Electronic Supplementary Information

Functional Fluorinated Polymer Materials and Preliminary Self-Healing Behavior

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1- Materials. All reagents were used as received unless stated otherwise. 2-Trifluoromethyl acrylic acid (MAF) was kindly offered by Tosoh FineChemical Company (Shunan, Japan). *tert*-butyl peroxypivalate (TBPPi) was kindly supplied by Akzo Nobel (Compiègne, France). 2,2,2-Trifluoroethyl α -fluoroacrylate (FATRIFE) was purchased from Scientific Industrial Application P and M, Russia. (1,1'-Methylenedi-4,1-phenylene) bismaleimide (purity 95%), thionyl chloride (purity 97%), furfuryl alcohol (purity 98%), pyridine (purity \geq 99%) hydrochloric acid, and laboratory reagent grade methanol were purchased from Sigma-Aldrich. Deuterated acetone (acetone- d_6) used for NMR spectroscopy was purchased from Euriso-top (Grenoble, France) (purity > 99.8%).

2- Experimental Procedures.

2.1. Synthesis of Cyclopenta-1,3-dien-1-ylmethyl 2-(trifluoromethyl)acrylate (MAF-Furan). (*i*) Synthesis of Dimethyl 2-(Trifluoromethyl)acryloyl Chloride (MAF-COCl). MAF-COCl was synthesized from 2-trifluoromethyl acrylic acid (MAF) using thionyl chloride following a procedure reported earlier in the literature.¹ Typically, MAF (20.0 g, 142 mmol) and SOCl₂ (12.4 mL, 170.4 mmol) were taken in a 100 mL round bottomed flask equipped with a vertical condenser. An oil bubbler was attached on the top of the condenser to monitor the evolution of the gases during the progress of the reaction (HCl and SO₂). The reaction mixture was heated at 80 °C and evolution of the gas (by-products HCl and SO₂) indicated the progress of the reaction. The reaction was stopped when the evolution of gases ceased. The product (MAF-COCl), as a colorless liquid, was purified by fractional distillation of the crude materials.

(*iii*) Synthesis of Cyclopenta-1,3-dien-1-ylmethyl 2-(Trifluoromethyl)acrylate (MAF-Furan). Furfuryl alcohol (6.2 mL, 71 mmol) and pyridine (11.5 mL, 142 mmol) were added to dichloromethane (40 mL) in a two-necked round bottom flask equipped with a dropping funnel. The mixture was stirred magnetically while purging with nitrogen for 20 min. After cooling at -10 °C in an ice-NaCl bath, MAF-COCl (11.3 g, 71 mmol) was transferred to the dropping funnel and slowly added into the reaction mixture (for 30 min) while maintaining the flask at - 10 °C. The reaction mixture was stirred magnetically at -10 °C for 2 hr and then at room temperature for another 14 hr. After completion of reaction, diethyl ether (200 mL) was added to the reaction mixture and it was washed with water followed by dilute HCl to remove unreacted MAF/pyridinium hydrochloride. Further, organic layer was washed with saturated solution of NaHCO₃ and water and dried over MgSO₄, filtered and the solvent was removed under vacuum to obtain MAF-Furan as a clear to slightly yellow liquid (yield = 44%). The structure and purity of such a monomer was confirmed by ¹H (Fig.S1), ¹⁹F (Fig.S2), ¹³C (Fig.S3), ¹H-¹³C HSQC (Fig.S4) NMR and FTIR (Fig.S5) spectroscopies, and GC-MS spectrometry (Fig.S6).

¹H NMR (400 MHz, CDCl₃, δ ppm, Fig. S1): 5.23 (s, 2H); 6.35 – 6.39 (m, 1H)); 6.45 (d, ³*J*_{HH} = 1.1 Hz, 1H); 6.47 (d, ³*J*_{HH} = 3.3 Hz, 1H); 6.72 (dd, ³*J*_{HH} = 1.2, 0.4 Hz, 1H); 7.39 – 7.49 (m, 1H).

¹⁹F NMR (376 MHz, CDCl₃, δ ppm, Fig. S2): -65.8 (-C<u>F</u>₃).

¹³C NMR (100 MHz, CDCl₃, δ ppm, Fig. S3): 59.6 (s, $-O\underline{C}H_2$, i), 111.2 (s, $-O-C(CH_2O)=\underline{C}H$ in furan ring, b), 111.9 (s, $-O-CH=\underline{C}H$ in furan ring, g), 120.3 (${}^{1}J_{CF} = 272$ Hz, $-\underline{C}F_3$, e), 131.5 (q, ${}^{2}J_{CF} = 32$ Hz, $-\underline{C}(CF_3)=CH_2$, d), 133.6 (q, ${}^{3}J_{CF} = 5$ Hz, $-C(CF_3)=\underline{C}H_2$, f), 144.1 (s, -O-CH=CH in furan ring, c), 149.0 (s, $-O-\underline{C}(CH_2O)=CH$ in furan ring, h), 161.4 (s, $-\underline{C}=O$, a).²⁻⁴ IR (cm⁻¹): (Fig. S5) 1735 (C=O stretching of ester), 1648 (C=C stretching of MAF), 1502 (C-O frequency), 1347, 1016-1205 (C-F stretching), 745 (Furan ring). GC-MS (Fig. S6): m/z = 220 (MAF-Furan; C₉H₇F₃O₃), 123 (H₂C=C(CF₃)C=O, C₄H₂F₃O), 97(-OCH₂-Furan, C₅H₅O₂), 95 (H₂C=CCF₃, C₃H₂F₃), 81 (CH₂-Furan, C₅H₅O), 69 (CF₃).

2.2. Radical Copolymerization of FATRIFE with MAF-Furan

All copolymerizations were performed using Schlenk techniques under nitrogen atmosphere. Typically a copolymerization (P2, Table 1) of FATRIFE with MAF-Furan was performed as described below (Scheme 1): TBPPi (46 mg of 75% solution, 0.2 mmol) and MAF-Furan (0.44 g, 2 mmol) were placed into a Schlenk flask which was then purged by three vacuum-nitrogen cycles. Then, degassed AcN (2.0 mL) and FATRIFE (3.1 g, 18 mmol) were added one after another under a dry nitrogen flux and the reaction mixture was heated at 56 °C under stirring for 18 h. At the end of the reaction, the crude product was precipitated twice from chilled methanol, filtered through a filter funnel, and then dried under vacuum (10^{-3} bar, 60 °C) for 16 h. The purified copolymer, was characterized by ¹H and ¹⁹F NMR spectroscopies.

¹H NMR (400 MHz, CDCl₃, δ ppm of P5, Table 1, Fig. 1): 0.8 to 1.5 (s, {-C(C<u>H</u>₃)₃ signal of the α -*tert*-butyl end group arising from TBPPi fragment}; 2.45 to 3.35 (-C<u>H</u>₂ groups in FATRIFE and MAF); 4.45 to 4.95 (m, -OC<u>H</u>₂CF₃ of FATRIFE), 5.23 (s, 2H), 6.35 – 6.39 (m, 1H), 7.49 – 7.39 (m, 1H).

¹⁹F NMR (376 MHz, CDCl₃, δ ppm of P5, Table 1, Fig. S7): -69 (s, -C<u>F</u>₃ of MAF in the copolymer); -75 (s, -C<u>F</u>₃ of FATRIFE in the copolymer); multiplets centered in the -162 to - 178 ppm range (α -F atom of FATRIFE units in the copolymer).

The molar fractions of FATRIFE in the copolymer were determined by ¹H NMR spectroscopy using the integrals of the $-OCH_2$ signals (signal *a*, Fig. 1) assigned to FATRIFE units and subtract its intensity from the peak labeled with (b, b', ranging from 2.45 to 3.35 ppm) to get the signal intensity b' (corresponding to $-CH_2$ signals MAF),⁵ as displayed in equation (S1):

$$FATRIFE \ mol\% \ in \ copolymers = \frac{\int_{4.45}^{4.95} OCH_{2(a)}}{\int_{4.45}^{4.95} OCH_{2(a)} + \int_{2.45}^{3.35} CH_{2(b+b')} - \int_{4.45}^{4.95} OCH_{2(a)}} \times 100$$
(S1)

The MAF-Furan amount in the copolymer was assessed from the ¹⁹F NMR spectra using the integrals of the -CF₃ signals attributed to FATRIFE and MAF units,⁶ as in equation (S2):

FATRIFE mol% in copolymers =
$$\frac{\int_{-73}^{-77} CF_3}{\int_{-73}^{-77} CF_3 + \int_{-68}^{-70} CF_3} \times 100$$
 (S2)

2.3. Preparation of Thermally Reversible Cross-Linked Polymers (Diels Alder Reaction). Typically, 20 mg of poly(FATRIFE-*c*o-MAF-Furan) copolymer, dissolved in 1 mL of acetone, were mixed with 0.5 equivalent of bis-maleimide solubilized in acetone. The mixture was heated at 50 °C for 10 min in a closed glassware and deposited into a Teflon mold. The solvent was evaporated for 24 h at room temperature, and the sample was completely dried under vacuum at 30 °C for an extra 24 h to obtain a pale yellow film without air bubbles.

3- Characterization.

Nuclear Magnetic Resonance (NMR) Spectroscopy. ¹H and ¹⁹F NMR spectra of the copolymers were recorded on a Bruker AC 400 Spectrometer (400 MHz for ¹H and 376 MHz for ¹⁹F) using acetone- d_6 as the solvent. Coupling constants and chemical shifts are provided in Hertz (Hz) and parts per million (ppm), respectively. The typical instrumental parameters for recording ¹H [or ¹⁹F] NMR spectra were as mentioned here: flip angle 90 ° [or 30 °, acquisition time 4.5 s [or 0.7 s], pulse delay 2 s [or 5 s], number of scans 32 [or 64], and a pulse width of 5 µs for ¹⁹F NMR.

Fourier Transform Infrared (FTIR) Spectroscopy. FTIR analyses of the copolymers were carried out using a PerkinElmer Spectrum 1000 in ATR mode, with an accuracy of ± 2 cm⁻¹.

Size Exclusion Chromatography (SEC) Measurements. Molar masses (M_n s) and dispersities (Ds) of the poly(VDF-co-MAF-Furan) copolymers were determined using a size exclusion chromatography (SEC) with triple-detection GPC (from Agilent Technologies) using a

PL0390-0605390 LC light scattering detector capable of detecting at two diffusion angles (15° and 90°), a PL0390-06034 capillary viscometer, and a 390-LC PL0390-0601 refractive index detector and two PL1113-6300 ResiPore 300×7.5 mm columns. DMF (containing 0.1 wt % of LiCl) was used as the eluent for this study at a flow rate of 0.8 mL min⁻¹ and toluene as the flow-marker. The entire SEC-HPLC system was thermostated at 35 °C during the entire duration of the measurement. Poly(methyl methacrylate) standards were used to calibrate the SEC instrument. The results were processed using the corresponding Agilent software.

Thermogravimetric Analysis (TGA). TGA of the purified and dried poly(FATRIFE-*co*-MAF-Furan) copolymers samples were performed under air using a TGA 51 apparatus from TA Instruments, at a heating rate of 10 °C min⁻¹ from room temperature to 580 °C.

Differential Scanning Calorimetry (DSC). DSC analyses of the purified and dried poly(FATRIFE-*co*-MAF-Furan) copolymers were carried out using a Netzsch DSC 200 F3 instrument under N₂ atmosphere. The instrument was calibrated with noble metals and checked before analysis with an indium sample ($T_m = 156.6 \text{ °C}$). The heating (or cooling) range was from -40 °C to 170 °C at a scanning rate of 10 °C min⁻¹. The sample was initially stabilized at 20 °C for 10 min. Then, the first scan was made at a heating rate of 10 °C min⁻¹ up to 170 °C. It was then cooled to -40 °C. Finally, a second scan was performed at a heating rate of 10 °C min⁻¹ up to 170 °C. T_g was evaluated from the second heating, taken at the half-height of the heat capacity jump of the glass transition. This procedure ensured elimination of the thermal history of the polymers during the first heating.

Gas Chromatography Mass Spectrometry (GC-MS) Analysis. The total product mixture was analyzed using a Shimadzu GC (GC-2010 Plus) and a quadripole MS (GCMS-QP2010 SE) equipped with a Zebron ZB-5 ms column, 20 m \times 0.18 mm id, 0.18 µm df. The detector and the injector temperatures were 200 °C and 280 °C, respectively. The temperature program started from 50 °C with a 2 minutes hold and then the heating rate was 25 °C.min⁻¹ until

reaching 250 °C and holding at 250 °C for 2 minutes. The total pressure was108 kPa, the total flow 25.9 mL.min⁻¹, column flow 0.74 mL.min⁻¹, purge flow 3 mL.min⁻¹, linear velocity 38.2 cm.s⁻¹, and a split injection of 30 : 1.

Optical Microscopic Analysis (OM). Optical microscopic study was carried on the polymer thin film spin-coated from acetone solution (20 mg mL^{-1}) on silicon wafer followed by drying in vacuum at room temperature for 16 h. A sharp knife was used to make a scratch on the surface of the polymer film. The scratched cross-linked polymer film samples were heated to induce healing. At time zero, and after various irradiation times, images of the scratch area were recorded by means of an Olympus polarized optical microscope (Model BX51) equipped with a camera system at room temperature.

Atomic Force Microscopic Analysis (AFM). AFM study was carried on the polymer thin film spin-coated from acetone solution (20 mg mL⁻¹) on silicon wafer followed by drying in vacuum at room temperature for 16 h. A rigid Veeco (TESP) Si tip with nominal spring constant, k ~ 42 N m⁻¹, and resonant frequency, $f_0 \sim 320$ kHz was used to make a scratch on the surface of the polymer film. The scratched cross-linked polymer film samples were heated to induce healing. At time zero, and after various irradiation times, images of the scratch area were obtained in a Veeco Multimode Nanoscope IIIa AFM operating in tapping mode at room temperature.

4- Supplementary Tables.

Table S1. Experimental conditions and results for the conventional radical copolymerization of FATRIFE and MAF-Furan using TBPPi in AcN at 56 °C.^a

entry	FATRIFE mol%		yield (%)	$M_{n,SEC}^{c}$	D^c	<i>T_{d10%}^d</i> (°C)	<i>T_g^e</i> (°C)
	feed	copolymer ^b	_				
P1	95	97 (96)	100	81400	1.86	365	51, 113
P2	90	93 (94)	87	67500	1.93	290	48, 116
P3	85	88 (87)	75	63200	1.94	245	29, 103

Acronyms: FATRIFE: 2,2,2-trifluoroethyl α -fluoroacrylate; MAF-Furan: cyclopenta-1,3-dien-1-ylmethyl 2-(trifluoromethyl)acrylate; TBPPi: *tert*-butyl peroxypivalate; time = 2 h, solvent, AcN: acetonitrile. ^aConditions: Solvent used = 2.0 mL. [TBPPi]₀/([FATRIFE]₀+[MAF-Furan]₀) = 1 mol%. %. ^b Copolymer compositions were calculated by ¹H NMR spectroscopy using equation (S1) and ¹⁹F NMR spectroscopy (value provided in brackets) using equation (S2). ^cDetermined by SEC in DMF (containing 0.1 wt% LiCl), system was calibrated using poly(methyl methacrylate) standards. ^dAssessed by thermogravimetric analysis (TGA), under air; 10 °C/min. ^e Determined by differential scanning calorimetry (DSC).



Scheme S1. Synthesis of cyclopenta-1,3-dien-1-ylmethyl 2-(trifluoromethyl)acrylate (MAF-Furan).

5- Supplementary Fig.s.



Fig. S1. ¹H NMR spectrum of MAF-Furan, recorded in CDCl₃ at 20 °C. (*) Solvent (chloroform) peak.



Fig. S2. ¹⁹F NMR spectrum of MAF-Furan, recorded in CDCl₃ at 20 °C.



Fig. S3. ¹³C NMR spectrum of MAF-Furan, recorded in CDCl₃ (*) at 20 °C.²⁻⁴



Fig. S4. ¹H-¹³C HSQC NMR spectrum of MAF-Furan, recorded in CDCl₃ at 20 °C. The correlations (red crosses) are highlighted from the black solid/dashed lines.



Fig. S5. ATR-IR spectrum of MAF-Furan.



Fig. S6. GC chromatogram of the final product during MAF-Furan synthesis and the corresponding GC-MS spectrum of the fraction at 5.34 min in the GC trace.



Fig. S7. Representative ¹⁹F NMR spectrum of poly(FATRIFE-*co*-MAF-Furan) copolymer prepared by conventional radical copolymerization of FATRIFE and MAF-Furan using TBPPi in AcN at 56 °C (P2, Table S1), recorded in acetone-d6 at 20 °C.



Fig. S8. ATR-IR spectra of PFATRIFE (top) and poly(FATRIFE-*co*-MAF-Furan) copolymers (P1-P3, Table S1).

Table S2: Characteristic frequencies in IR spectra of the poly(FATRIFE-*co*-MAF-Furan) copolymer⁷

Frequency	v cm-1
C=O in ester of MAF-Furan units	1730
C=O in ester of FATRIFE units	1720
C=C in MAF-Furan units	1600
CH ₂ bend	1400
C-F	1100-1200
C-O in MAF-Furan units and FATRIFE units	950



Fig. S9. SEC traces of poly(FATIRFE-*co*-MAF-Furan) copolymers prepared by conventional radical copolymerization of FATRIFE and MAF-Furan using TBPPi in acetonitrile at 56 °C (P1–P3, Table S1). Because such fluorinated poly(VDF-*co*-MAF-Furan) copolymers have lower refractive indices (RIs) compared to that of the eluent and since the detector is RI, the SEC signals are negative.⁸⁻¹⁰



Fig. S10. TGA thermograms (in air) and their derivative curves of poly(FATIRFE-*co*-MAF-Furan) copolymers prepared by conventional radical copolymerization of FATRIFE and MAF-Furan using TBPPi in acetonitrile at 56 °C (P1–P3, Table S1) heated at 10 °C min⁻¹.



Fig. S11. DSC thermogram of poly(FATRIFE-*co*-MAF-Furan) copolymer containing 97 mol% FATRIFE (P1, Table S1).



Fig. S12. DSC thermogram of poly(FATRIFE-*co*-MAF-Furan) copolymer containing 93 mol% FATRIFE (P2, Table S1).



Fig. S13. DSC thermogram of poly(FATRIFE-*co*-MAF-Furan) copolymer containing 88 mol% FATRIFE (P3, Table S1).



Fig. S14. Plot showing correlation between MAF-Furan mol% in the poly(FATRIFE-*co*-MAF-Furan) copolymer with the glass transition temperatures exhibited by the copolymer. Tg of poly(FATRIFE) was reported earlier⁶ and used here to construct the plot.



Fig. S15. Self-healing study of cross-linked polymer network. Optical micrographs of (a) the knife-cut sample and (b) thermally self-repaired sample of cross-linked copolymer.

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