Supporting Information

Thermo-reversible Self-healing in Fluorous Crosslinked Copolymer

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Synthesis of Furfurylmethacrylate (FMA):

A Schlecke 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. Methacryloyl 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$_2$SO$_4$. 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): ($^1$H, CDCl$_3$, δ ppm: δ 7.51 – 7.36 (s, 1H, -C=CH-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$_2$C), 1.94 (dt, J = 1.7, 0.9 Hz, 3H, CH$_3$). ($^{13}$C, CDCl$_3$, δ ppm: 167.17 (s, -OC=O), 149.71 (s, CH=C-O), 1463.31(s, -CH=C-O), 136.11 (s, CH$_2$=C-CH$_3$), 126.18 (s, CH$_2$=C-), 110.71 (s, CCHCH), 110.65 (s, CCHCH), 58.40 (s, OCH$_2$C), 18.42 (s, CH$_3$).

Scheme S1. Synthesis of furfurylmethacrylate (FMA)
Figure S1. $^1$H NMR of FMA in CDCl$_3$

Figure S2. $^{13}$C NMR of FMA in CDCl$_3$
**Figure S3.** $^{19}$F NMR of 3d in CDCl$_3$

**Figure S4.** $^{13}$C NMR of 1 in CDCl$_3$
Figure S5. $^{13}$C NMR of 2 in CDCl$_3$

Figure S6. $^{13}$C NMR of 3d in CDCl$_3$
HFBA (%) = \frac{0.90}{(0.90 + 2.14)} \times 100 = 29.61

Figure S7. $^1$H NMR of 3a in CDCl$_3$

HFBA (%) = \frac{1.42}{(1.42 + 2.25)} \times 100 = 38.69

Figure S8. $^1$H NMR of 3b in CDCl$_3$
HFBA (%) = 2.24 / (2.24 + 2.38) × 100
= 48.49

Figure S9. $^1$H NMR of 3c in CDCl$_3$

HFBA (%) = 3.07 / (3.07 + 2.25) × 100
= 57.71

Figure S10. $^1$H NMR of 3d in CDCl$_3$
HFBA (%) = \frac{5.39}{(5.39 + 2.44)} \times 100
= 68.84

Figure S11. $^1$H NMR of 3e in CDCl$_3$
Figure S12. Diffusion ordered spectroscopy of a) 1, b) 2, c) 3b and d) 3d
Figure 13: $^1$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) $^{19}$F NMR after 4 h heating at 60 °C.
Figure S14. $^1$H NMR of 5d taken after 4 h heating at 120 °C in DMSO-d$_6$

Figure S15. $^{19}$F NMR of 5d taken after 4 h heating at 120 °C in DMSO-d$_6$
Figure S16. $^1$H NMR of 5d taken after 4 h heating at 60 °C in DMSO-d$_6$
Figure S17. $^1$H NMR of 5b taken after 4 h heating at 120 °C in DMSO-d$_6$. 
Figure S18. $^{19}$F NMR of 5b taken after 4 h heating at 120 °C in DMSO-d$_6$
Figure S19. $^1$H NMR of 5b taken after 4 h heating at 60 °C in DMSO-d$_6$

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 S25. TGA and first derivative curve of 3b

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. S33. Diffusion Coefficient from PGSE of 2
Fig. S34. Diffusion Coefficient from PGSE of 3b

Fig. S35. Diffusion Coefficient from PGSE of 3d