Electronic Supplementary Material (ESI) for Polymer Chemistry.

Synthesis of Fluorinated Gradient Copolymers via In-Situ Transesterification with Fluoroalcohols in Tandem Living Radical Polymerization

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Supporting Data

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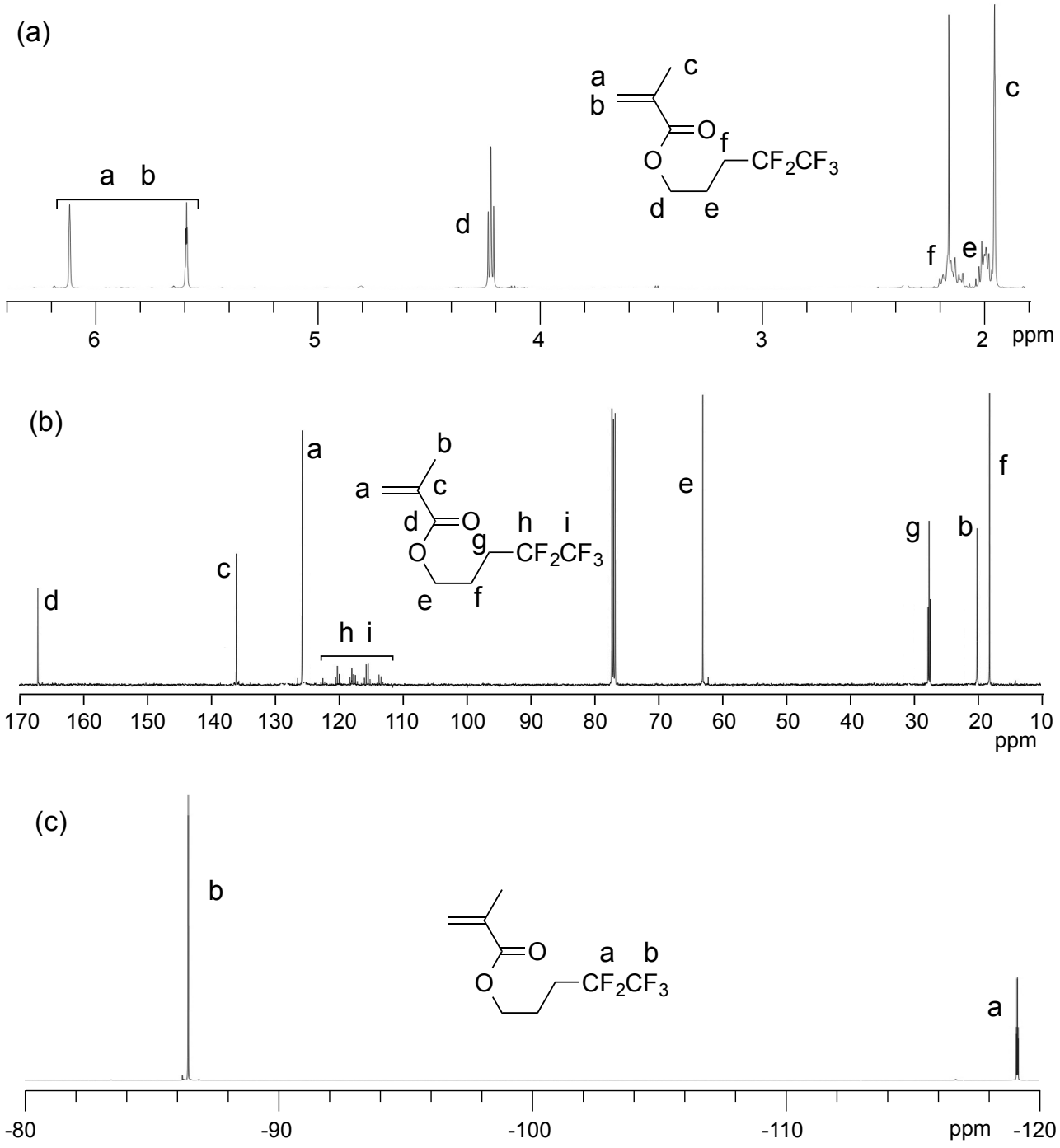

Figure S1. (a) ^{1}H, (b) ^{13}C and, (c) ^{19}F NMR spectra of 5FPMA in $CDCl_3$ at 25 ^{o}C.

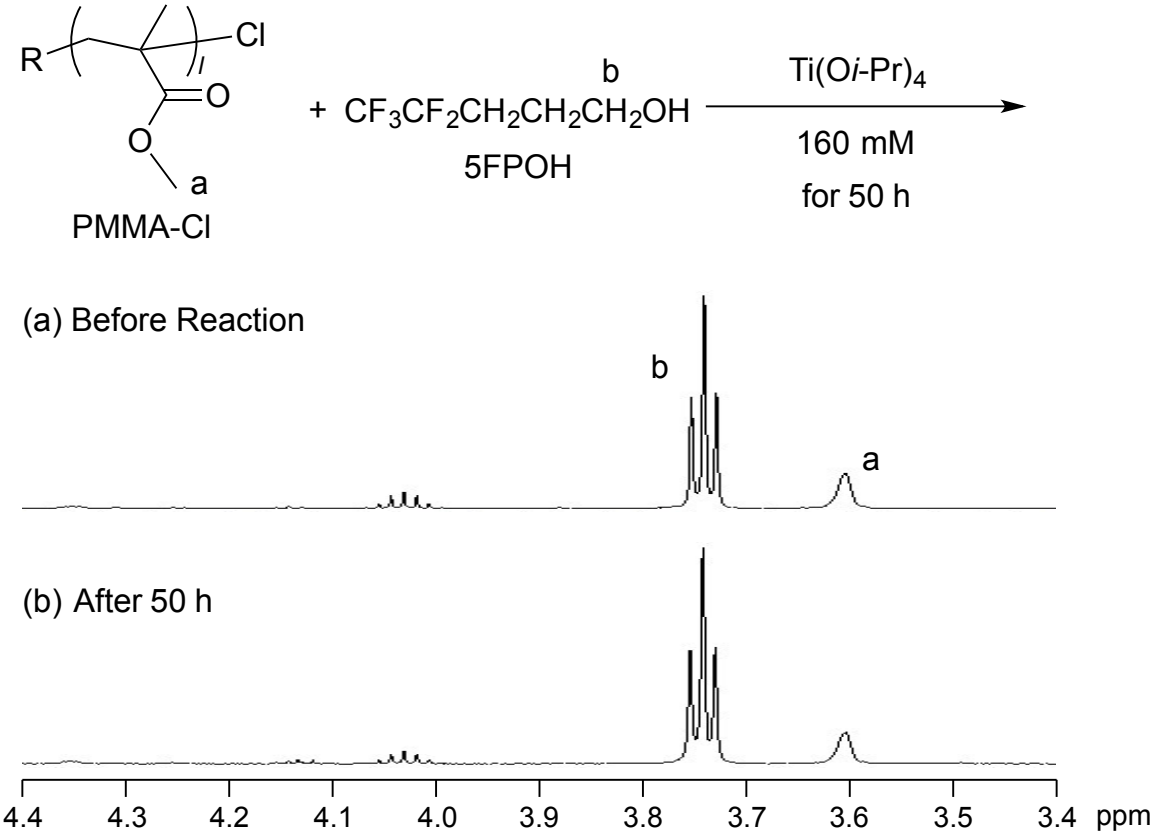

Figure S2. Transesterification of a chlorine-capped poly(methyl methacrylate) (PMMA-Cl: M_n = 12000, M_w/M_n = 1.14) with 5FPOH and Ti(O*i*-Pr)$_4$: [PMMA-Cl]/[Ti(O*i*-Pr)$_4$] = 20/160 mM in toluene/5FPOH (1/1, v/v) at 80 ^oC for 50 h. ^1H NMR spectra (in $CDCl_3$ at 25 ^oC) of the solution (a) before and (b) after the reaction for 50 h.

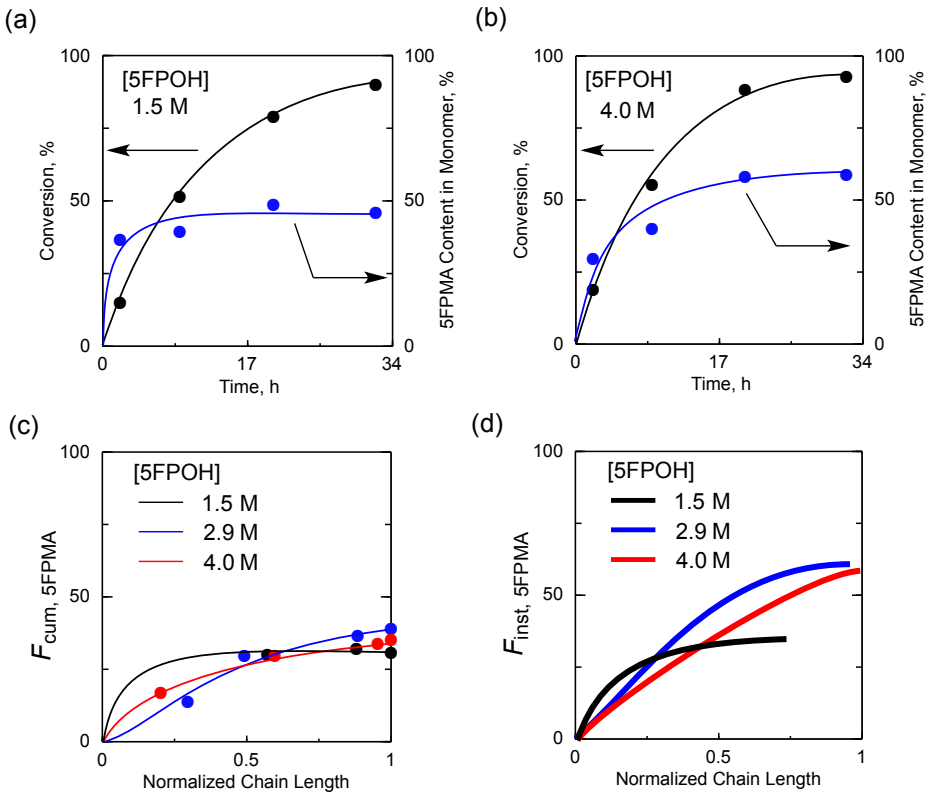

Figure S3. Tandem living radical polymerization of MMA with Ti(O*i*-Pr)$_4$ and 5FPOH: [MMA]/[ECPA]/[Ru(Ind)Cl(PPh$_3$)$_2$]/[Ti(O*i*-Pr)$_4$] = 2000/20/2/80 mM in toluene/5FPOH (1.5, 2.9, and 4.0 M) at 80 °C. (a,b) Total conversion and 5FPMA content in monomer: [5FPOH] = (a) 1.5 M and (b) 4.0 M. (c) Cumulative 5FPMA content ($F_{cum,5FPMA}$) and (d) instantaneous 5FPMA content ($F_{inst,5FPMA}$) of MMA/5FPMA gradient copolymers.

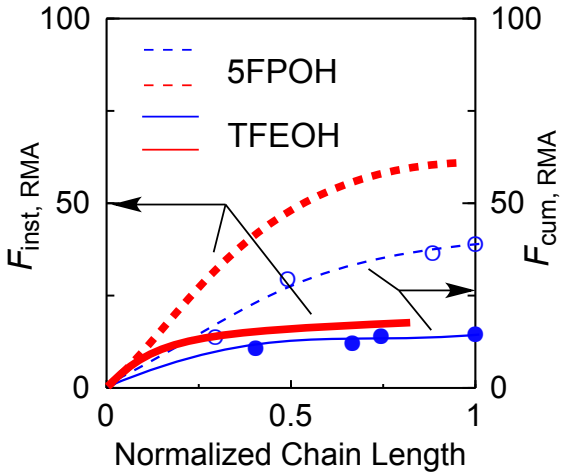

Figure S4. Cumulative or instantaneous RMA content ($F_{cum,\ RMA}$ or $F_{inst,\ RMA}$) of MMA/R$_F$MA gradient copolymers obtained from concurrent tandem polymerization of MMA with Ti(O*i*-Pr)$_4$ and TFEOH or 5FPOH: [MMA]/[ECPA]/[Ru(Ind)Cl(PPh$_3$)$_2$]/[Ti(O*i*-Pr)$_4$] = 2000/20/2/80 mM in toluene/TFEOH or 5FPOH (1/1, v/v) at 80 °C.

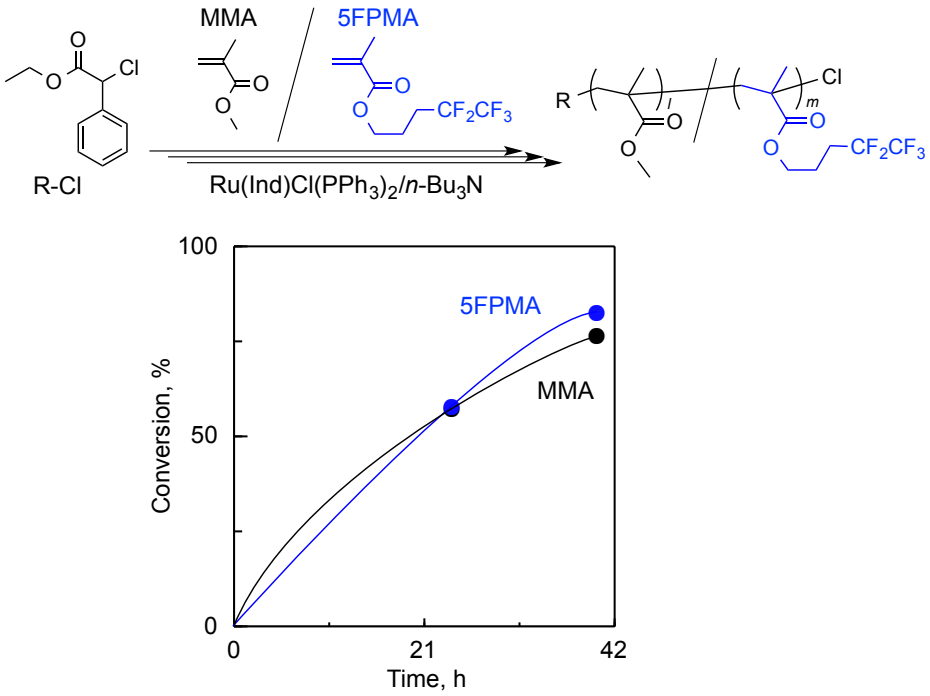

Figure S5. Time-conversion curve of monomers in ruthenium-catalyzed living radical random copolymerization of MMA and 5FPMA with a chloride initiator in toluene: [MMA]/[5FPMA]/[ECPA]/[Ru(Ind)Cl(PPh_3)$_2$]/[*n*-Bu_3N] = 1500/1500/15/1.5/15 mM in toluene at 80 ^oC.