

Supporting Information for

Dendrimeric Organosiloxane with Thermopolymerizable -OCF=CF₂ Groups as the Arms: Synthesis and Transformation to the Polymer with both Ultra-low *k* and low Water Uptake

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Experimental Section

Reagents and Instruments. 1,2-Dibromotetrafluoroethane was purchased from Top Fluorochem Co., Ltd, China and used as received. 2,4,6,8-Tetravinyl-2,4,6,8-tetramethylcyclotetrasiloxane (D₄^V) was purchased from Shanghai Enchem Industry Co., Ltd and distilled under reduced pressure before use. Other starting materials were purchased from Aldrich and used without further purification. All the solvents were distilled before use.

¹H NMR, ¹⁹F NMR, ¹³C NMR, and ²⁹Si NMR spectra were measured on a JEOL 400YH instrument. Elemental analysis was determined with Elementar vario EL III instrument. Molecular weights were determined by gel permeation chromatography (GPC) with a Waters Breeze2a 200 GPC system equipped with a refractive index (RI) detector using polystyrene as the standard and tetrahydrofuran (THF) as the eluent at a flow rate of 1.0 mL/min. Matrixassisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) was measured on Thermo Fisher Scientific

LTQ FT Ultra. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet spectrometer with KBr pellets at room temperature. Differential scanning calorimetric (DSC) analysis was determined with TA Instrument DSC Q200 at a heating rate of 10 °C min⁻¹ in nitrogen atmosphere. Thermogravimetric analysis (TGA) was measured on a TG 209F1 apparatus with a heating rate of 10 °C min⁻¹ in nitrogen atmosphere. Dielectric properties were investigated at room temperature on a 4294A Precision Impedance Analyzer (Agilent) by the non-contact method in a range of frequencies from 40 Hz to 30 MHz.

Synthesis. Compound **1** was prepared according to a procedure previously reported.¹

D₄-TFVE was synthesized by the following route: a mixture of D₄^V (2.17 g, 6.3 mmol), compound **1** (6.57 g, 28 mmol) and H₂PtCl₆ (6 drops, 1 g/mL in *i*-PrOH) was stirred at 70 °C for 3 h until vinyl groups were converted completely according to ¹H NMR. After being cooled to room temperature, the crude product was purified by column chromatography using *n*-hexane and dichloromethane as eluents on silica gel. Pure **D₄-TFVE** (6.35 g) was obtained as a transparent and colorless liquid with a yield of 79%. ¹H NMR (CDCl₃, 400 MHz), δ (ppm) 0.00~0.04 (m, 3H, Si-Me), 0.20~0.24 (m, 6H, Me-Si-Me), 0.36~0.65 (m, 4H, Si-CH₂-CH₂-Si), 7.05~7.07 (d, 2H, Ar), 7.45~7.47 (d, 2H, Ar). ¹⁹F NMR (CDCl₃, 376 MHz), δ (ppm) -133.99~-133.54 (m, 1F), -126.65~-126.10 (m, 1F), -119.67~-119.26 (m, 1F). ¹³C NMR (CDCl₃, 100 MHz), δ (ppm) -3.45, -1.38, 7.18, 9.34, 115.31, 133.70, 135.56, 135.79, 147.18, 155.97. ²⁹Si NMR (CDCl₃, 59.6 MHz), δ (ppm) -19.26, -0.42. MALDI-TOF (*m/z*): Calcd, 1273.29. Found 1273.96 (M⁺ + H⁺); GPC: *M_w* = 1,414, *M_n* = 1,398, PDI = 1.01. Elemental

analysis, Calcd. for $C_{52}H_{68}F_{12}O_8Si_8$: C, 49.03; H, 5.38; F, 17.90. Found: C, 50.32; H, 5.26; F, 17.58.

Synthesis of D₄-Ph. To a stirred mixture of D₄^V (8.12 g, 23.6 mmol) and dimethylphenylsilane (17.28 g, 130 mmol), chloroplatinic acid (6 drops, 1 g/mL in *i*-PrOH) was added. The mixture was stirred at 70 °C for 3 h until vinyl groups were converted completely according to ¹H NMR. After being cooling to room temperature, the crude product was purified by column chromatography using *n*-hexane and dichloromethane as eluents on silica gel. Pure monomer (17.8 g) was obtained as a clear, colorless liquid with a yield of 87%. ¹H NMR (CDCl₃, 400 MHz), δ (ppm) 0.02~0.04 (m, 3H, Si-Me), 0.23~0.26 (m, 6H, Me-Si-Me), 0.40~0.67 (m, 4H, Si-CH₂-CH₂-Si), 7.33~7.35 (d, 2H, Ar), 7.49~7.50 (d, 2H, Ar). ¹³C NMR (CDCl₃, 100 MHz), δ (ppm) -3.40, -1.33, 7.07, 9.37, 127.87, 128.93, 133.75, 139.43. ²⁹Si NMR (CDCl₃, 59.6 MHz), δ (ppm) -19.20, -0.59. MALDI-TOF (*m/z*): Calcd, 888.36. Found 906.39 (M⁺ + NH₄⁺).

Preparation of the Samples for Measurement of Dielectric Properties. D₄-TFVE (520 mg) was placed into a flat-bottomed glass tube with a diameter of 10.0 mm and filled with argon. The tube was heated to 170 °C and kept at this temperature for 1 h. Then the temperature was elevated slowly and maintained at 180 °C for 2 h, 200 °C for 3 h, 220 °C for 5 h, and 250 °C for 5 h, respectively. After being cooled to room temperature, a cured sample was obtained, which was polished before measurement of dielectric properties.

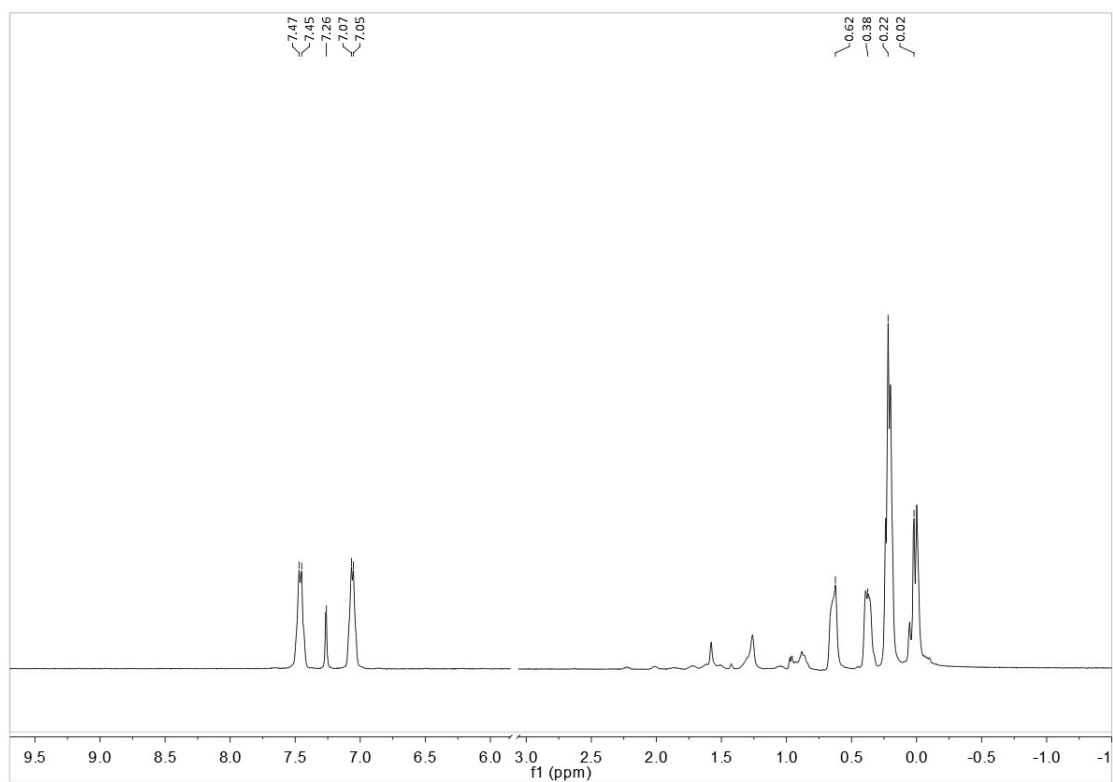


Fig. S1 ^1H NMR spectrum of $\text{D}_4\text{-TFVE}$ (CDCl_3 , 400 MHz).

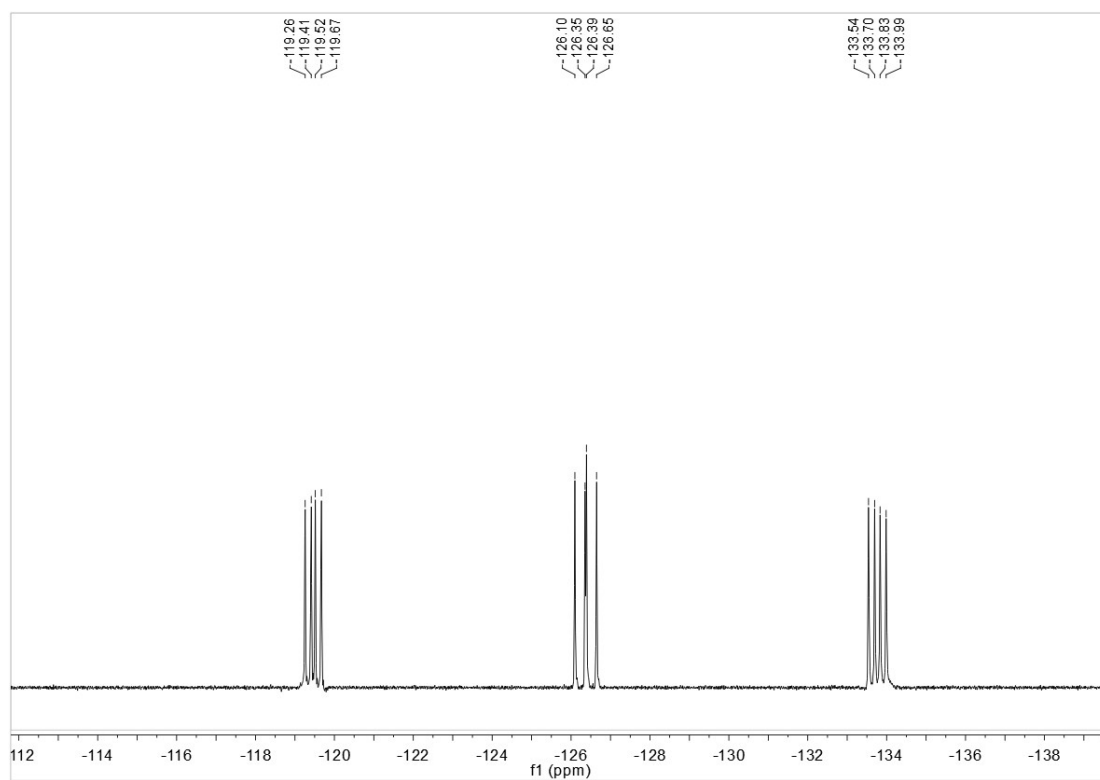


Fig. S2 ^{19}F NMR spectrum of $\text{D}_4\text{-TFVE}$ (CDCl_3 , 376 MHz).

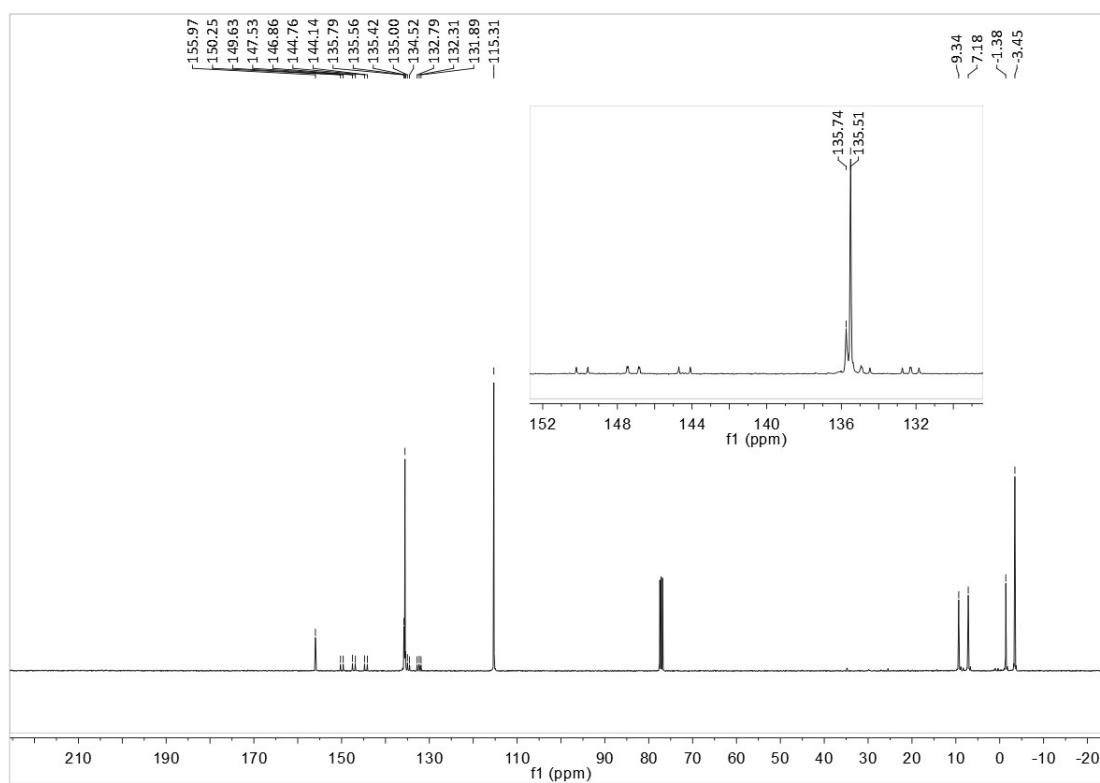


Fig. S3 ¹³C NMR spectrum of **D₄-TFVE** (CDCl₃, 100 MHz).

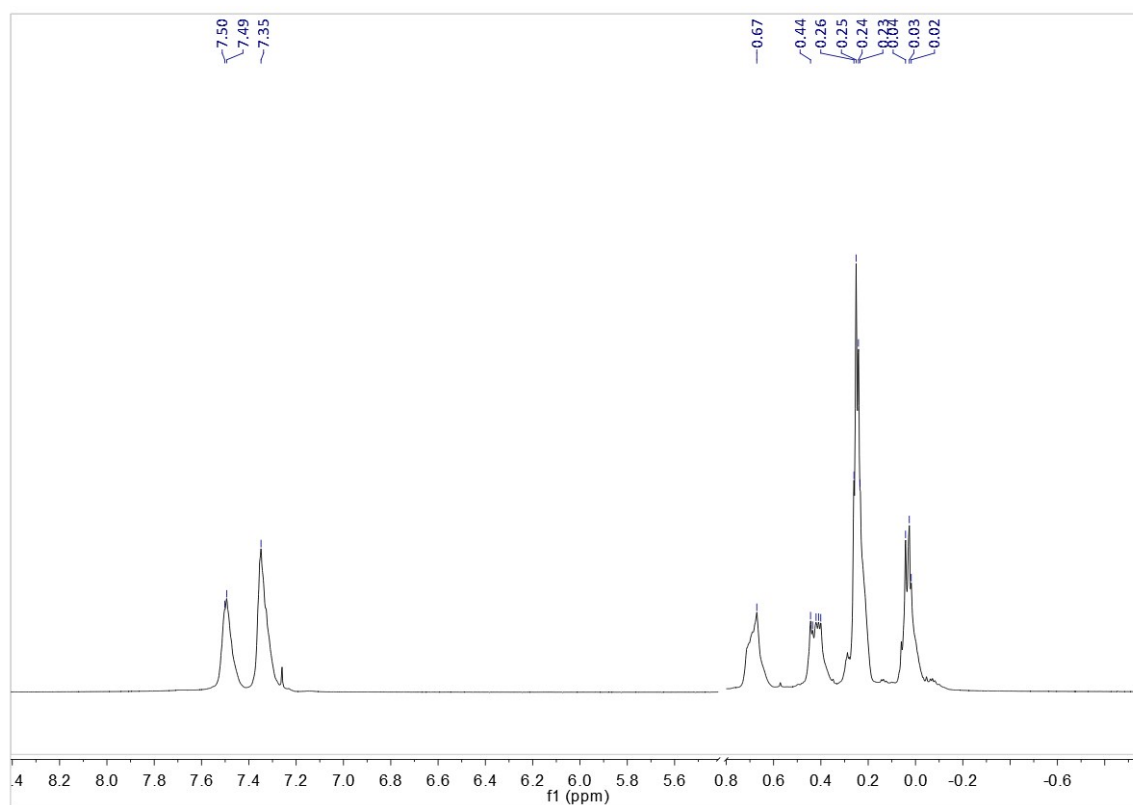


Fig.S4 ^1H NMR spectrum of $\text{D}_4\text{-Ph}$ (CDCl_3 , 400 MHz).

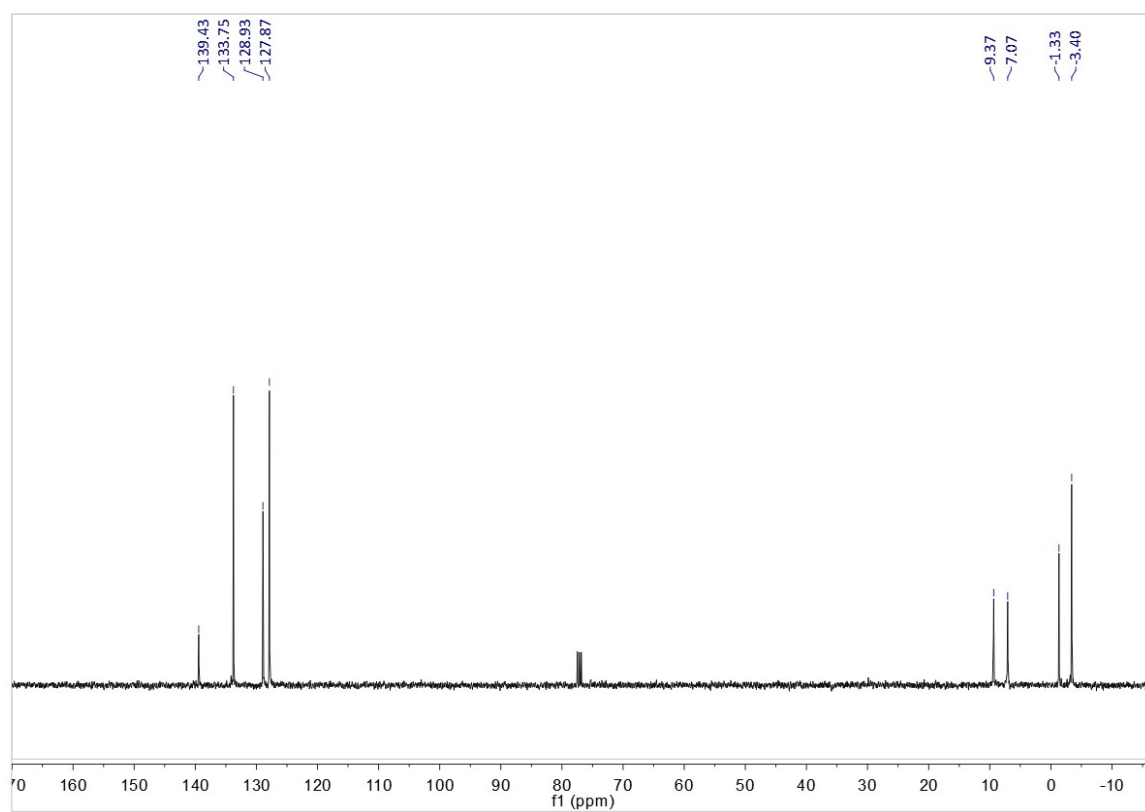


Fig. S5 ^{13}C NMR spectrum of $\text{D}_4\text{-Ph}$ (CDCl_3 , 100 MHz).

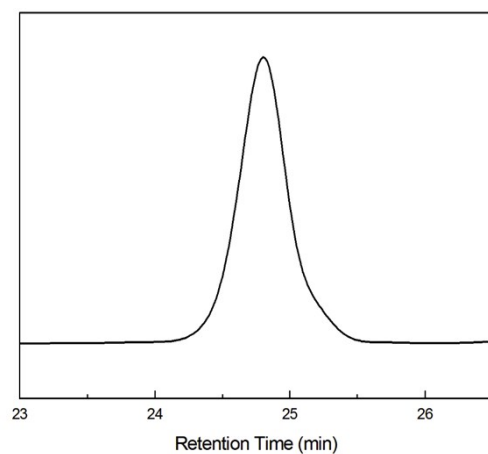


Fig. S6 GPC trace of D_4 -TFVE.

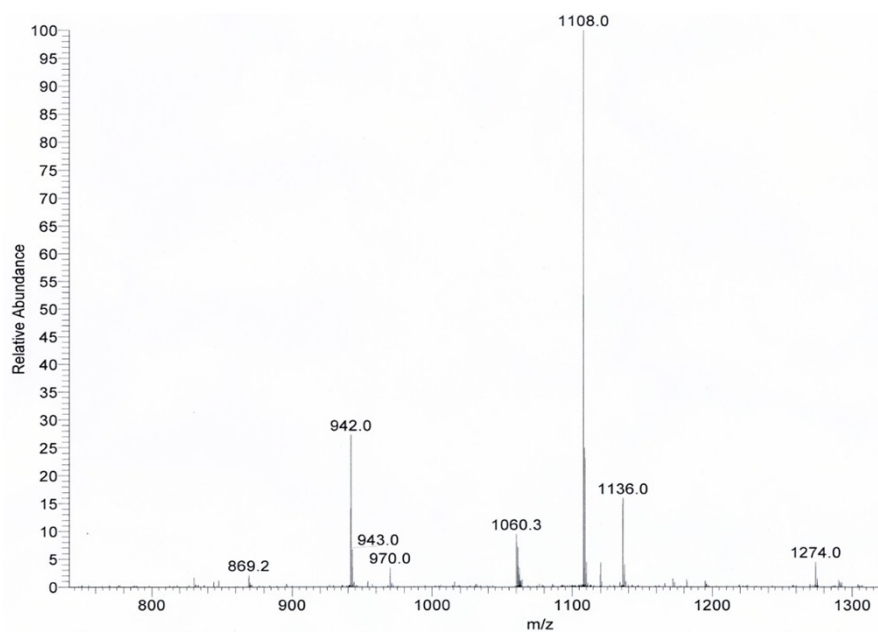


Fig. S7 MALDI-TOF-MS of **D₄-TFVE**.

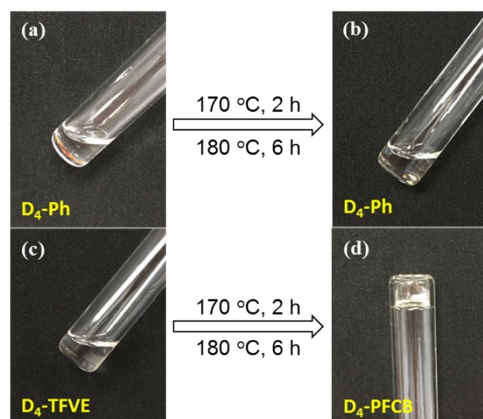


Fig. S8 Effect of heating treatment on the appearance of **D₄-Ph** and **D₄-PFCB**. (a) freshly prepared **D₄-Ph**, (b) **D₄-Ph**, heated at 170 °C for 2 h and 180 °C for 6 h, (c) freshly prepared **D₄-TFVE**, (d) **D₄-PFCB**, obtained by heating **D₄-TFVE** at high temperature.

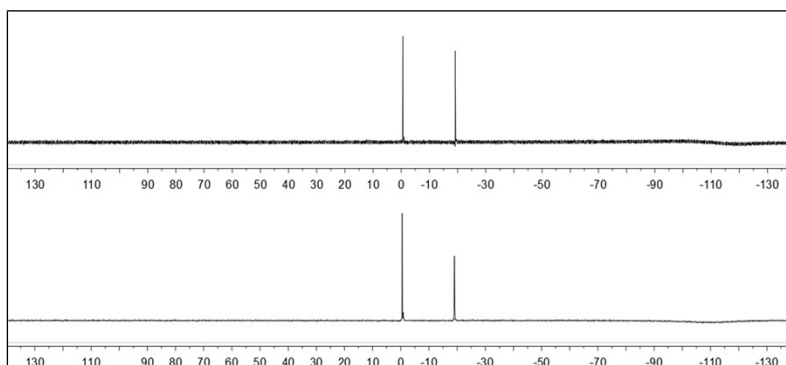


Fig. S9 A comparison of ^{29}Si NMR spectra of **D₄-Ph** before (up) and after (down) being heated at high temperature.

1. J. Rizzo and F. W. Harris, *Polymer*, 2000, **41**, 5125-5136.