Electronic Supplementary Information

Modular Segmented Hyperbranched Copolymers

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Experimental

Materials and Measurements

All reagents were obtained from commercial sources and used as provided, with the exception of 1,4-dioxane, which was purified via basic alumina plug and di(ethyleneglycol) diacrylate (75%), which was purified by column chromatography. Anhydrous solvents were collected from an anhydrous solvent system and used immediately after being obtained. All ^{1}H NMR (300 MHz and 500 MHz) spectra were recorded on a Varian Mercury 300 or Varian Mercury 500 spectrometer. Chemical shifts were referenced to residual signals from $CDCl_3$ (7.27 ppm). Gel permeation chromatography (GPC) was conducted in DMAC (with 0.05 M LiCl) at 50 °C with a flow rate of 1.0 mL/min (Pump: Agilent 1260 Infinity Isocratic Pump G1310B, Columns: Guard + two ViscoGel I-series G3078 mixed bed columns, molecular weight range 0–20 × 10^3 and 0–100 × 10^4 g mol^{-1}). Detection consisted of a Wyatt Optilab T-rEX refractive index detector operating at 658 nm and a Wyatt miniDAWN TREOS laser light scattering detector (operating at 50 mW, 658 nm with detection angles of 49°, 90°, and 131°). Molecular weights were determined using the 100%-mass recovery method.

Synthesis of pentafluorophenylacrylate (PFPA)

PFPA was synthesized in a modified procdure reported by Theato et al.[1] Pentafluorophenol (5.00 g, 27.2 mmol, 1.00 equiv.) and triethylamine (3.02 g, 29.9 mmol, 1.10 equiv.) were

dissolved in 75 mL dry CH_2Cl_2 and the solution was stirred in an ice bath. Acryloyl chloride (2.95 g, 32.6 mmol, 1.20 equiv.) was added drop-wise to the solution under constant stirring. After 2 h, the solution was extracted with water (2x50 mL) and dried over anhydrous $MgSO_4$. The remaining solvent was removed by rotary evaporation to give a viscous, slightly yellow oil. The crude product was purified by vacuum distillation at 70 °C to give a colorless oil in 73% yield. ^{1}H NMR ($CDCl_3$): δ/ppm: 6.70 (d, 1H), 6.35 (dd, 1H), 6.16 (d, 1H). ^{19}F NMR ($CDCl_3$): δ/ppm: -153.23 (2F), -158.12 (1F), -162.54 (2F)

Synthesis of 2,3,5,6-tetrafluorophenylacrylate (TFPA)

TFPA was synthesized as reported previously,[2] following the same protocol as for PFPA but using tetraflurophenol instead of pentafluorophenol. After vacuum distillation the clear oil was recovered in 81% yield. ^{1}H NMR ($CDCl_3$): δ/ppm: 6.98 (m, 1H) 6.70 (d, 1H), 6.35 (dd, 1H), 6.16 (d, 1H). ^{19}F NMR ($CDCl_3$): δ/ppm: -153.8 (2F), -139.9 (2F)

Synthesis of (S)-1-Doceyl-(S)-(α,α′-dimethyl-α′′-acidic acid) Trithiocarbonate, DDMAT

DDMAT was synthesized as reported previously.[3] Dodecanethiol (40.5 g, 0.200 mol, 1.00 equiv.), acetone (96.12 g, 1.655 mol, 8.275 equiv.) and tricaprylylmethyl ammonium chloride (3.23 g, 8.00 mmol, 0.04 equiv.) were combined in a three neck round bottom flask and cooled to 10 °C while kept under argon. A solution of 50% NaOH (16.8 g, 0.210 mol, 1.05 equiv.) was added over a 20 min period and stirred for an additional 15 min. A white precipitate formed. Carbon disulfide (15.2 g, 0.200 mol, 1.00 equiv.) was added to acetone (20.2 g, 0.340 mol, 1.70 equiv.) and the resulting solution was added to the reaction over a 20-min period. The previously formed precipitate dissolved and the solution turned a red-orange color. After 10 min, chloroform (35.6 g, 0.300 mol, 1.50 equiv.) was added. After that, 50% NaOH (80.0 g, 1.00 mol, 5 equiv.) was added dropwise over a 30 min period. The solution was stirred overnight and a heavy orange precipitate was formed. The next day, 300 mL of

water was added along with 50 mL of concentrated HCl. The flask was purged with argon and stirred vigorously to evaporate acetone. The solid was collected by filtration, stirred into 2-propanol (0.5 L) and the undissolved solid removed by filtration. The filtrate was concentrated to dryness and recrystallized from hexanes to provide 27.78 g of yellow solid (41% yield). ^{1}H NMR (300 MHz, $CDCl_3$): 3.32−3.26 (t,2H, CH_2CH_2S), 1.72 (s, 6H, $COC(CH_3)_2S$), 1.64−1.70 (m, 2H, $CH_2CH_2CH_2S$), 1.25−1.45 (m, 20H, $CH_3(CH_2)_{10}CH_2$), 0.85−0.90 (t, 3H, CH_3CH_2).

Synthesis of 2-((2-(((Dodecylthio)carbonothioyl)thio)-2-methylpropanoyl)oxy)ethyl Acrylate, ACDT

ACDT was synthesized following a procedure by Gao and coworkers.[4] DDMAT (2.00 g, 5.49 mmol, 1.00 equiv.) was dissolved in dry chloroform (50 mL) in a three neck round bottom flask. An oil bubbler was attached to the flask to allow gas formed during the reaction to escape. Oxalyl chloride (1.05 g, 8.24 mmol, 1.50 equiv.) was added to the flask using a syringe followed by the addition of 5 drops of *N*,*N*-dimethylformamide. Vigorous bubbling was observed. The solution was allowed to stir at room temperature for 2 h, after which no gas evolution was evident. Dichloromethane and excess oxalyl chloride were evaporated under reduced pressure. The resulting oil was redissolved in 100 mL dry dichloromethane and put in an ice bath where it was stirred. A solution of hydroxyethylacrylate (0.637 g, 5.49 mmol, 1.00 equiv.) and triethylamine (0.611 g, 6.04 mmol, 1.10 equiv.) was added to the reaction flask drop-wise. After the addition was complete, the reaction was removed from the ice bath and continued to stir at room temperature overnight. The next day, the solution was washed with 1M HCl (2x50 mL) and brine (2x50 mL) and dried over anhydrous $MgSO_4$. The remaining solvent was removed using rotary evaporation. The crude product was purified using column chromatography with a 10:1 hexane: ethyl acetate mixture to yield 2.50 g of a viscous orange oil (97 % yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) 6.37−6.44, 6.06−6.16, and

5.81−5.86 (m, 3H, CH_2CHCO), 4.31−4.39 (m, 4H, $COO(CH_2)_2OCO$), 3.25 (t, 2H, $SCH_2(CH_2)_{10}CH_3$), 1.69 (s, 6H, $COC(CH_3)_2S$), 1.20−1.41 (m, 20H, $CH_3(CH_2)_{10}CH_2$), 0.88 (t, 3H, CH_3CH_2).

Typical Protocol for RAFT-SCVP of PFPA

PFPA (0.50 g, 2.1 mmol) was added to a vial. Stock solutions of ACDT and AIBN in 1,4-dioxane were prepared. Appropriate amounts of AIBN stock solution, ACDT stock solution, and additional 1,4-dioxane were added to the vials to achieve a concentration of 1.5 M. Vials were purged with argon for 20 min, then placed in a silicon oil bath at 70 °C for 48 h. To quench the polymerizations, the vials were cooled in an ice bath and exposed to air. Additional 1,4-dioxane (1.5 mL) was added to the vials and the solutions were precipitated into cold hexanes. A white solid was obtained upon filtration. ^{1}H NMR ($CDCl_3$): δ/ppm: 4.31−4.39 (br s), 3.25 (br s), 3.10 (br s), 2.51 (br s), 2.13 (br s), 1.69 (s), 1.20−1.41 (br m) 0.88 (t).

Typical Protocol for RAFT-SCVP of TFPA

The same protocol as for PFPA was used, but TFPA was used instead. ^{1}H NMR ($CDCl_3$): δ/ppm: 6.9 (br s), 4.31−4.39 (br s), 3.25 (br s), 3.10 (br s), 2.51 (br s), 2.13 (br s), 1.69 (s), 1.20−1.41 (br m) 0.88 (t).

Polymerization Protocol for PFPA with Crosslinker

PFPA (0.50 g, 2.1 mmol) was added to a vial. Stock solutions of DDMAT, DEGDA and AIBN in 1,4-dioxane were prepared. AIBN stock solution, DDMAT stock solution, DEGDA stock solution and additional 1,4-dioxane were added to the vials to achieve a concentration of 1.5 M. Vials were purged with argon for 20 min, then placed in a silicon oil bath at 70 °C for

48 h. After removal from the oil bath and cooling in an ice bath, additional 1,4-dioxane was added to the vial and the solution was precipitated into cold hexanes. Filtration yielded 0.48g of white solid. ^{1}H NMR ($CDCl_3$): δ/ppm: 3.3-3.6 (br s), 3.10 (br s), 2.51 (br s), 2.13 (br s).

Polymerization Protocol for PFPA with Crosslinker

The same protocol as for PFPA was used, but TFPA was used instead. ^{1}H NMR ($CDCl_3$): δ/ppm: 6.9 (br s), 3.3-3.6 (br s), 3.10 (br s), 2.51 (br s), 2.13 (br s).

General Reaction Protocol for Functionalization of PPFPA and PTFPA with Nucleophile

PPFPA/ PTFPA was dissolved in a minimal amount of dry THF. Triethylamine (1.2 equiv.) and the appropriate nucleophile (1.1 equiv.) were added and the solution was stirred at room temperature overnight. Solvent was removed by rotary evaporation. The resulting solid was redissolved in a small amount of THF, precipitated into cold hexanes and filtered by vacuum filtration to yield a white powdery solid. When hydrophilic nucleophiles (i.e., aminophosphonic acid or aminosulfonic acid) were employed, the polymers were dialyzed against DI water for 3 days, followed by lyophilization.

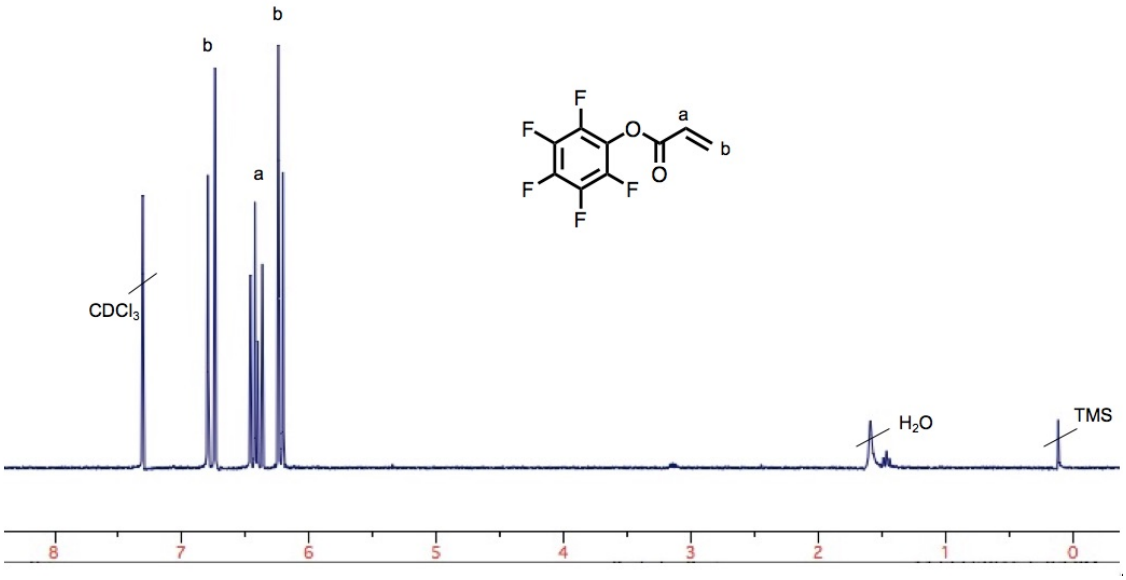


Figure S1. ^{1}H NMR spectrum of pentafluorophenylacrylate (PFPA).

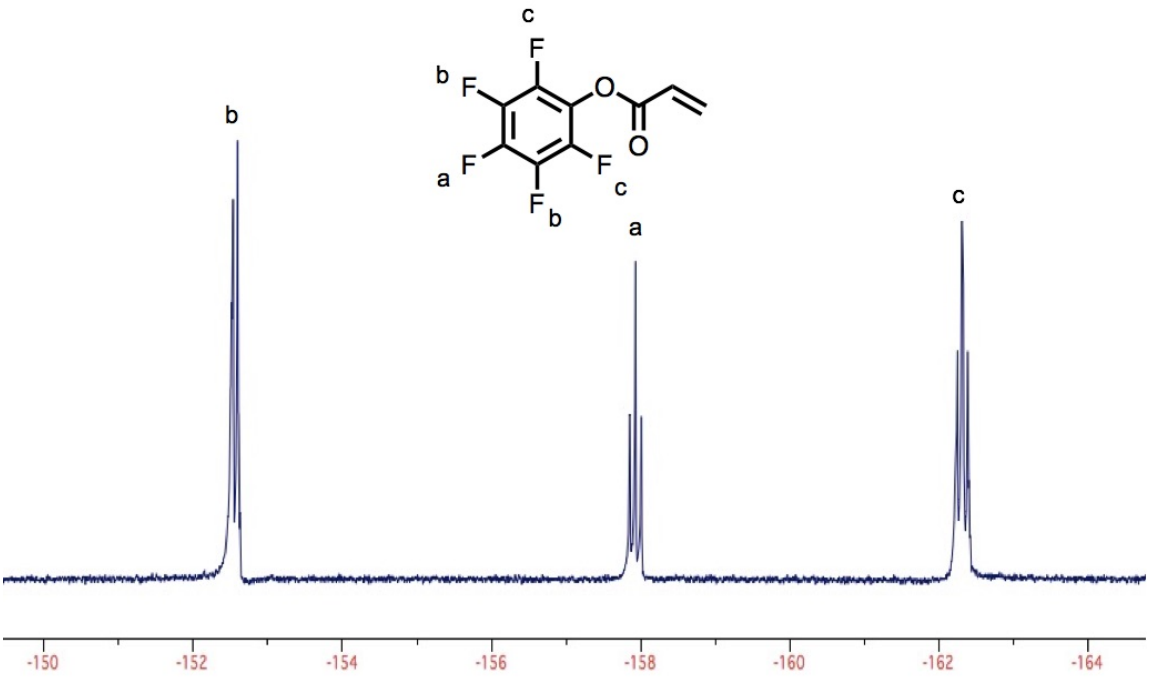
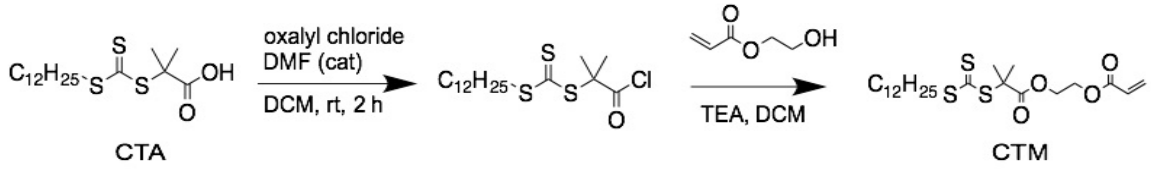


Figure S2. ^{19}F NMR spectrum of pentafluorophenylacrylate (PFPA)



Scheme S1. Synthesis of chain-transfer monomer (CTM) from chain transfer agent (CTA)

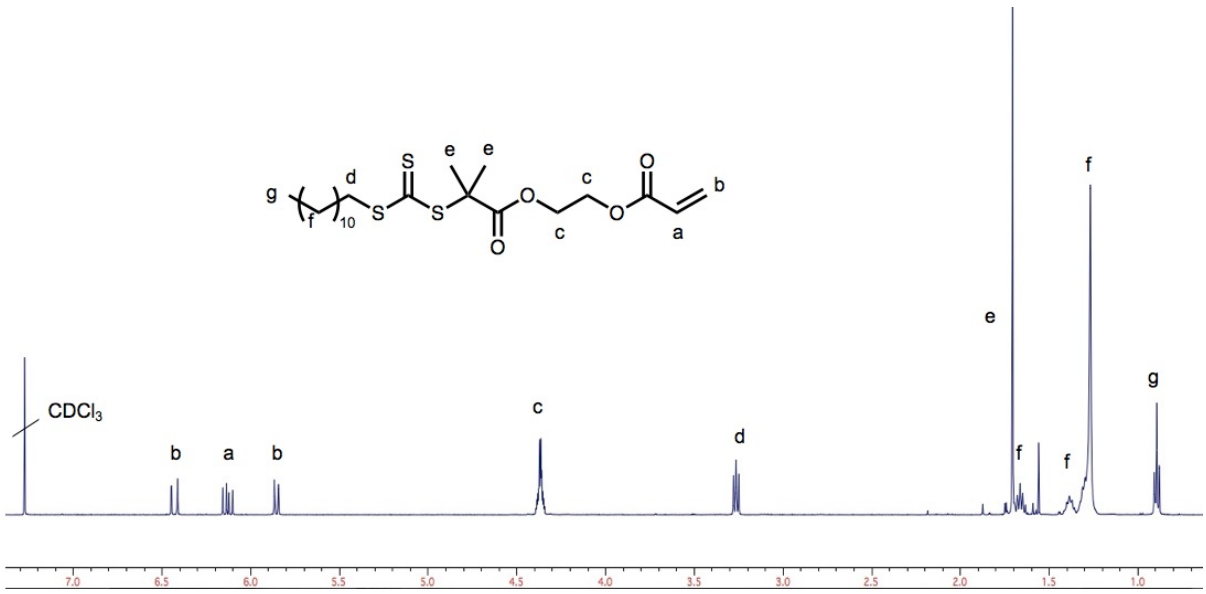


Figure S3. ^{1}H NMR spectrum of chain transfer monomer (CTM)

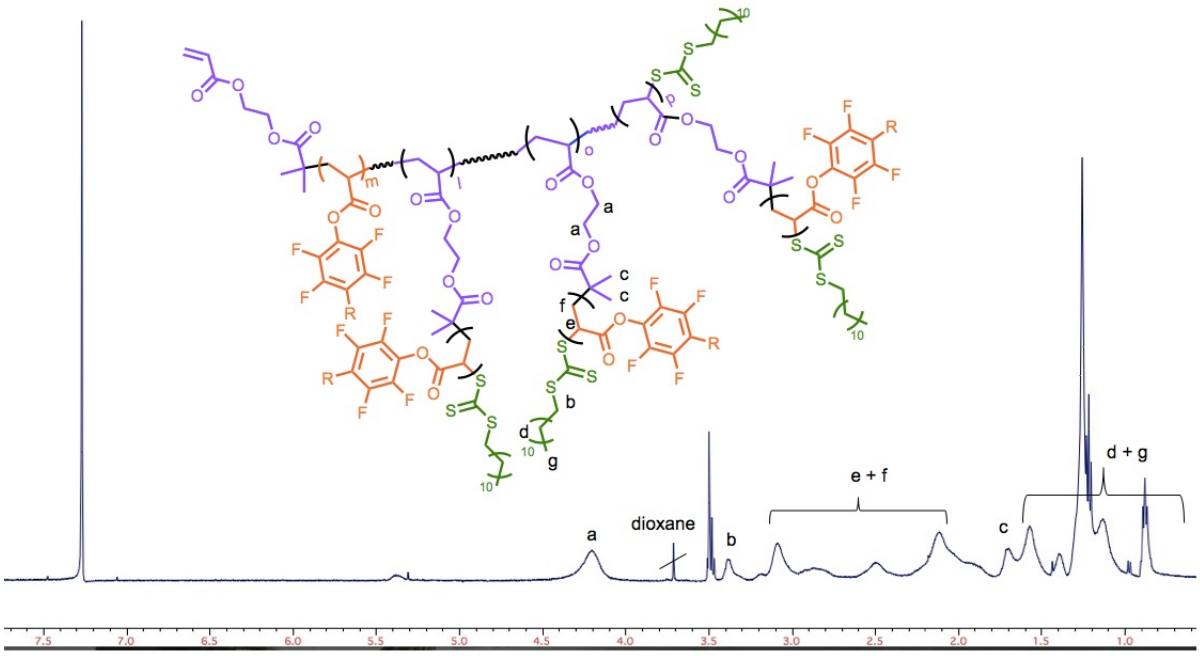


Figure S4. Example of a typical ^{1}H NMR spectrum of hyperbranched poly(pentafluorophenylacrylate) (PPFPA) prepared by self-condensing vinyl polymerization (SCVP). DB was calculated using signal *c* for the dendritic unit and signal *a* for the linear unit.

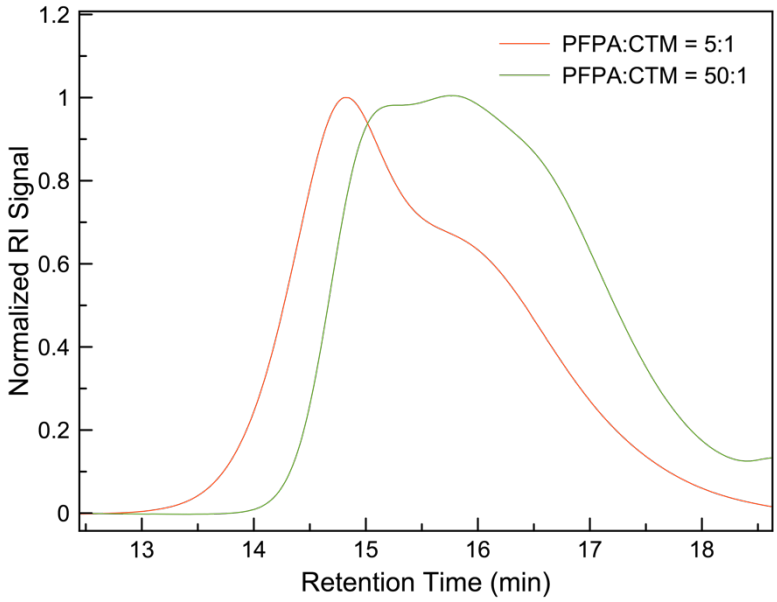


Figure S5. Gel permeation chromatography traces of hyperbranched polymer from entries **1** and **4** from Table 1. Red trace = entry **4** (5:1), green = entry **1** (50:1).

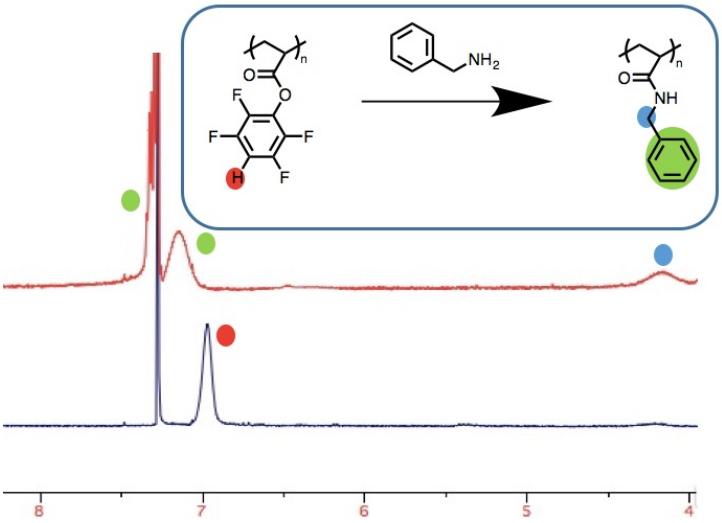


Figure S6. ^{1}H NMR spectra before (bottom) and after (top) functionalization of hyperbranched poly(tetrafluorophenylacrylate) (entry **5**, Table 1) with benzylamine.

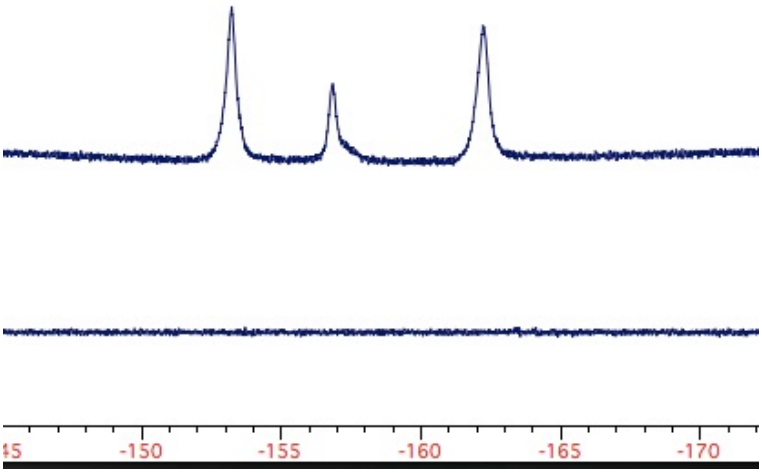


Figure S7. ^{19}F NMR spectrum before (top) and after (bottom) functionalization with benzylamine.

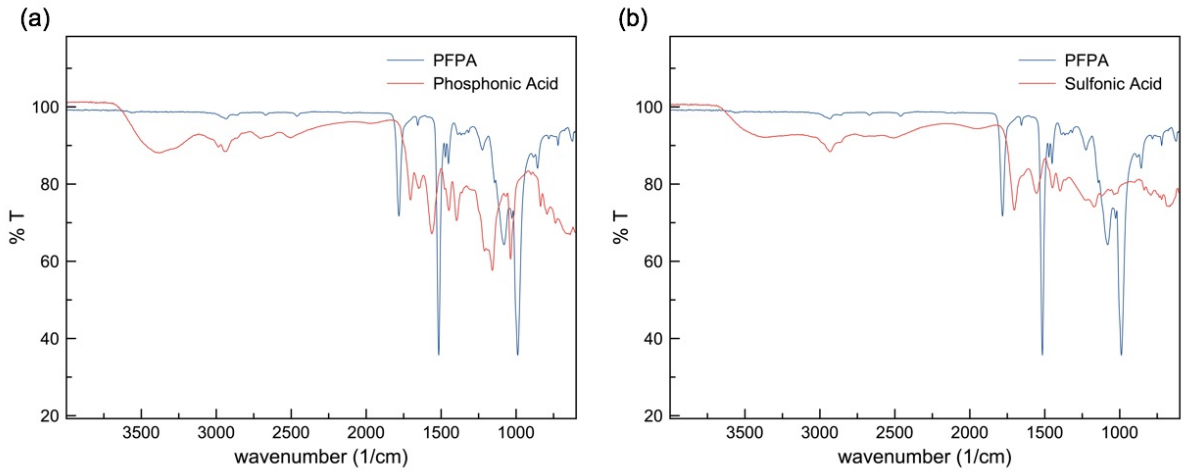


Figure S8. FTIR spectra of functionalized PPFPA (entry **1**, Table 1) with nucleophiles **1** (a) and **2** (b). Blue trace represents original polymer (PPFPA) and red trace represents functionalized polymer.

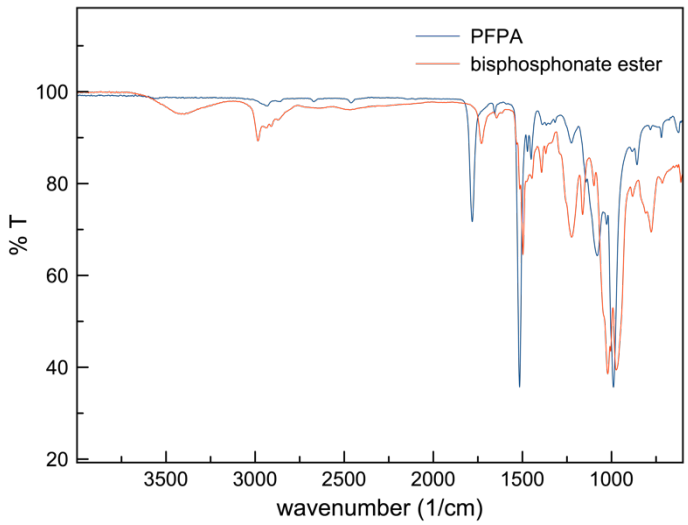


Figure S9. Infrared spectrum of poly(pentafluorophenyl acrylate) before and after functionalization with 2-hydroxyethyl aminobisphosphonate ester.

References

1. F. D. Jochum and P. Theato, *Macromolecules*, 2009, **42**, 5941-5945.
2. D. Roy, B. J. Nehilla, J. J. Lai and P. S. Stayton, *ACS Macro Lett.*, 2013, **2**, 132-136.
3. J. T. Lai, D. Filla and R. Shea, *Marcomolecules*, 2002, **35**, 6754-6756.
4. J. Han, S. Li, A. Tang and C. Gao, *Macromolecules*, 2012, **45**, 4966-4977.