Electronic Supplementary Material (ESI) for Polymer Chemistry.

Self-Healing Hydrophobic POSS-functionalized Fluorinated Copolymers via RAFT Polymerization and dynamic Diels-Alder Reaction

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Supporting information

Analytical Methods

The prepared samples were characterized using a Fourier transform infrared spectrophotometer (FTIR) (Perkin Elmer, model spectrum-2) over 400 cm^{-1} - 4000 cm^{-1}. At ambient temperature, using $CDCl_3$ as NMR solvent, the ^{1}H-NMR spectroscopy of all the polymer samples were recorded on a Bruker 600 MHz nuclear magnetic resonance spectroscopy (NMR) instrument. Tetramethylsilane (TMS) was used as an internal standard. The molecular weights (M_n) and the dispersity ($Đ$) of the copolymers were determined by size exclusion chromatography (SEC) using a Viscotek SEC instrument equipped with two ViscoGel mix bed columns (17360-GMHHRM) connected in series with a RI detector. THF was used as the eluent at a flow rate of 1 mL min^{-1}. Narrow molecular weight distribution polystyrene and poly (methyl methacrylate) standards were used to calibrate the instrument. The Differential scanning calorimetry (DSC) analysis was carried out under a nitrogen atmosphere using a TA Instrument (Discovery DSC 25) at a heating rate of 10 °C min^{-1} within a temperature range of -30°C to +200°C. For the DSC analysis, 5-6 mg of samples were taken in the Tzero aluminium pan. Initially, the polymer sample in the pan was quenched to liquid nitrogen temperature and then heated to +200°C at a heating rate of 10°C/min. After 1 min of equilibration time at a cooling rate of 10°C/min, the sample was again cooled to -30°C, followed by reheating to +200°C at the heating rate of 10°C/min. The inflexion point in the second heating scan is taken as the glass transition temperature (T_g). Thermogravimetric analysis (TGA) (of 5-6 mg individual polymer samples) was carried out on a Shimadzu Instrument at a heating rate of 20°C/min within the temperature range of 30°C to 600°C under a nitrogen atmosphere. Surface topographies of copolymers (prepared via drop-casting 50 mg/mL polymer solution in THF on a glass slide) were studied using atomic force microscopy (AFM) (Agilent 5500 (USA) instrument) operated at room temperature (r.t.) in air. Water contact angles (WCA) were measured on a CA Goniometer (Rame-Hart instrument co., USA Model no. 260F4). A water-drop (about 0.5 μL) was placed on the polymer surface (prepared via drop-casting 50 mg/mL polymer solution in THF on a glass slide) to measure the static contact angle using the DROP image Advanced CA software. Self-healing analysis of scratched polymer samples (prepared via drop-casting 50 mg/mL polymer solution in THF on a glass slide) was monitored under an optical microscope (Leica DMLM, made in Germany). Herein, the thickness of the (drop-cast) polymer film (50 mg/mL in THF solvent) was maintained within the range of 0.1-0.2 mm.

Molar composition calculation

The molar composition of the copolymer was determined from the ^{1}H NMR spectrum of the copolymer using the following formula.

$$Composition\ of\ FMA\ (M_{FMA})(\%) = \frac{M_{FMA}/2}{M_{FMA}/2 + M_{TFEMA}/2} \times 100$$

(Equation S1)

Where,

M_{FMA} = integral area of the H^5 protons; M_{TFEMA} = integral area of the H^{11} protons.

Theoretical molecular weight calculation

The theoretical molecular weight of DA copolymers was calculated using the following formula:

$$M_n(P1) + (Z \times Molecular\ weight\ of\ POSS - M)$$

(Equation S2)

Where,

Z is the molar ratio of POSS-M incorporated while DA modification of **P1** copolymer.

Degree of Polymerization (DP) calculation using NMR analysis

The degree of polymerization (DP) of FMA and TFEMA within the **P1** copolymer and the **P1C** modified copolymer was calculated using the integral area of -CH_2 protons of FMA (H^5) and TFEMA (H^{11}) w.r.t the -CH_2 proton of the RAFT end group (H^2) using the following equation.

$$DP\ of\ FMA = \left[(I_5/2)/(I_2/2)\right]$$

$$DP\ of\ TFEMA = \left[(I_{11}/2)/(I_2/2)\right]$$

(Equation S3)

Where,

I_5 = integral area of the H^5 protons; I_{11} = integral area of the H^{11} protons; I_2 = integral area of the H^2 protons.

Healing efficiency (E_H) calculation

The self-healing efficiency of the copolymers were determined from the following equation.

$$Healing\ efficiency\ (E_H)(\%) = \frac{(Original\ scratch\ width) - (Healed\ scratch\ width)}{(Original\ scratch\ width)} \times 100$$

(Equation S4)

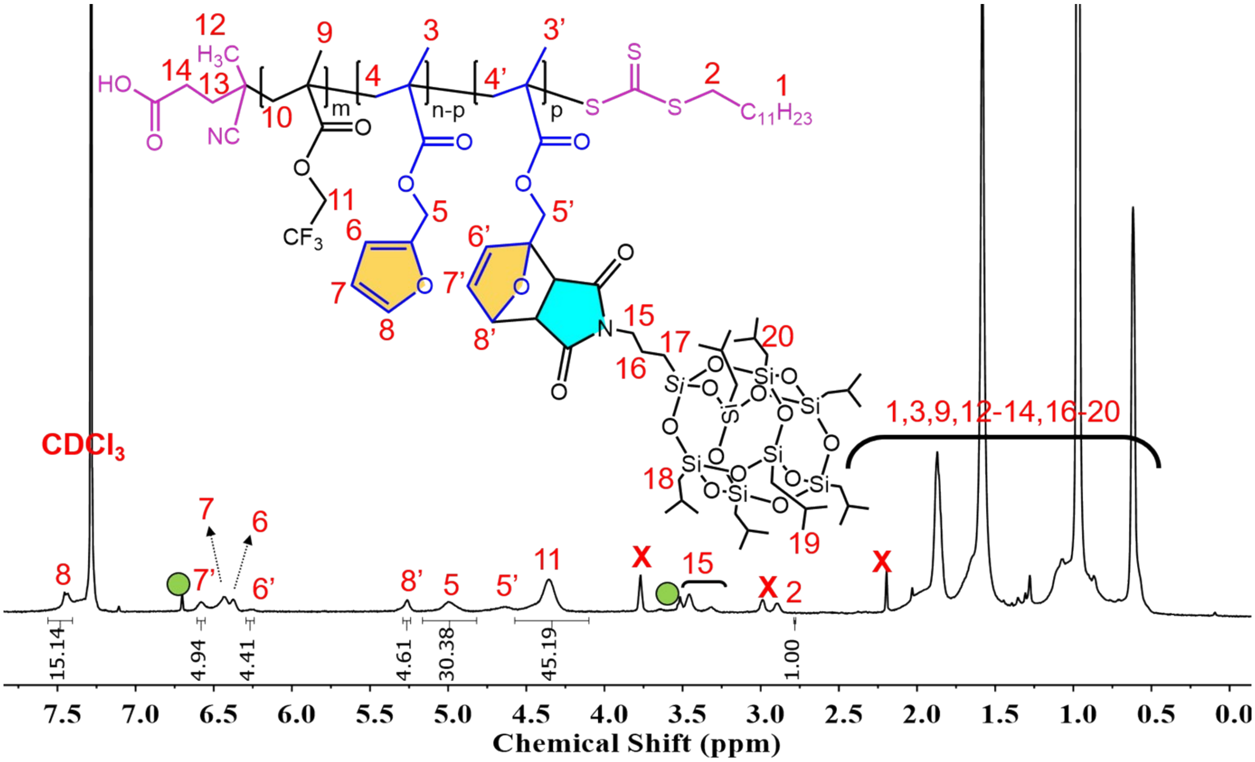

Figure S1. ^{1}H NMR spectrum of **P1A**.

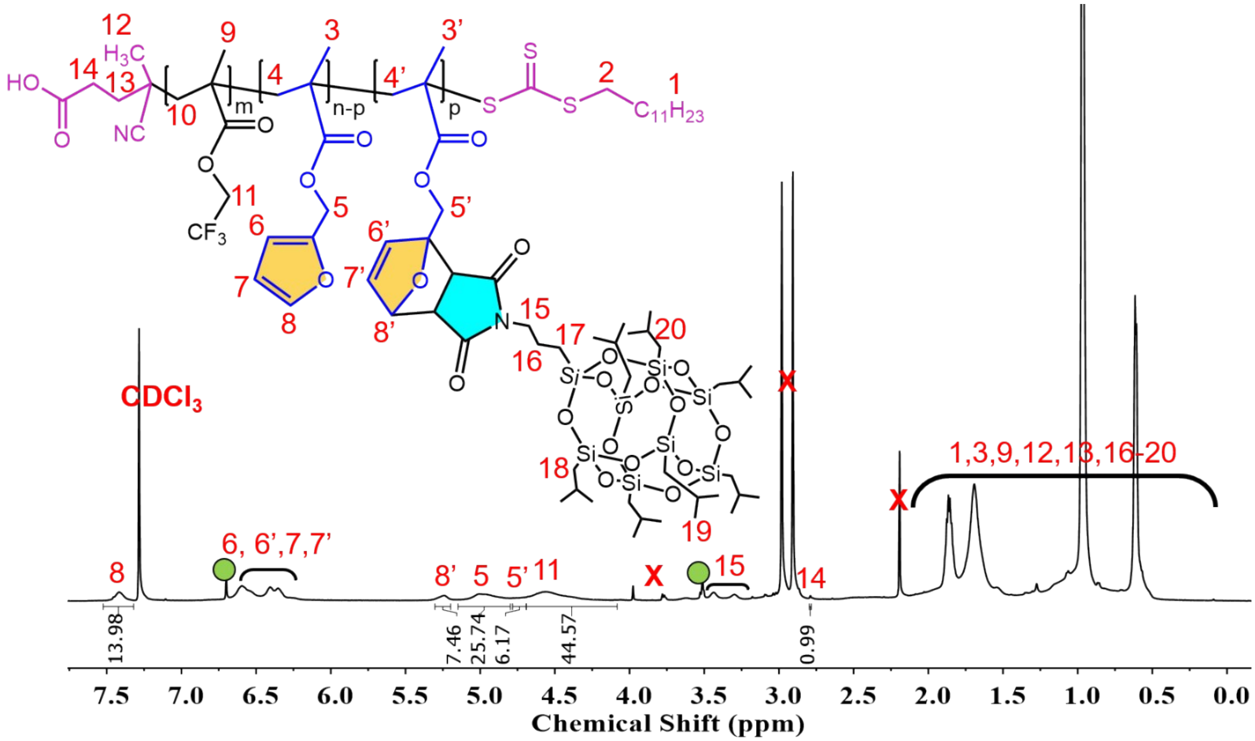

Figure S2. ^{1}H NMR spectrum of **P1B.**

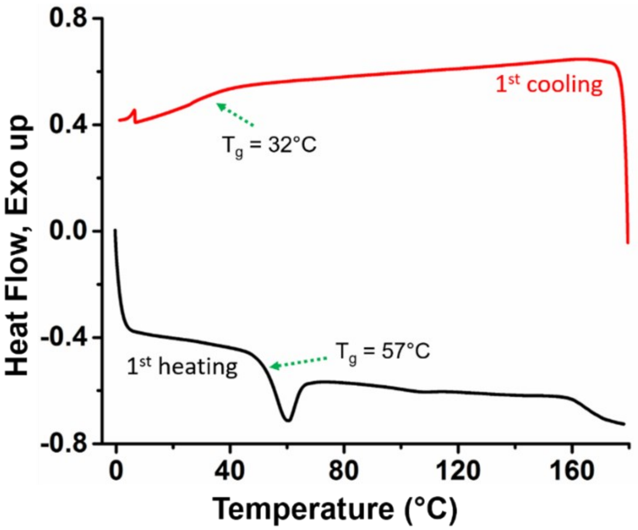

Figure S3. DSC thermogram of P1 copolymer

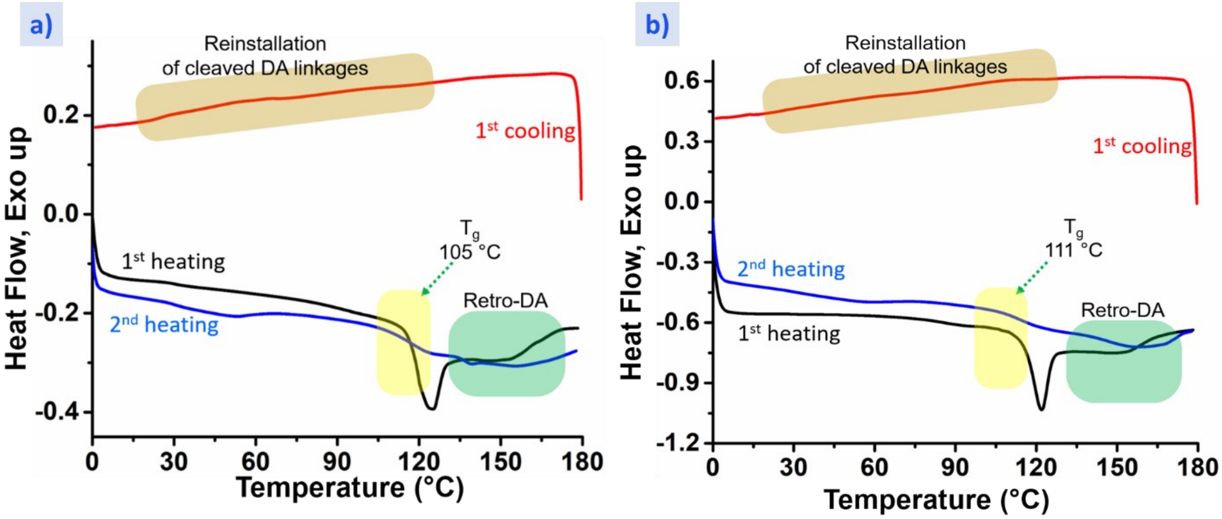

Figure S4. DSC analysis of P1A and P1B POSS-M modified polymer

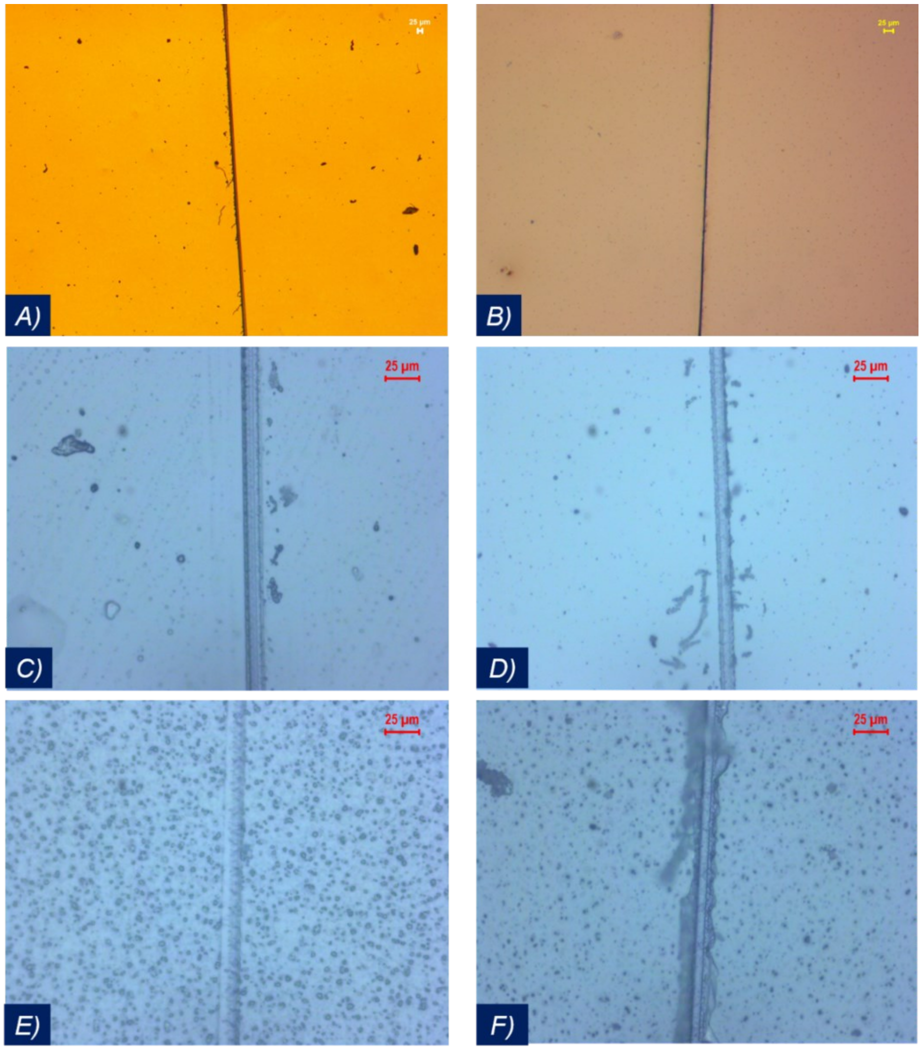

Figure S5. Optical microscopy images of scratched and healed samples of P1 (A-B) (unmodified copolymer), and P1A (C-D), P1B (E-F) (POSS-M modified copolymer)