.M. *Macromolecules*, **1996**, 29, 3647.