Supporting Information for

A Novel One-pot Synthesized Organosiloxane: Synthesis and Conversion to Directly Thermocrosslinked Polysiloxanes with Low Dielectric Constant and Excellent Thermostability

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Experimental Section

Materials. All starting materials were obtained from Aldrich and used as received unless other illustration. 4-Bromobenzocyclobutene was purchased from Chemtarget Technologies Co., Ltd. and used without further purification. Triethoxyvinylsilane and diethoxydimethylsilane were purified by distillation before use. Tetrahydrofuran (THF) and acetic acid were dehydrated and distilled under inert atmosphere before use.

Measurement. ¹H NMR and ¹³C NMR spectra were obtained on Bruker AV400 and Bruker AV300 instruments. Molecular weights were measured at room temperature by gel-permeation chromatography (GPC) with a Waters Breeze2a 200 GPC system, equipped with a UV detector using tetrahydrofuran (THF) as the eluent. Fouriertransform infrared (FT-IR) spectra were recorded on a Nicolet spectrometer with KBr pellets. Differential scanning calorimetric (DSC) analysis was determined with a TA Instrument DSC Q200 at a heating rate of 10 °C min⁻¹ under nitrogen. Thermogravimetric analysis (TGA) was measured on a Netzsch TG 209F1 apparatus with a heating rate of 10 °C min⁻¹ under nitrogen atmosphere. The dielectric constants of the cured samples were investigated at room temperature on a 4294A Precision Impedance Analyzer (Agilent) in a range of frequencies from 40 Hz to 30 MHz. A TI 950 TriboIndenter (Hysitron) was used to measure the mechanical properties of cured polymer films. Thermo-mechanical analysis (TMA) was measured on a TMA/SDTS841e instrument with a heating rate of 5 °C min⁻¹ in air.

Synthesis. Synthesis of 4-[(1,1-diethoxyl-1-vinyl)silanyl]benzocyclobutene (**m**-Si-BCB). Triethoxyvinylsilane (45.15 g, 0.24 mol) and THF (50 mL) were mixed under an argon atmosphere. A solution of 4-bromobenzocyclobutene (27.45 g, 0.15 mol) in THF (30 mL) was added dropwise at room temperature. After being stirred for additional 4 hours, the reaction mixture was filtered to remove the solid and the filtrate solution was concentrated to give the crude product, which was distilled under vacuum to provide pure **m**-Si-BCB as a colorless liquid with a yield of 63%. ¹H NMR (400 MHz, CDCl₃, δ): 7.52~7.54 (d, 1H), 7.37 (s, 1H), 7.10~7.12 (d, 1H), 6.16~6.20 (m, 2H), 5.94~6.00 (m, 1H), 3.84~3.89 (m, 4H), 3.22 (s, 4H), 1.25~1.29 (t, 6H). ¹³C NMR (100 MHz, CDCl₃, δ): 148.54, 145.67, 136.75, 133.11, 132.53, 131.05, 128.40, 122.05, 58.82, 30.04, 30.02, 18.46. HRMS calcd for C₁₄H₂₀O₂Si: 248.1233; found: 248.1229.

Synthesis of oligomer **p-Si-BCB**. A solution of **m-Si-BCB** (12.42 g, 0.05 mol) in acetic acid (30.03 g, 0.5 mol) was refluxed for 24 h. After being cooled to room

temperature, the mixture was evaporated under reduced pressure and dried at vacuum at 90 °C for 8 h to afford a colorless viscous liquid **p-Si-BCB** with a yield of 95%. ¹H NMR (400 MHz, CDCl₃, δ): 6.93~7.60 (m, 3H), 5.81~6.30 (m, 3H), 3.18~3.25 (m, 4H). ¹³C NMR (100 MHz, CDCl₃, δ): 148.24, 145.40, 136.41, 135.43, 134.61, 132.68, 127.99, 121.88, 30.02, 30.00.

Synthesis of CP1. A solution of **m-Si-BCB** (2.48 g, 0.01 mol) and diethoxydimethylsilane (0.74 g, 0.005 mol) in acetic acid (9.00 g, 0.15 mol) was refluxed for 24 h. After being cooled to room temperature, the mixture was evaporated under reduced pressure and dried at vacuum at 90 °C for 8 h to afford a colorless viscous liquid CP1 with a yield of 93%. ¹H NMR (400 MHz, CDCl₃, δ): 7.13~7.70 (m, 3H), 6.03~6.43 (m, 3H), 3.30~3.34 (m, 4H), 0.21~0.42 (m, 3H). ¹³C NMR (75 MHz, CDCl₃, δ): 148.30, 145.42, 135.50, 135.18, 133.97, 132.60, 128.00, 121.90, 30.02, 29.96, 1.21.

Synthesis of CP2. A solution of **m-Si-BCB** (2.48 g, 0.01 mol) and diethoxydimethylsilane (1.48 g, 0.01 mol) in acetic acid (12.01 g, 0.20 mol) was refluxed for 24 h. After being cooled to room temperature, the mixture was evaporated under reduced pressure and dried at vacuum at 90 °C for 8 h to afford a colorless viscous liquid **CP2** with a yield of 93%. ¹H NMR (400 MHz, CDCl₃, δ): 7.31~7.64 (m, 2H), 7.06~7.19 (m, 1H), 5.91~6.31 (m, 3H), 3.26~3.29 (m, 4H), 0.15~0.31 (m, 6H). ¹³C NMR (75 MHz, CDCl₃, δ): 148.18, 145.39, 135.47, 135.04, 133.66, 132.40, 127.86, 121.82, 30.05, 29.99, 0.93.

Synthesis of CP3. A solution of m-Si-BCB (1.24 g, 0.005 mol) and

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diethoxydimethylsilane (1.48 g, 0.01 mol) in acetic acid (9.00 g, 0.15 mol) was refluxed for 24 h. After being cooled to room temperature, the mixture was evaporated under reduced pressure and dried at vacuum at 90 °C for 8 h to afford a colorless viscous liquid **CP3** with a yield of 92%. ¹H NMR (400 MHz, CDCl₃, δ): 7.18~7.72 (m, 3H), 6.02~6.40 (m, 3H), 3.33~3.35 (m, 4H), 0.20~0.50 (m, 12H). ¹³C NMR (100 MHz, CDCl₃, δ): 148.17, 145.44, 135.46, 134.63, 133.97, 132.57, 127.90, 121.84, 30.02, 29.96, 1.35.



Fig. S1 MALDI-TOF-MS of the oligmer p-Si-BCB.



Fig. S2 ¹³C NMR of m-Si-BCB (CDCl₃, 100 MHz).



Fig. S3 ¹³C NMR of p-Si-BCB (CDCl₃, 75 MHz).



Fig. S4 ¹³C NMR of CP1 (CDCl₃, 75 MHz).



Fig. S5 ¹³C NMR of CP2 (CDCl₃, 75 MHz).



Fig. S6 ¹³C NMR of **CP3** (CDCl₃, 100 MHz).



Fig. S7 FT-IR spectra of p-Si-BCB and c-Si-BCB.



Fig. S8 Nano indentation tests of the c-Si-BCB films.