## **Supporting Information**

## Thermo-reversible Self-healing in Fluorous Crosslinked Copolymer

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## Synthesis of Furfurylmethacrylate (FMA):

A Schleck flask was charged with furfuryl alcohol (5.000 g, 47.83 mmol) in 30.00 mL of dry dichloromethane (DCM) and triethylamine (4.836 g, 47.83 mmol) was added below 10 °C and stir for 1 h at ambient temperature. Methacrolyl chloride (4.689 g., 47.83 mmol) was added to the mixture at 10 °C. The reaction progress was checked by TLC and GC-MS. After 24 h completion of the reaction mixture was extracted from DCM and water (50 mL×3) and the organic phase was dried over  $Na_2SO_4$ . Solvent was removed under reduced pressure to give (FMA) light yellow liquid 5.730 g (72.1 %, 34.48 mmol). The crude product was purified by fractional distillation at 160-200 °C / 0.1 mbar. (Scheme **S1**)

**NMR (FMA):** (<sup>1</sup>H, CDCl<sub>3</sub>, δ ppm: δ 7.51 – 7.36 (s, 1H, -CH=C-O), 6.51 – 6.39 (m, 1H, CCHCH), 6.38 – 6.29 (m, 1H, CHCHCH), 6.12 (dt, *J* = 1.7, 0.9 Hz, 1H, CHH=C), 5.64 – 5.53 (m, 1H, CHH=C), 5.13 (s, 1H, OCH<sub>2</sub>C), 1.94 (dt, *J* = 1.7, 0.9 Hz, 3H, CH<sub>3</sub>). (<sup>13</sup>C, CDCl<sub>3</sub>, δ ppm: 167.17 (s, -OC=O), 149.71 (s, CH=C-O), 1463.31(s, =CH-C-O), 136.11 (s, CH<sub>2</sub>=C-CH<sub>3</sub>), 126.18 (s, CH<sub>2</sub>=C-), 110.71 (s, CHCHCH), 110.65 (s, CCHCH), 58.40 (s, OCH<sub>2</sub>C), 18.42 (s, CH<sub>3</sub>).



Scheme S1. Synthesis of furfurylmethacrylate (FMA)



















Figure S12. Diffusion ordered spectroscopy of a) 1, b) 2, c) 3b and d) 3d



**Figure 13:** <sup>1</sup>H NMR of a 1:1 mixture of copolymer PHFBA-co-PFMA (**3b**) and BM (a) at 0 h, (b) After 4 h heating at 60 °C and (c) <sup>19</sup>F NMR after 4 h heating at 60 °C.



Figure S15. <sup>19</sup>F NMR of 5d taken after 4 h heating at 120 °C in DMSO-d<sub>6</sub>





Figure S17. <sup>1</sup>H NMR of 5b taken after 4 h heating at 120 °C in DMSO-d<sub>6</sub>





Figure 20. Thermo-reversibility measurement (endo and exotherm peak) by DSC traces of 4



Figure 21. Thermo-reversibility measurement (endo and exotherm peak) by DSC traces of 5b



Figure S22. TGA and first derivative curve of 1



Figure S23. TGA and first derivative curve of 2



Figure S24. TGA and first derivative curve of 3a



Figure S26. TGA and first derivative curve of 3c



Figure S27. TGA and first derivative curve of 3d



Figure S28. TGA and first derivative curve of 3e



Figure S29. TGA and first derivative curve of 4



Figure S30. TGA and first derivative curve of 5b



Figure S31. TGA and first derivative curve of 5d



Fig. S32. Diffusion Coefficient from PGSE of 1











Fig. S35. Diffusion Coefficient from PGSE of 3d