Supporting Information

Hydrosilylation-Derived Silicon-Containing Hydrocarbon-Based Polymers Exhibiting Ultralow Dielectric Losses and High Thermal Stabilities

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Materials

Toluene, tetrahydrofuran, acetone, methanol, ethanol and ethyl acetate were purchased from GODO Co.,Ltd. (Japan). Dimethyl sulfoxide, *n*-hexane, *N,N*-dimethylformamide and chloroform were purchased from FUJIFILM Wako Pure Chemical Corporation (Japan). Dichloromethane was purchased from AGC Inc. (Japan).

Synthesis of the silicon-containing hydrocarbon-based polymers

Synthesis of HMTS-BPEB

HMTS (0.234 g, 1.1 mmol) and BPEB (0.284 g, 1.0 mmol) were placed in a test tube and purged with argon gas to create an inert atmosphere. Toluene (2 mL) was then added, and the mixture was stirred at 100 °C until completely dissolved. Subsequently, a catalytic amount of Karstedt's catalyst (5 drops) was added, and the mixture was stirred for 24 hours. After polymerization, the reaction mixture was precipitated into a large excess of methanol. The resulting precipitate was collected by vacuum filtration and dried under reduced pressure at 40 °C. The resulting compound was dissolved in acetone and subsequently recovered by evaporation. The yield was 0.513 g (99%).

Synthesis of DDSQ-BPEB

DDSQ (1.15 g, 1.0 mmol) and BPEB (0.279 g, 1.0 mmol) were placed in a test tube and purged with argon gas to create an inert atmosphere. Toluene (2 mL) was then added, and the mixture was stirred at 60 °C. Subsequently, a catalytic amount of Karstedt's catalyst (5 drops) was added, and the mixture

was stirred for 24 hours. After polymerization, the reaction mixture was precipitated into a large excess of methanol. The resulting precipitate was collected by vacuum filtration and dried under reduced pressure at 40 °C to afford the desired polymer. The yield was 1.35 g (94%).

Synthesis of TMDP/DDSQ-BPEB

TMDP (0.276 g, 0.8 mmol) and DDSQ (0.240 g, 0.2 mmol), BPEB (0.289 g, 1.0 mmol) were placed in a test tube and purged with argon gas to create an inert atmosphere. Toluene (2 mL) was then added, and the mixture was stirred at 60 °C. Subsequently, a catalytic amount of Karstedt's catalyst (5 drops) was added, and the mixture was stirred for 24 hours. After polymerization, the reaction mixture was precipitated into a large excess of methanol. The resulting precipitate was collected by vacuum filtration and dried under reduced pressure at 40 °C to afford the desired polymer. The yield was 0.744 g (92%).

Synthesis of 1,2-DMSB-BPEB

1,2-DMSB (0.205 g, 1.1 mmol) and BPEB (0.294 g, 1.1 mmol) were placed in a test tube and purged with argon gas to create an inert atmosphere. Toluene (2 mL) was then added, and the mixture was stirred at 100°C until completely dissolved. Subsequently, a catalytic amount of Karstedt's catalyst (5 drops) was added, and the mixture was stirred for 24 hours. After polymerization, the reaction mixture was precipitated into a large excess of methanol. The resulting precipitate was collected by vacuum filtration and dried under reduced pressure at 40 °C to afford the desired polymer. The yield was 0.188 g (38%).

Synthesis of 1,4-DMSB-BPEB

1,4-DMSB (0.209 g, 1.1 mmol) and BPEB (0.299 g, 1.1 mmol) were placed in a test tube and purged with argon gas to create an inert atmosphere. Toluene (2 mL) was then added, and the mixture was stirred at 100°C until completely dissolved. Subsequently, a catalytic amount of Karstedt's catalyst (5 drops) was added, and the mixture was stirred for 24 hours. After polymerization, the reaction mixture was precipitated into a large excess of methanol. The resulting precipitate was collected by vacuum filtration and dried under reduced pressure at 40 °C to afford the desired polymer. The yield was 0.462 g (91%).

Synthesis of DDSQ-MVSB

DDSQ (2.44 g, 2.1 mmol) and MVSB (0.520 g, 2.1 mmol) were placed in a test tube and purged with argon gas to create an inert atmosphere. Toluene (6 mL) was then added, and the mixture was stirred at 60 °C. Subsequently, a catalytic amount of Karstedt's catalyst (10 drops) was added, and the mixture was stirred for 24 hours. After polymerization, the reaction mixture was precipitated into a large excess

of methanol. The resulting precipitate was collected by vacuum filtration and dried under reduced pressure at 40 °C to afford the desired polymer. The yield was 2.846 g (96%).

Synthesis of 1,4-DMSB-MVSB

1,4-DMSB (0.814 g, 4.2 mmol) and MVSB (1.04 g, 4.2 mmol) were placed in a test tube and purged with argon gas to create an inert atmosphere. Toluene (6 mL) was then added, and the mixture was stirred at 60 °C until completely dissolved. Subsequently, a catalytic amount of Karstedt's catalyst (10 drops) was added, and the mixture was stirred for 24 hours. After polymerization, the reaction mixture was precipitated into a large excess of methanol. The resulting precipitate was collected by vacuum filtration and dried under reduced pressure at 40 °C to afford the desired polymer. The yield was 1.728g (93%).

Synthesis and characterization of the silicon-containing hydrocarbon-based polymers

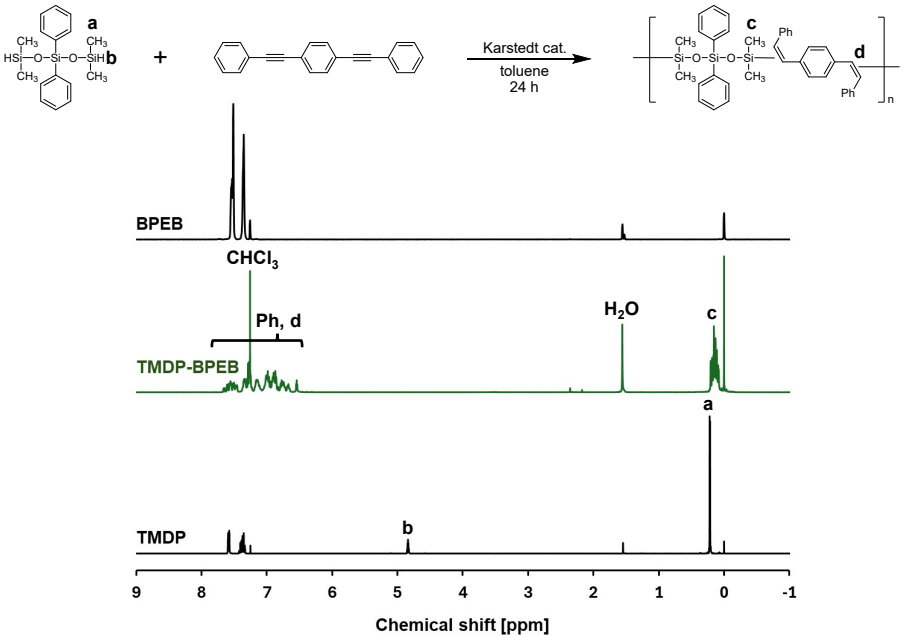

Figure. S1. ^{1}H NMR spectra of TMDP-BPEB.

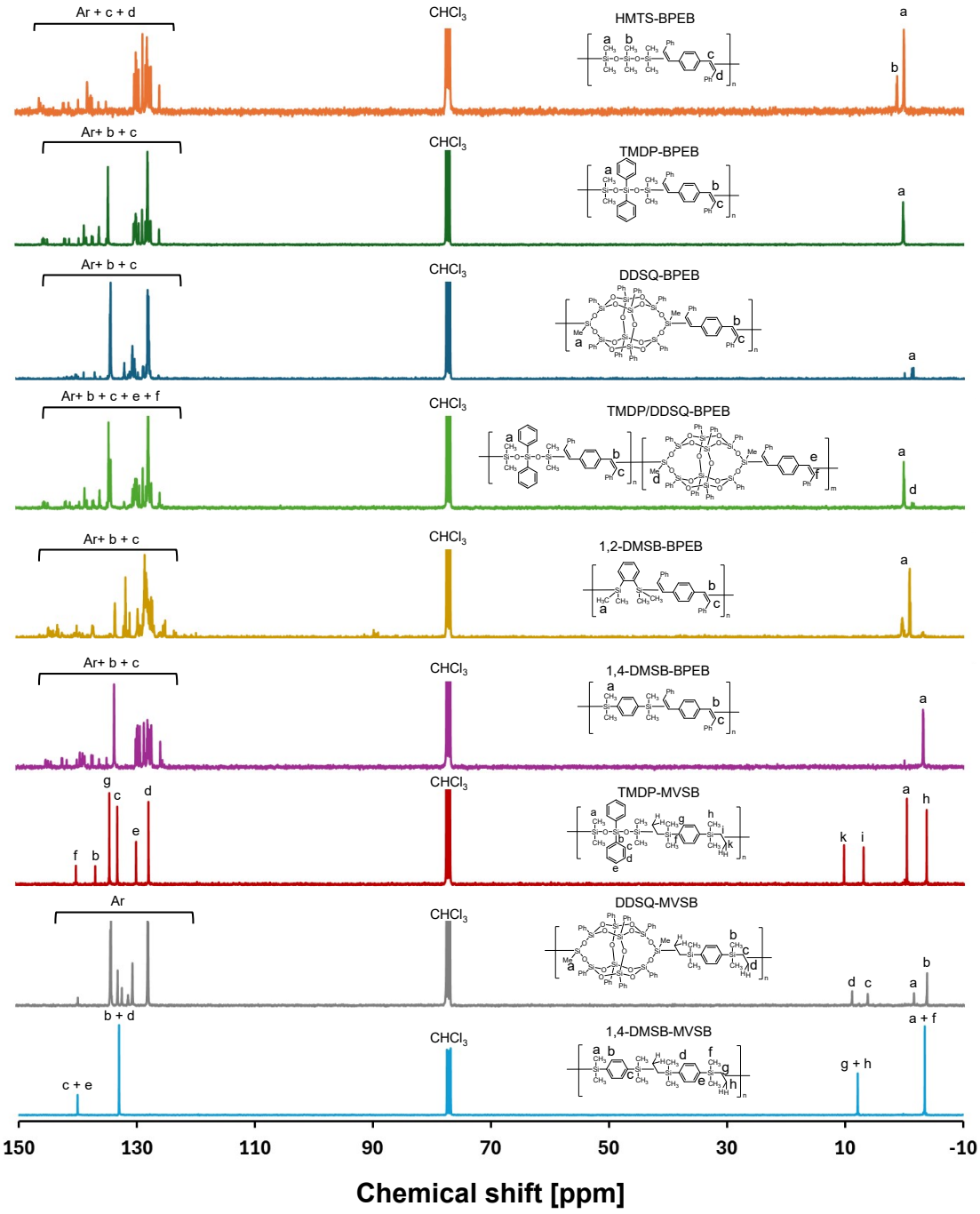

Figure. S2. ^{13}C NMR spectra of the silicon-containing hydrocarbon-based polymers.

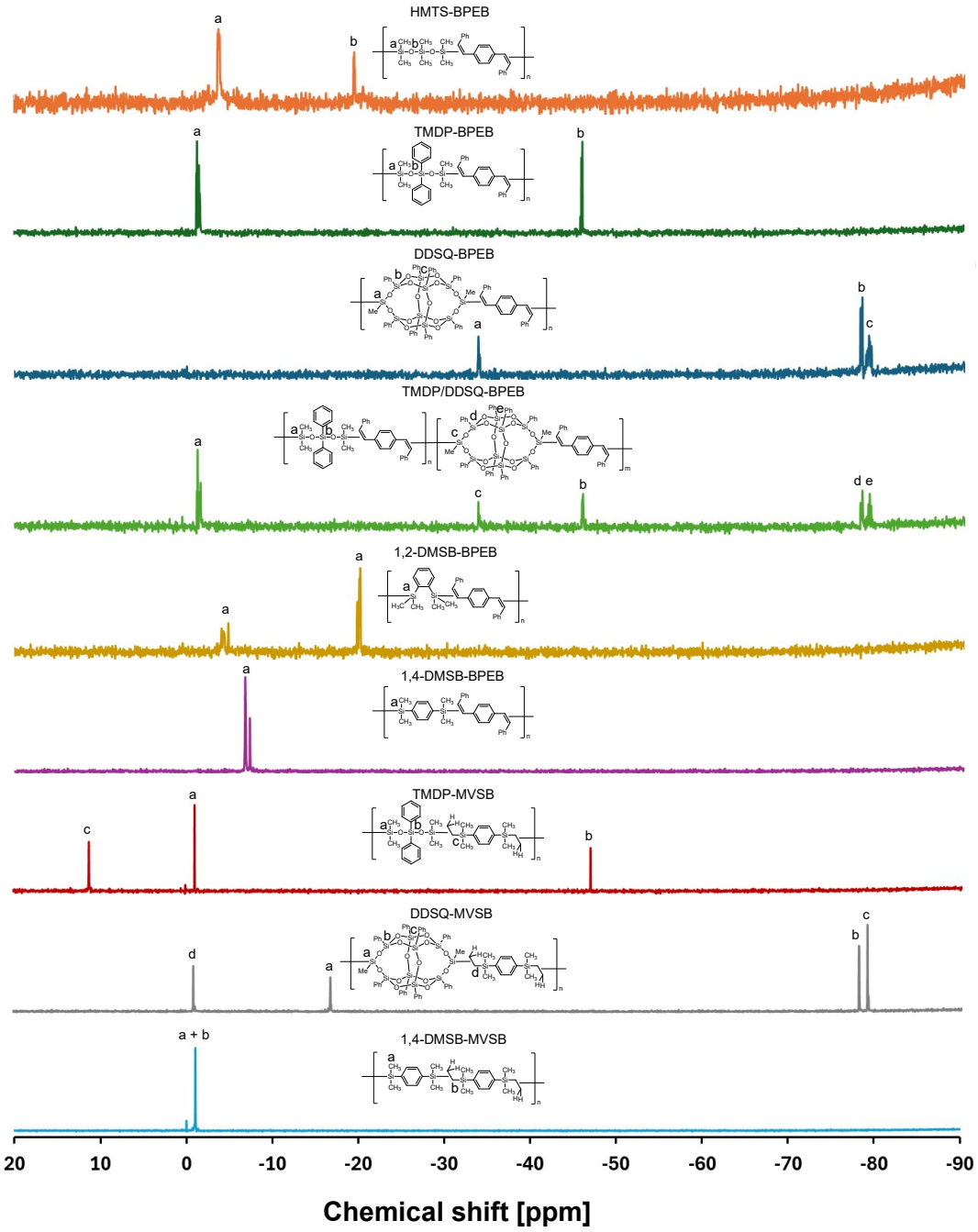

Figure. S3. ^{29}Si NMR spectra of the silicon-containing hydrocarbon-based polymers.

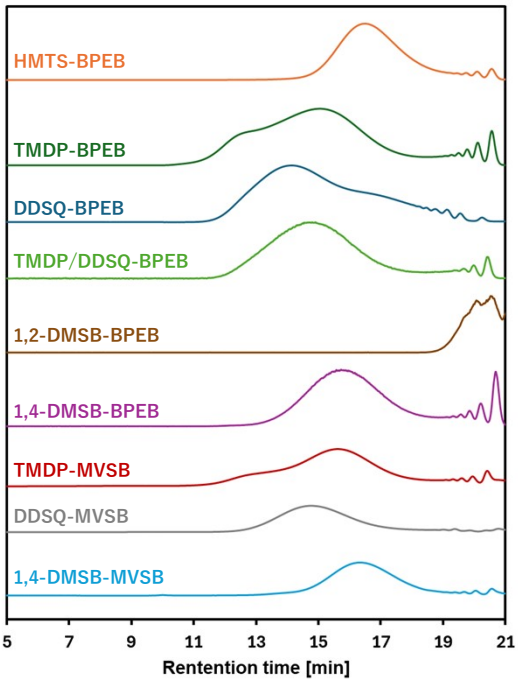

Figure. S4. SEC curves of the silicon-containing hydrocarbon-based polymers.

Thermal properties of the silicon-containing hydrocarbon-based polymers

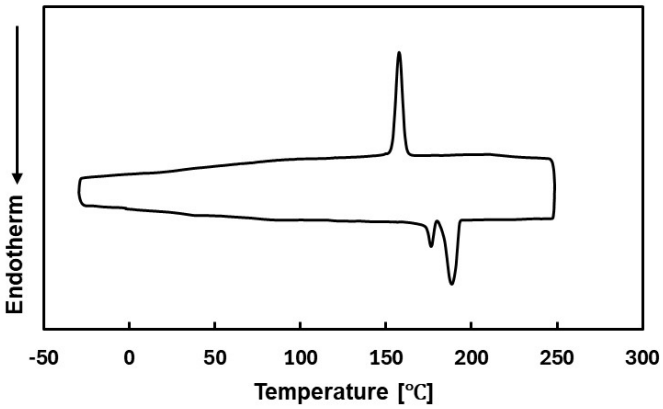

Figure. S5. DSC curve of 1,4-DMSB-MVSB.

WAXD analysis of the silicon-containing hydrocarbon-based polymers

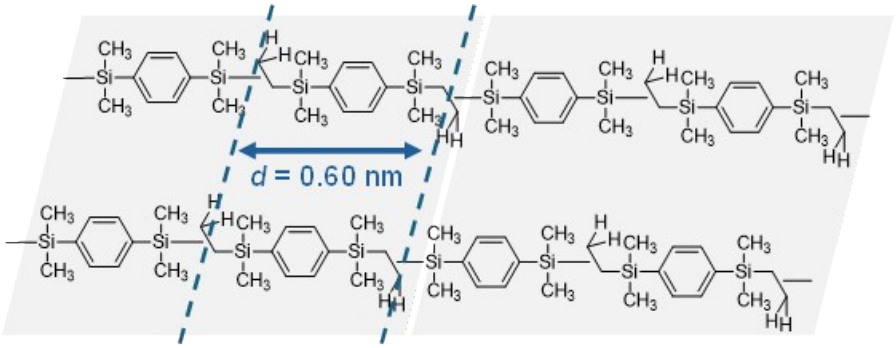

Figure.S6. Schematic image of 1,4-DMSB-MVSB estimated from WAXD analysis.