

Supporting Information for

Post-functionalization of Novolac Resins by Introducing Thermo-crosslinkable -OCF=CF₂ Groups as the Side Chains: A New Strategy for Production of the Thermosetting Polymer without Releasing Volatiles

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EXPERIMENTAL SECTION

Reagents and Instruments. A commercial Novolac resin with a brand of HK6812 was purchased from Huakai Resin Factory (Jining, Shandong province, China), and purified by precipitating a solution of ethyl acetate of the resin in large of stirring toluene. GPC (polystyrene standard) exhibited that the purified resin had M_n of about 2,400 and a polydispersity of 2.3. 1,2-Dibromotetrafluoroethane was purchased from Top Fluorochem Co., Ltd, China and used as received. Dimethylchlorosilane was purchased from Co., Ltd. Other starting materials were purchased from Aldrich and Acros companies and used without further purification. All solvents were dehydrated over CaH₂ and distilled under an inert atmosphere before use. Zinc powder was activated by washing with 0.1 M HCl followed by drying at 150 °C in vacuum for 8 h before use.

^1H and ^{13}C NMR spectra were recorded on JEOL ecz400 or Agilent 500/54/ASP instrument using CDCl_3 as solvent and TMS as internal standard. Molecular weights were measured on a Waters Breeze2a 200 GPC instrument using polystyrene as the standards and tetrahydrofuran (THF) as the eluent, respectively. Mass spectrometry was performed on Agilent Technologies 5973N and Thermo Fisher Scientific LTQ FT Ultra. Elemental Analysis was performed on Elementar vario MicroCube. FT-IR spectra were obtained on a Thermo Scientific Nicolet spectrometer with KBr pellets. Differential Scanning Calorimetry (DSC) was determined with TA Instrument of DSC Q200 at a heating rate of 10 or 20 $^\circ\text{C min}^{-1}$ under nitrogen flow. Thermogravimetric analysis (TGA) was performed on a TG 209F1 apparatus with a heating rate of 10 $^\circ\text{C min}^{-1}$ in nitrogen. The dielectric properties of the cured resin were measured from an Agilent 4294A precision impedance analyzer at room temperature. Surface toughness of the polymer film was measured by atom force microscopy (AFM) on a Nanonavi E-Sweep. The contact angle of water on the film was characterized on at 20 ± 1 $^\circ\text{C}$ using a spin coating method on a dynamic contact angle measurement instrument (JC2000C)

Synthesis. Synthesis of **Allyl-Novolac** (see Scheme 1): a mixture of the purified Novolac resin (31.2 g, 292 mmol), allyl bromide (78 mL, 900 mmol), anhydrous K_2CO_3 (74 g, 535 mmol) and acetone (550 mL) was heated to reflux and kept at the temperature for 14 h. After being cooled to room temperature, the mixture was filtered and the filtrate was evaporated. The obtained residue was extracted with hot ethanol (100×3 mL) to give **Allyl-Novolac** as a pale yellow sticky liquid. 23.7 g, yield of 56%. $M_n = 3,500$ and polydispersity (PDI) = 3.4. ^1H NMR (400 MHz, CDCl_3 , ppm): δ 7.22~6.39 (m, 3H, Ar-

H), 6.18~5.61 (m, 1H, -CH=C), 5.52~4.82 (m, 2H, =CH₂), 4.69~3.46 (m, 4H, Ar-CH₂ and O-CH₂-).

Synthesis of compounds **1**, **2** and **3** (see Scheme 1): these compounds were synthesized according to the previously reported routes.²¹

Synthesis of **Fluoro-Novolac** (see Scheme 1): a solution of **Allyl-Novolac** (3.35 g, 23.0 mmol) and compound **3** (7.0 g, 30.2 mmol) in toluene (4 mL) was heated to 70 °C with stirring until a homogenous solution was formed, followed by adding a solution of H₂PtCl₆ in isopropanol (10 wt%, 4 drops). The mixture was stirred at room temperature for 5h and filtered. After removed the volatiles under reduced pressure, **Fluoro-Novolac** was obtained as a yellow viscous liquid. Yield of 89%. $M_n = 9,000$ and polydispersity (PDI) = 3.4. ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.82~6.52 (m, 7H, Ar-H), 4.21~3.44 (m, 4H, Ar-CH₂ and O-CH₂), 1.97~1.51 (m, 2H, -CH₂-), 1.06~0.65 (m, 2H, -CH₂-Si), 0.54~0.05 (m, 6H, Si-CH₃). ¹⁹F NMR (376 MHz, CDCl₃, ppm): δ -118.93~-120.40 (m, 1F), -125.85~-127.20 (m, 1F), -132.99~-134.71 (m, 1F). Anal. Calcd. for: [(C₂₀H₂₁O₂SiF₃)_n] C, 63.47; H, 5.59; F, 15.06. Found: C, 63.42; H, 5.54; F, 14.07.

Preparation of the samples for measurement of dielectric properties. The obtained **Fluoro-Novolac** resin mentioned above was poured to a flat-bottomed tube (φ 1.0 cm) filled with Argon. The tube was maintained at 170 °C for 8 h and then at 200 °C for 2 h, 210 °C for 2 h, 220 °C for 2 h, 240 °C for 2h respectively. A completely cured sample thus obtained.

Characterization of the Novolac Derivatives

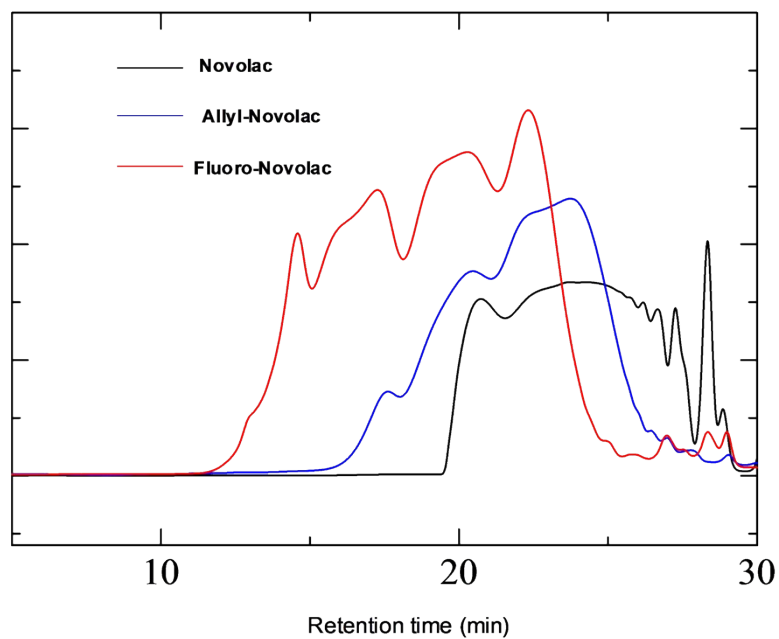


Fig. S1 GPC curves of the Novolac derivatives.

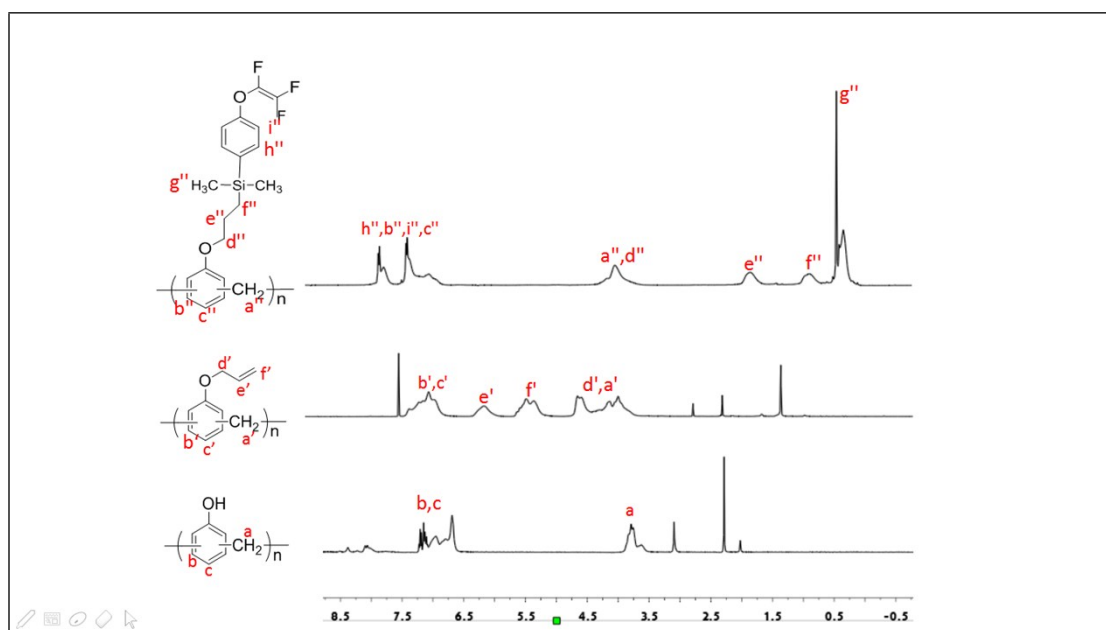


Fig. S2 ¹H NMR spectra of the Novolac derivatives (400 MHz, Acetone-*d*₆ or CDCl₃).

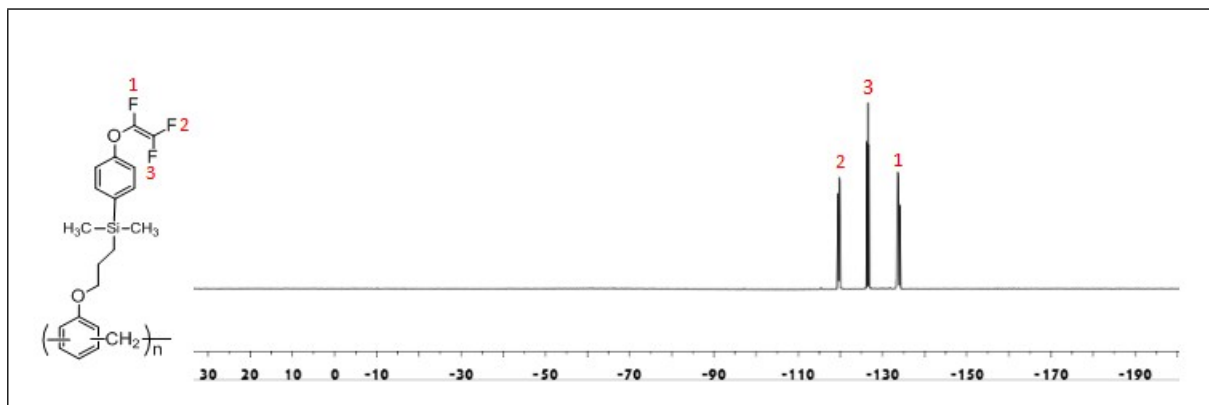


Fig. S3 ^{19}F NMR spectrum of **Fluoro-Novolac** (376 MHz, CDCl_3).

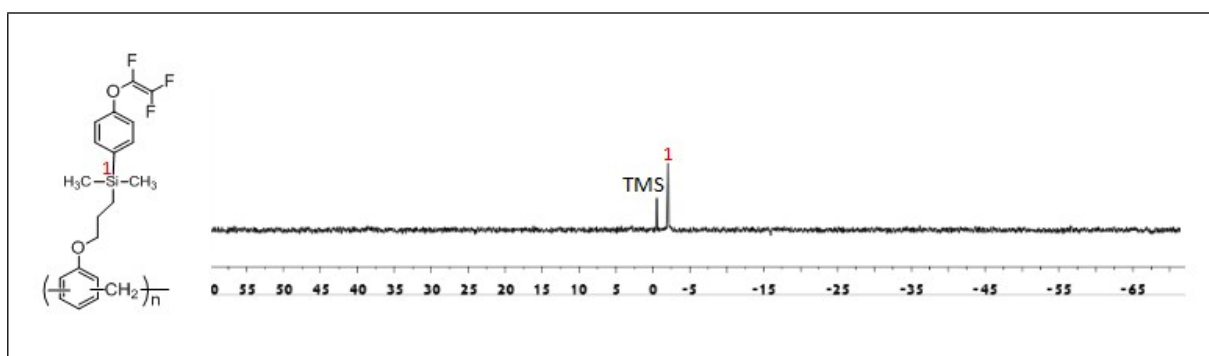


Fig. S4 ^{29}Si NMR spectrum of **Fluoro-Novolac** (59.6 MHz, CDCl_3).

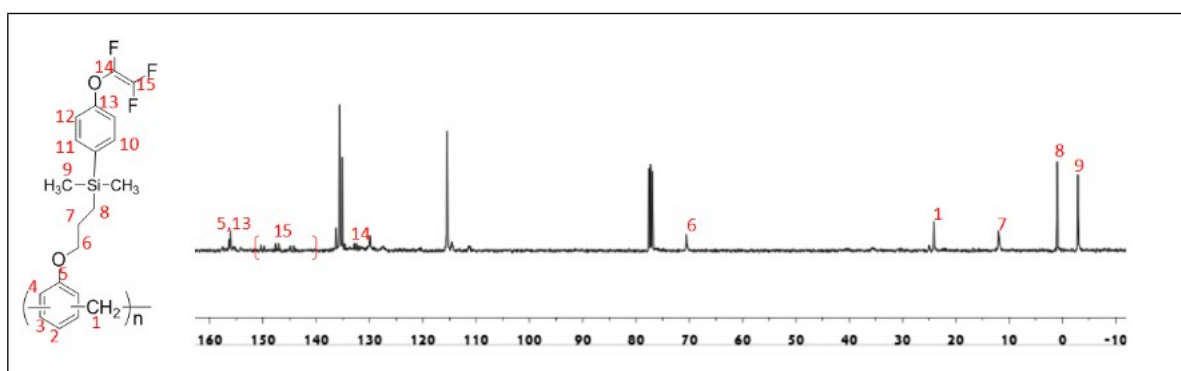


Fig. S5 ^{13}C NMR spectrum of **Fluoro-Novolac** (100 MHz, CDCl_3).