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Supporting Information

First RAFT/MADIX Radical Copolymerization of *tert*-Butyl 2-Trifluoromethacrylate with Vinylidene Fluoride Controlled by Xanthate

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Received (in XXX, XXX) Xth XXXXXXXX 20XX, Accepted Xth XXXXXXXX 20XX 5 DOI: 10.1039/b000000x



Figure S1: ¹⁹F NMR spectrum (recorded in CDCl₃) of the poly(MAF-TBE-*co*-VDF)-*b*-PVAc block copolymer (Run 15 in Table 2).

Electronic Supplementary Material (ESI) for Polymer Chemistry This journal is The Royal Society of Chemistry 2013

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Figure S2: ¹H NMR spectrum (recorded in deuterated acetone) of the poly(MAF-TBE-*co*-VDF)-*b*-PVDF block copolymer (Run 16 in Table 2)



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Figure S3: ¹⁹F NMR spectrum (recorded in d₆ acetone) of the poly(MAF-TBE-*co*-VDF) copolymer in absence of xanthate (Run 4 in Table 1)





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Figure S4: ¹H NMR spectrum (recorded in d₆ acetone) of the poly(MAF-TBE-co-VDF) copolymer in absence of xanthate (Run 4 in

Table 1)

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Figure S5: ¹H NMR spectrum (recorded in d₆ acetone) of the poly(MAF-TBE-*co*-VDF) copolymer in 2,2,2-trifluoroethanol (Run 10 in Table 1)



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Figure S6. ¹⁹F NMR spectrum (recorded in d₆ acetone) of the poly(MAF-TBE-*co*-VDF) copolymer in 2,2,2-trifluoroethanol (Run 10 in Table 1)

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Figure S7: ¹⁹F NMR spectra (recorded in d₆ acetone) of the poly(MAF-TBE-*co*-VDF) copolymer in 20, 40, 60, and 120 min to determine the conversion of MAF-TBE

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Figure S8: Size exclusion chromatograms (SEC) of poly(VDF-*co*-MAF-TBE)-xanthate copolymers at 40, 60, and 120 min, respectively. Initial concentrations = $[VDF]_0$: $[MAF-TBE]_0$: $[tert-butyl peroxypivalate]_0$: $[Xanthate]_0 = 0.420$: 0.110: 0.010: 0.012 at 74 °C

10

15



Figure S9: Evolution of -CF₂SC(S)OEt versus time