

## Supplementary Information

### **RAFT-Polymerized Poly(hexafluoroisopropyl methacrylate)s as Precursor for Functional Water-Soluble Polymers**

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## 1. Spectroscopic data of HFIPMA

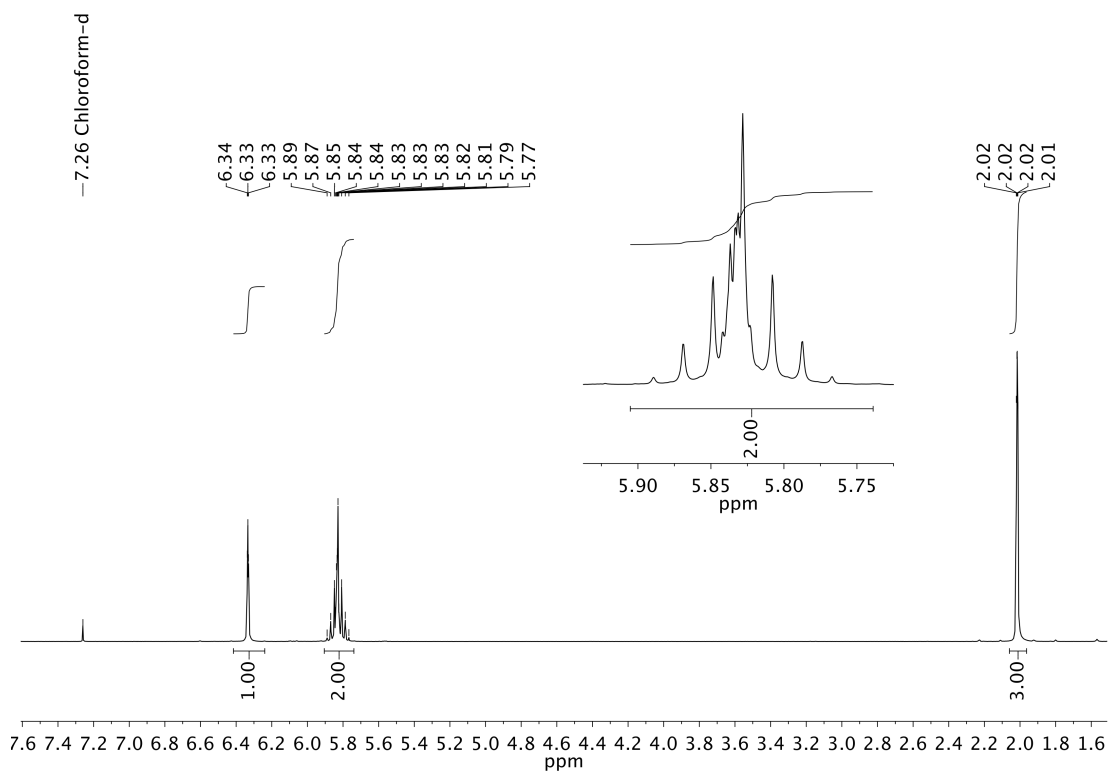


Figure S1:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) of HFIPMA.

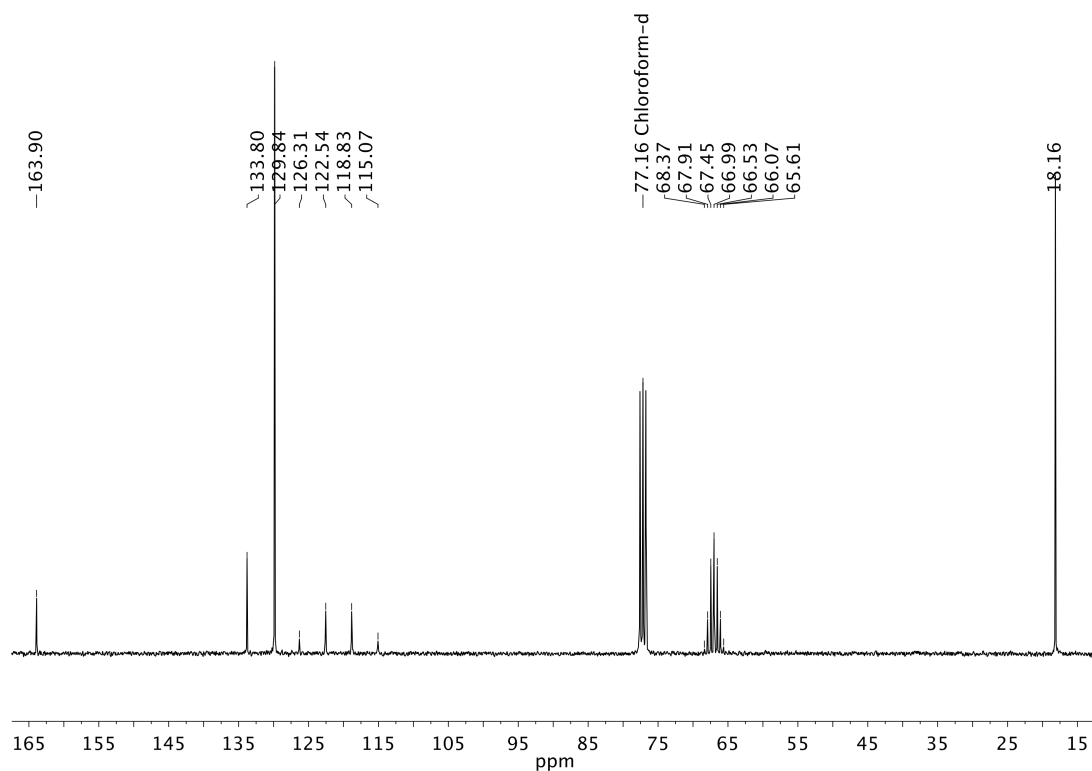


Figure S2:  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ) of HFIPMA.

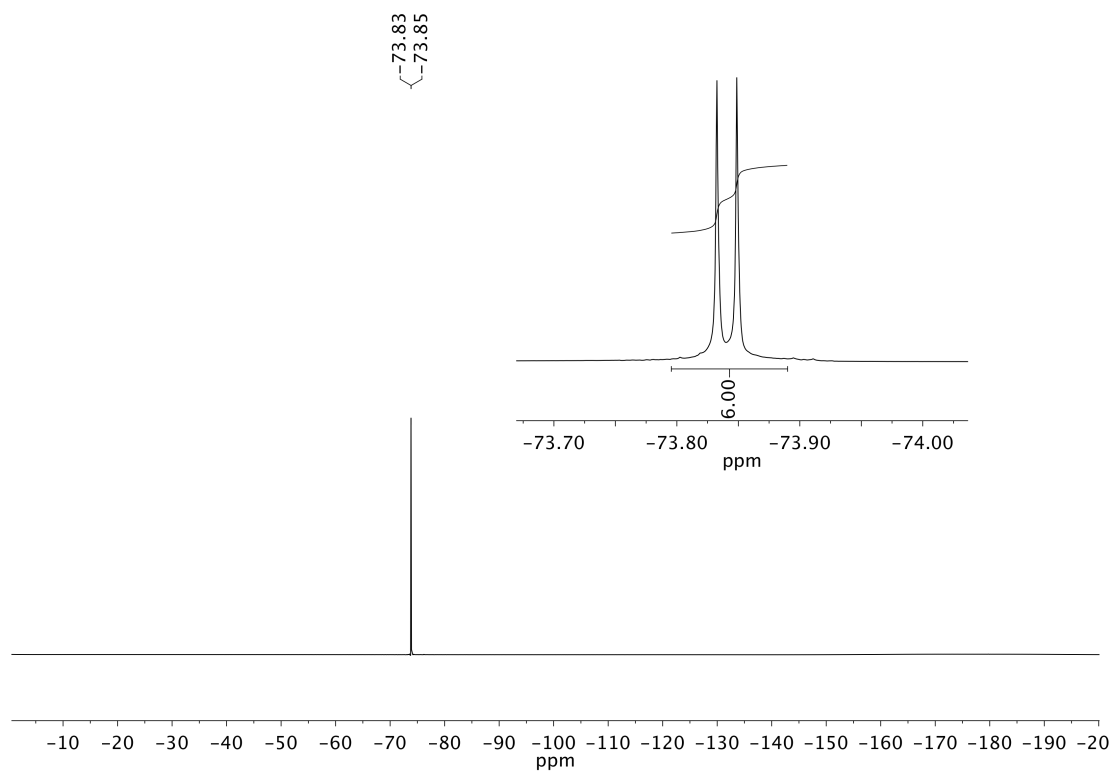


Figure S3:  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) of HFIPMA.

## 2. Solubility properties of P(HFIPMA)

Table S1: Solubility of PHFIPMA was studied in various common solvents.

Solvent	Solubility	Solvent	Solubility
THF	Yes	Water	No
Acetone	Yes	DMSO	No
Dioxane	Yes (at 65°C)	DMF	No
Diethyl Ether	Yes	Chloroform	No
n-Hexane	Yes	Dioxane	No (at 20°C)

### 3. Spectroscopic data of P(HFIPMA)

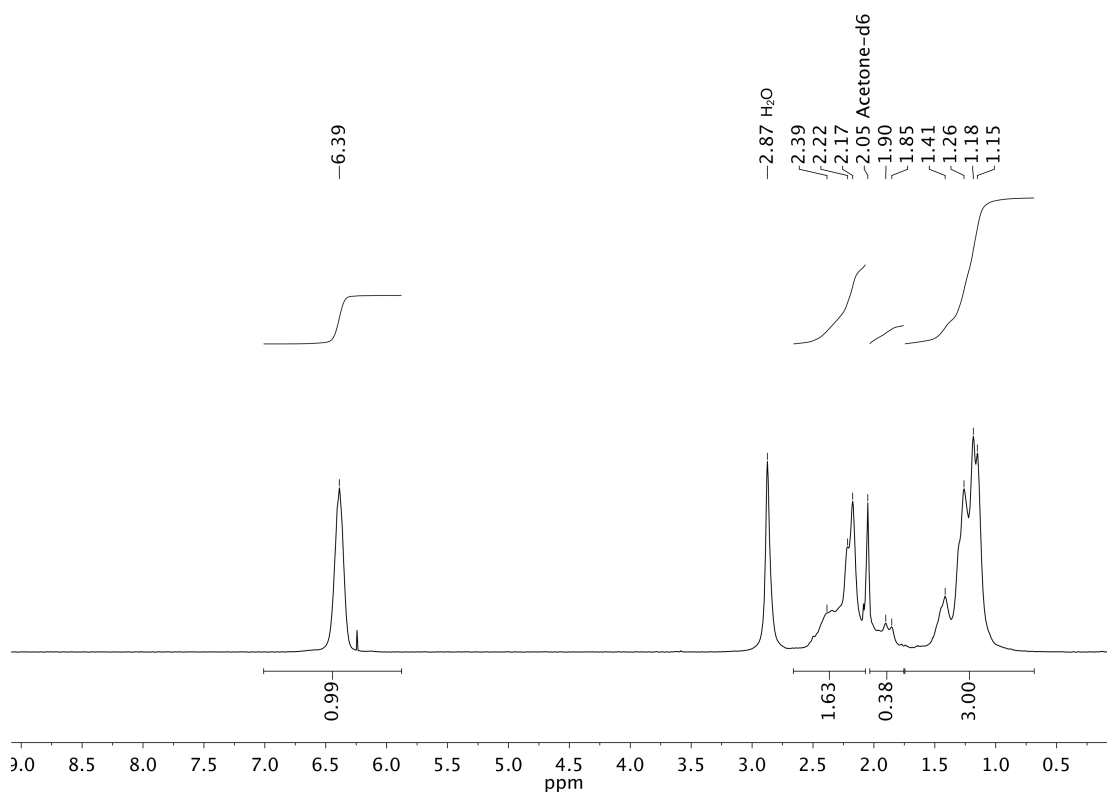


Figure S4:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) of P(HFIPMA) P2'.

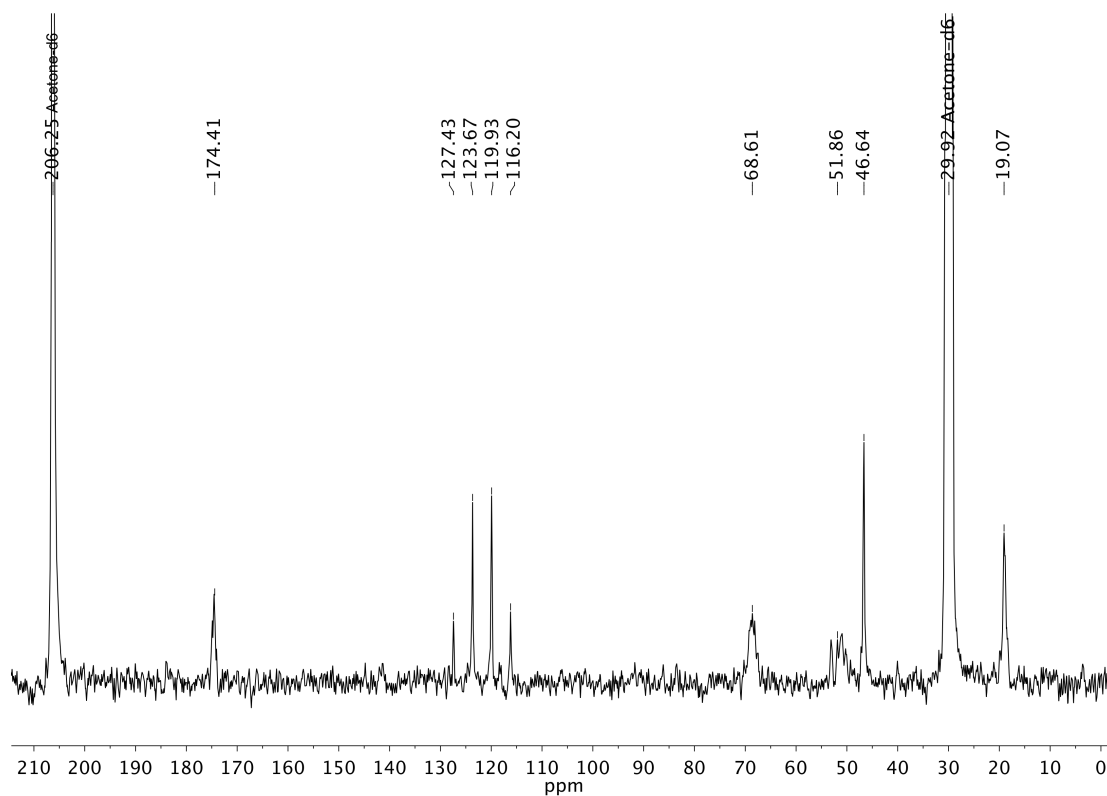


Figure S5:  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ) of P(HFIPMA) P2'.

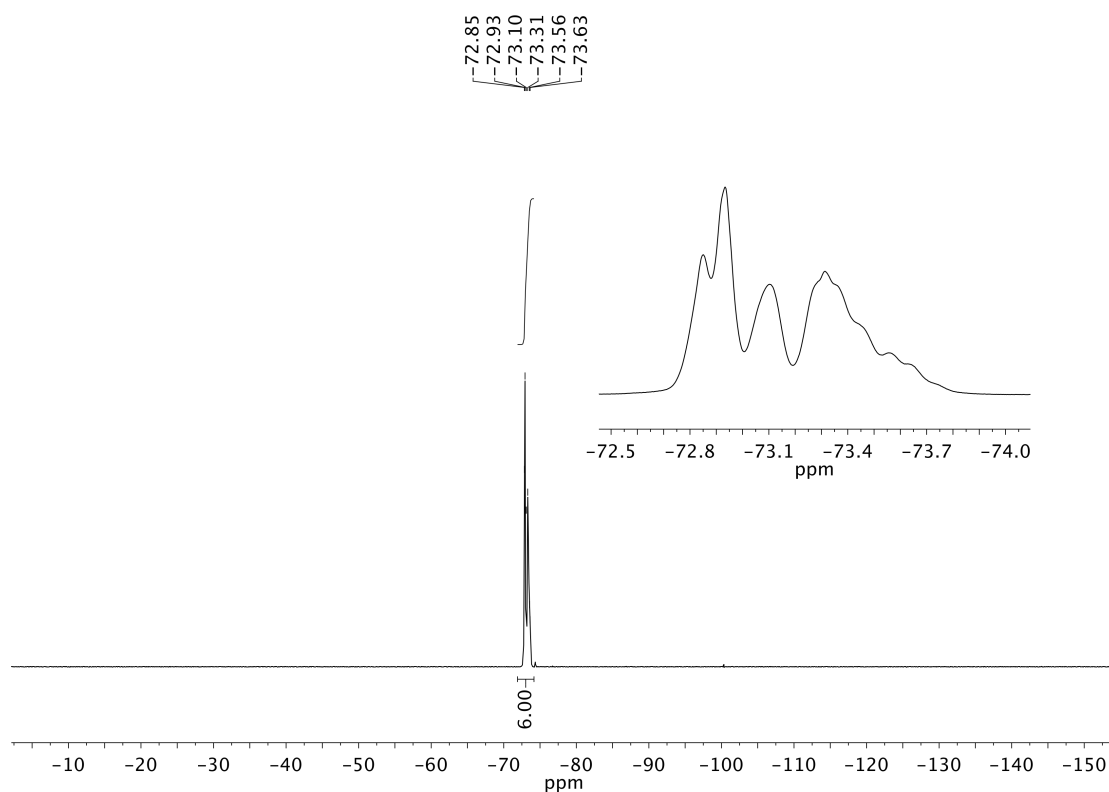


Figure S6:  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) of P(HFIPMA) P2'.

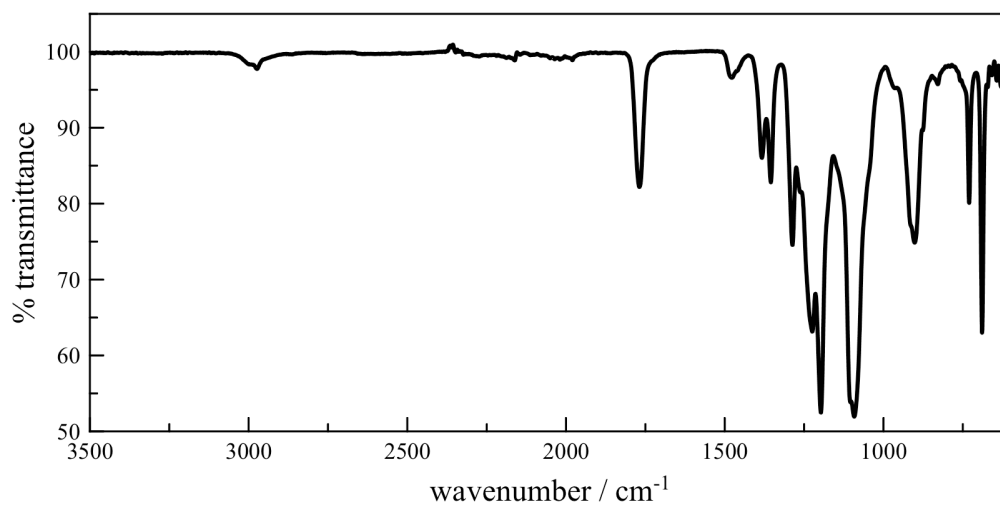


Figure S7: ATR-FT-IR of P(HFIPMA) P2'.

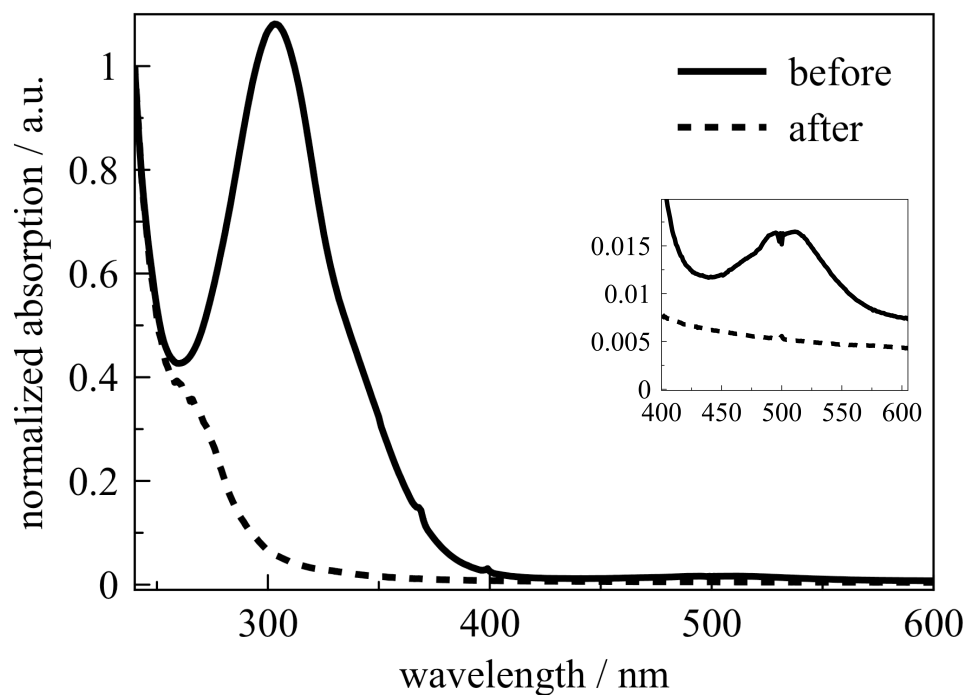


Figure S8: UV-vis of P(HFIPMA) P2 (before) and P2' (after) in dioxane.

#### 4. SEC data of P(HFIPMA)

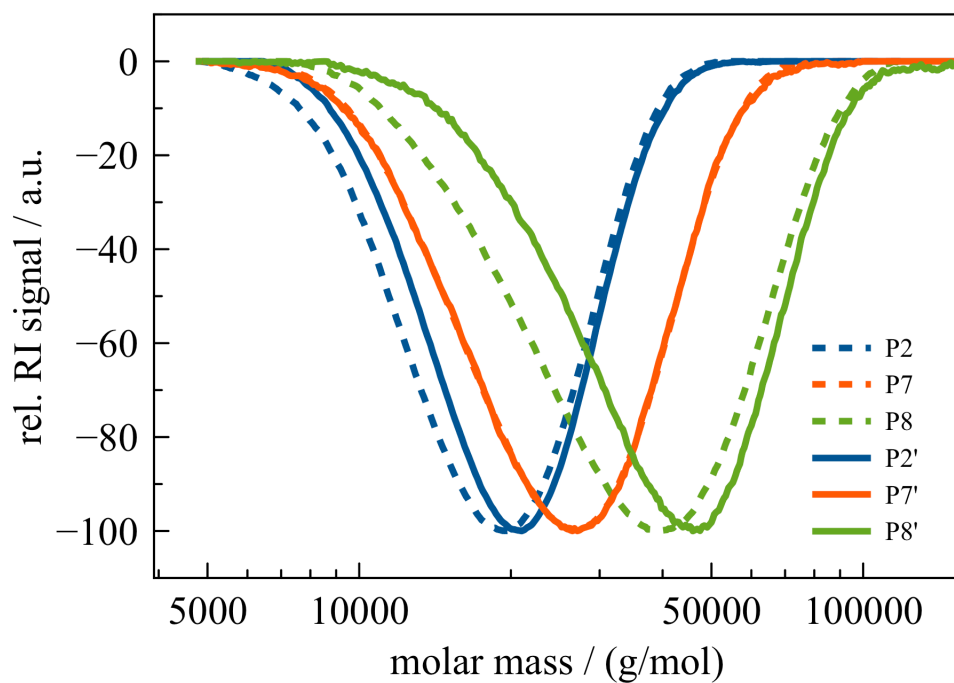


Figure S9: SEC traces of P(HFIPMA) polymers before (dashed lines) and after (solid line) dithiobenzoate end group removal.

### 5. Spectroscopic data of P(HFIPMA)-*b*-P(MEO<sub>3</sub>MA)

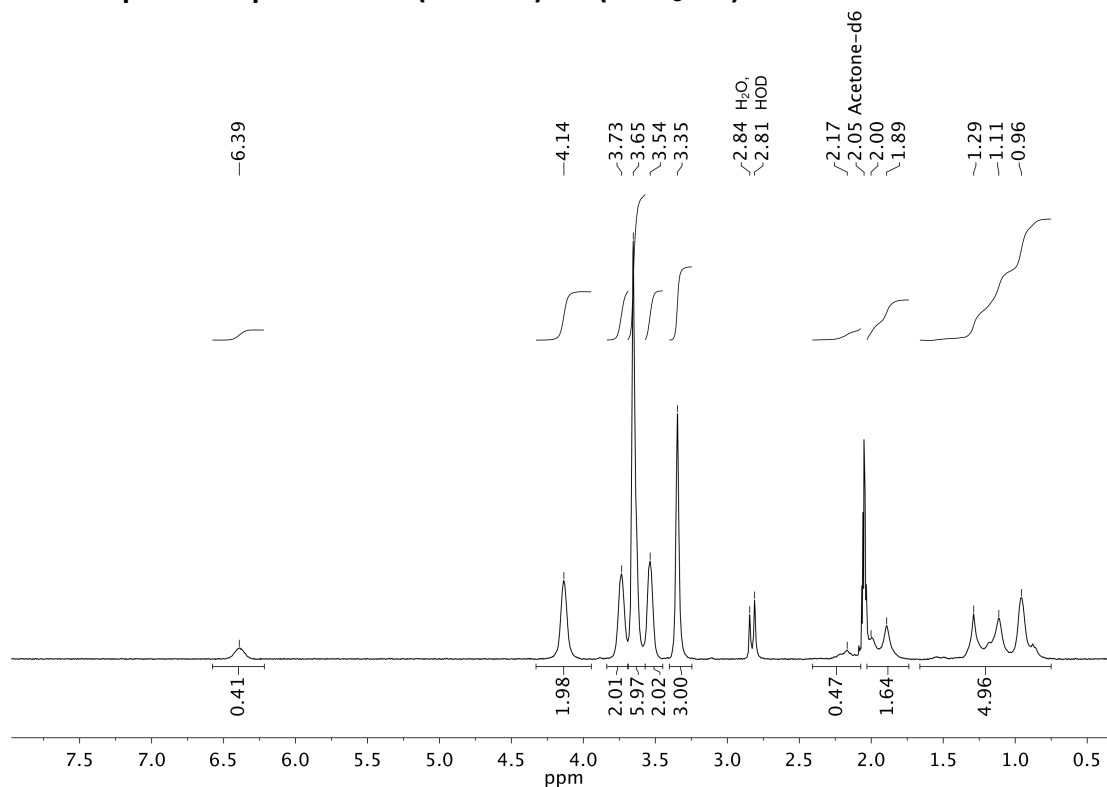


Figure S10: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of P(HFIPMA)-*b*-P(MEO<sub>3</sub>MA) P12'.

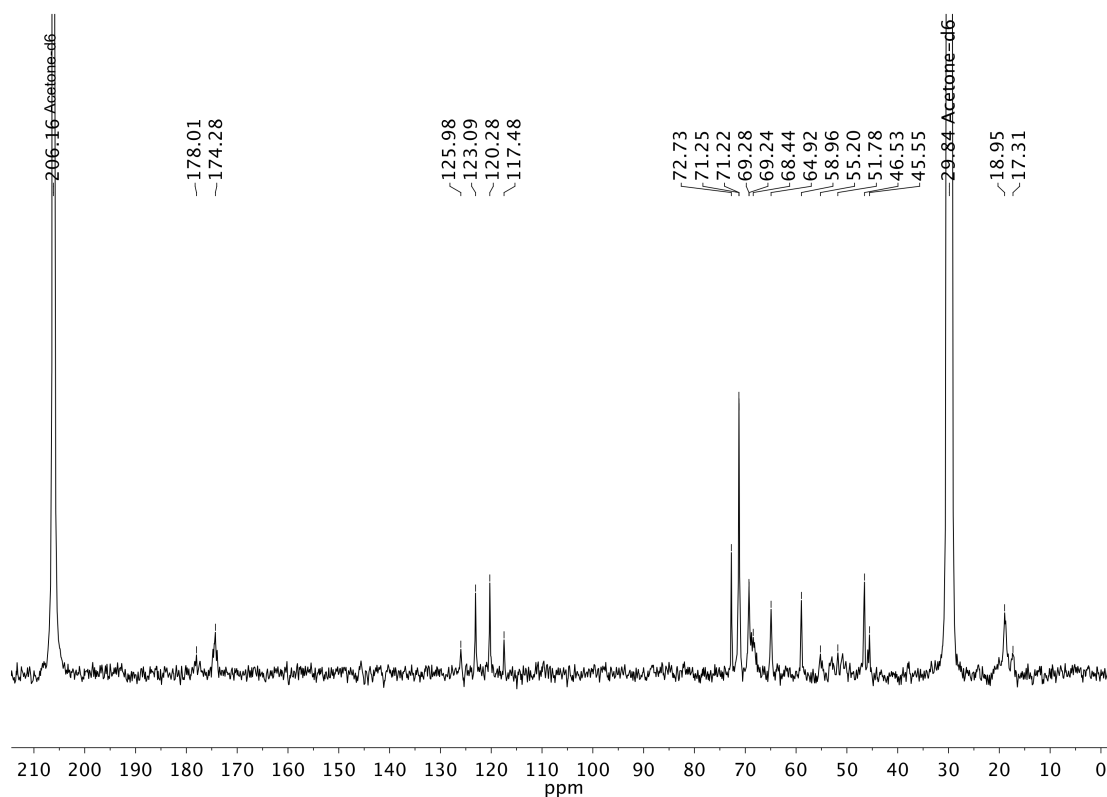


Figure S11: <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of P(HFIPMA)-*b*-P(MEO<sub>3</sub>MA) P12'.

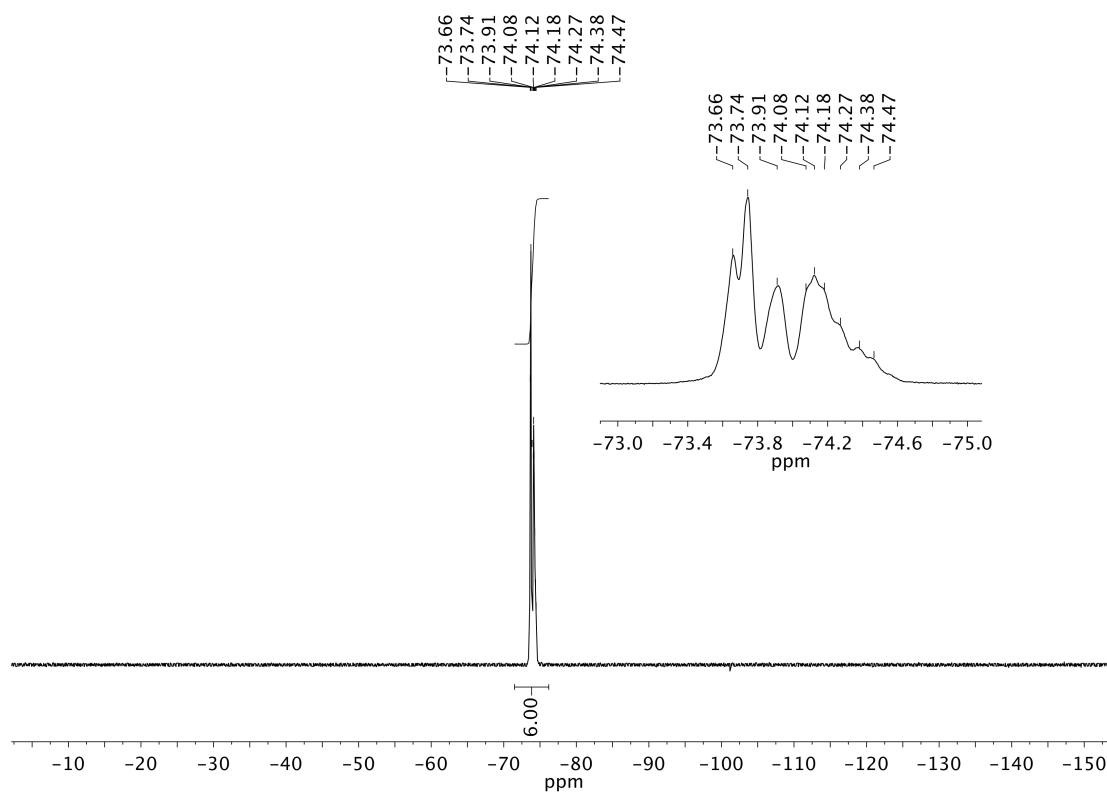


Figure S12:  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) of P(HFIPMA)-*b*-P(MEO<sub>3</sub>MA) P12'.

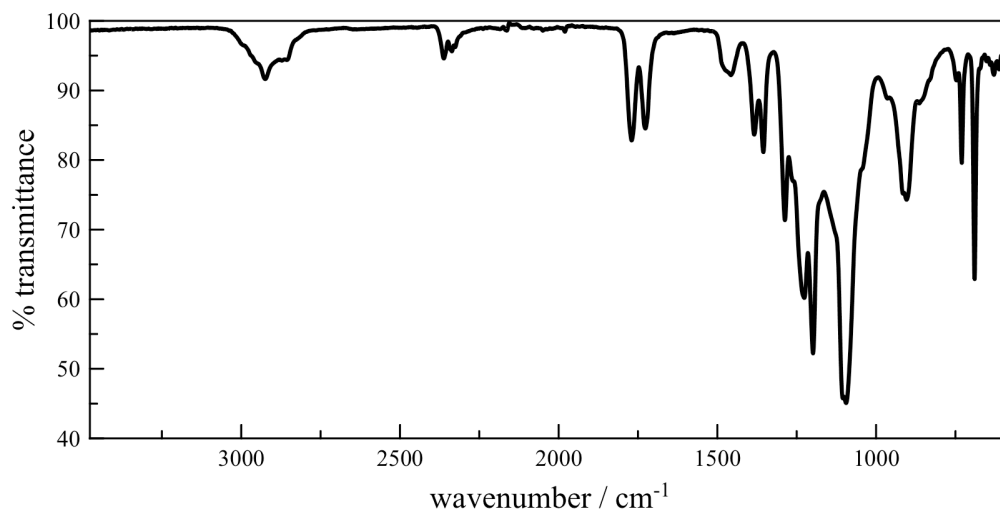


Figure S13: ATR-FT-IR of P(HFIPMA)-*b*-P(MEO<sub>3</sub>MA) P12'.



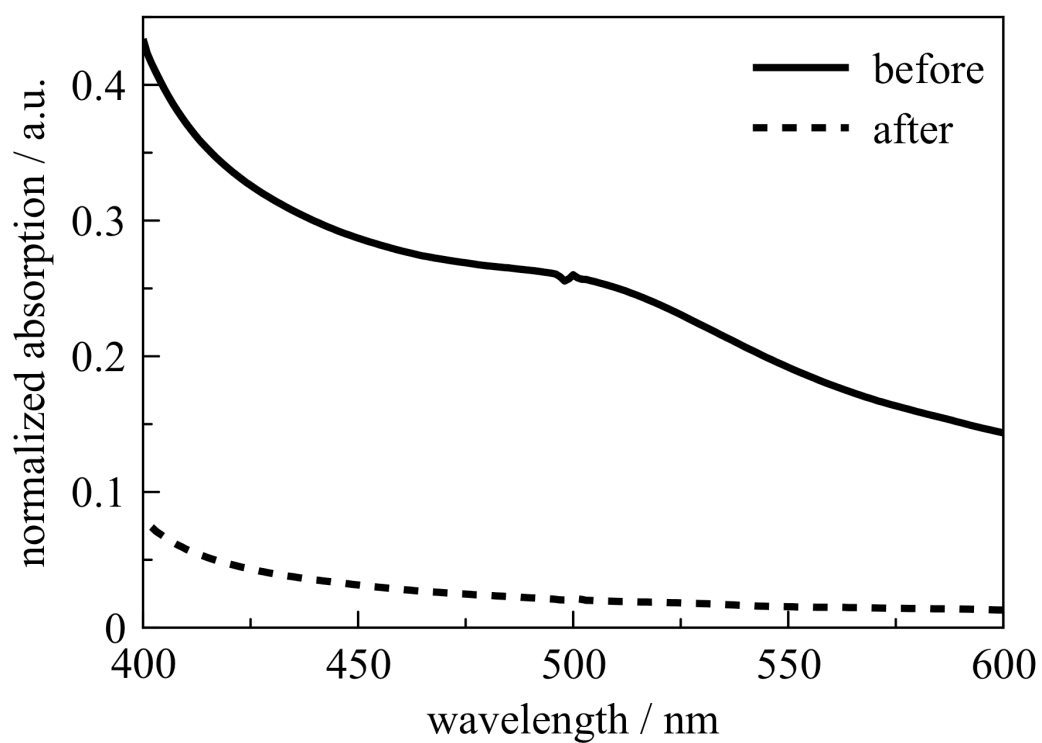


Figure S14: UV-vis of P(HFIPMA) P12 (before) and P12' (after) in acetone.

## 6. Reaction monitoring: Polymer analogous model reaction of P(HFIPMA)

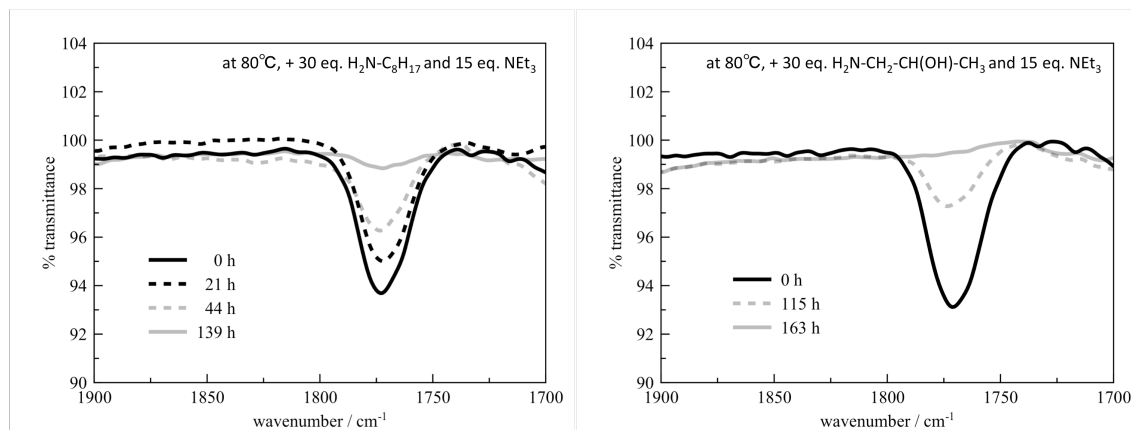


Figure S15: ATR-FT-IR reaction monitoring - polymer analogous reaction of P(HFIPMA) with n-octylamine (left) and 2-hydroxypropyl amine (right).

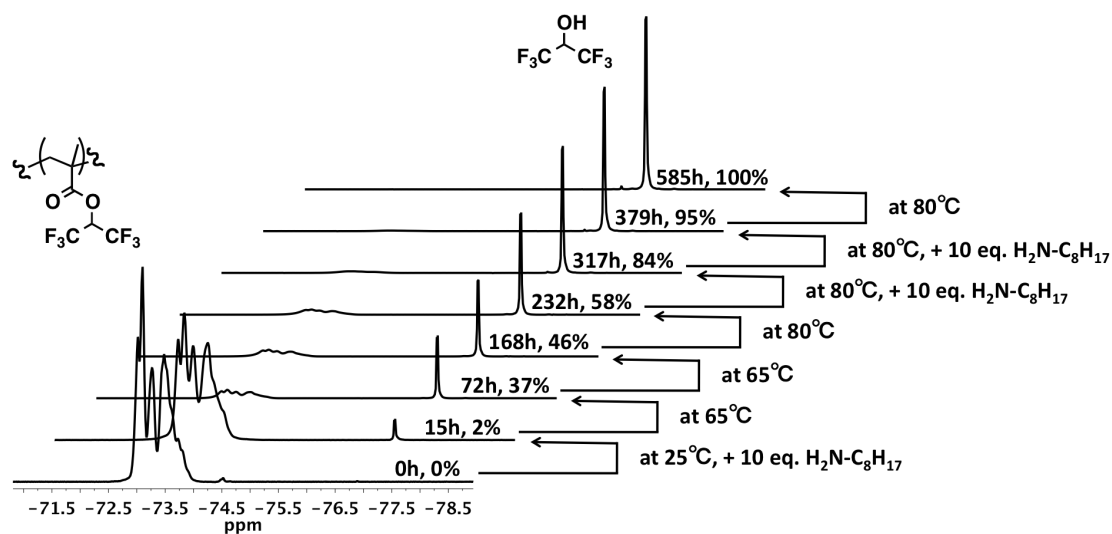


Figure S16:  $^{19}\text{F}$  NMR (376 MHz,  $\text{THF-}d_8$ ) reaction monitoring - polymer analogous reaction of P(HFIPMA) with n-octylamine.

## 7. Polymer analogous reaction of P(HFIPMA) with methoxy tri(ethylene glycol) amine

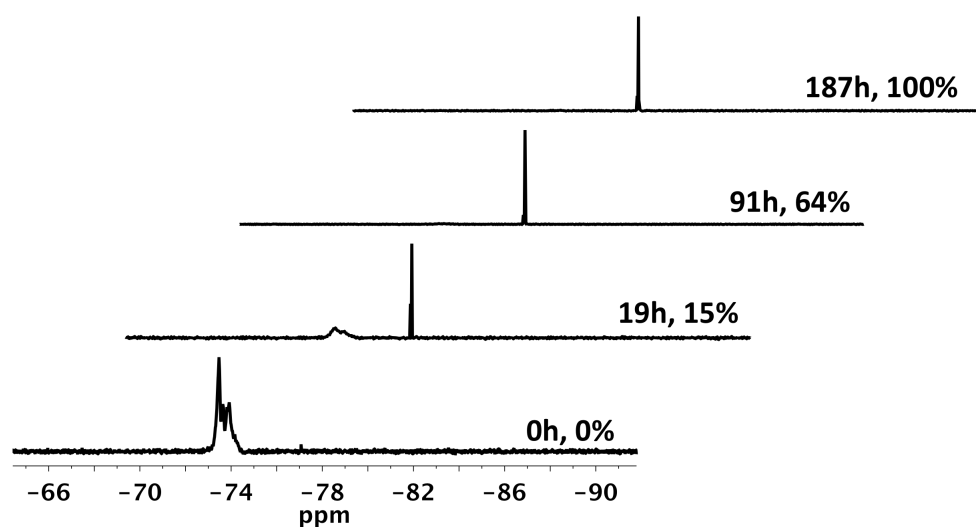


Figure S17:  $^{19}\text{F}$  NMR (376 MHz, acetone- $d_6$ ) P(HFIPMA) P1' with methoxy tri(ethylene glycol) amine.

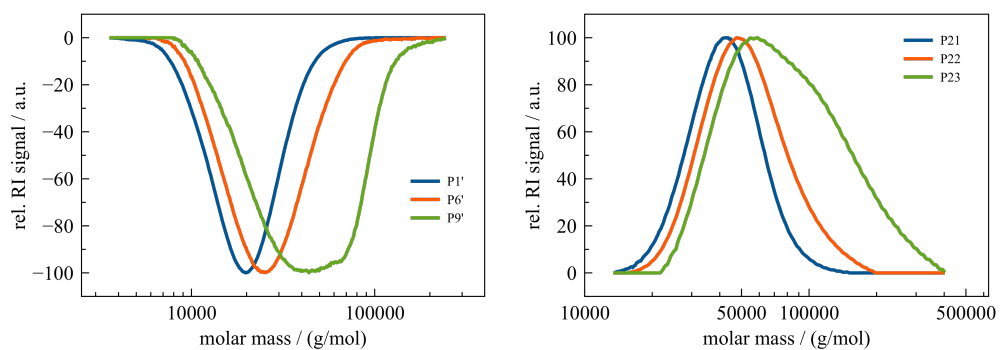


Figure S18: SEC traces of P(HFIPMA) polymers before (left, SEC in THF) and after treatment with methoxy tri(ethylene glycol) amine affording P(MEO<sub>3</sub>MAM) (right, SEC in HFIP).

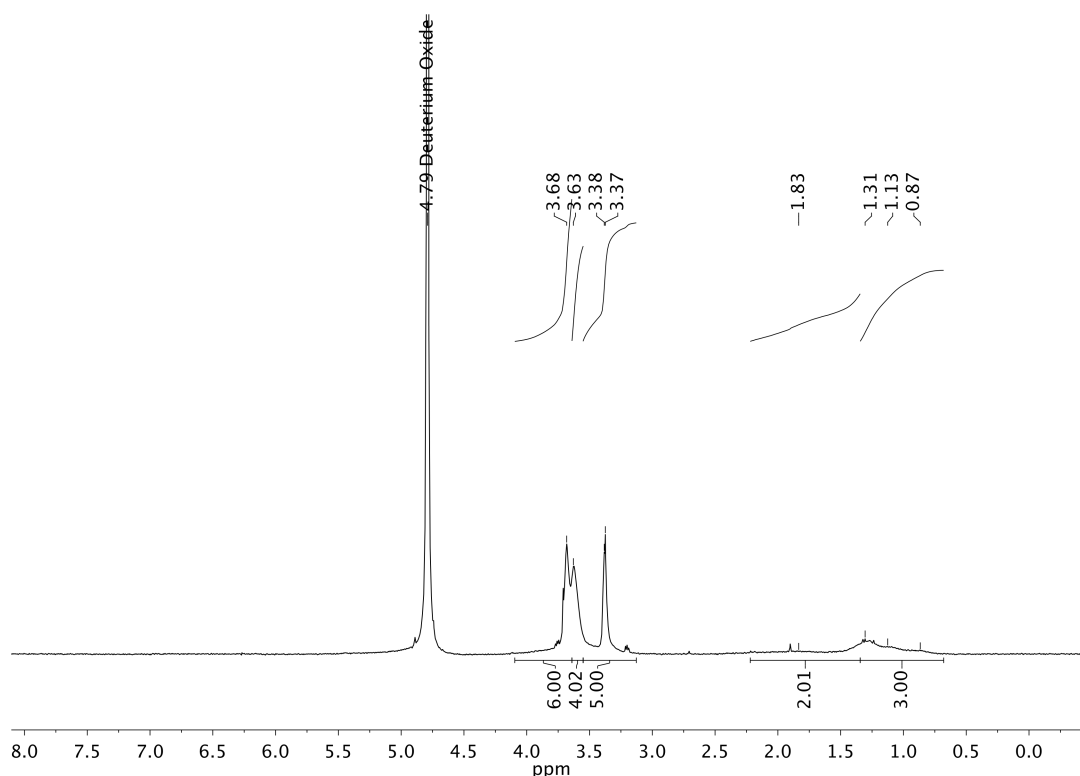


Figure S19:  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ ) of P(MEO<sub>3</sub>MAM) P21.

## 8. Polymer analogous reaction of P(HFIPMA) with 2-hydroxypropyl amine

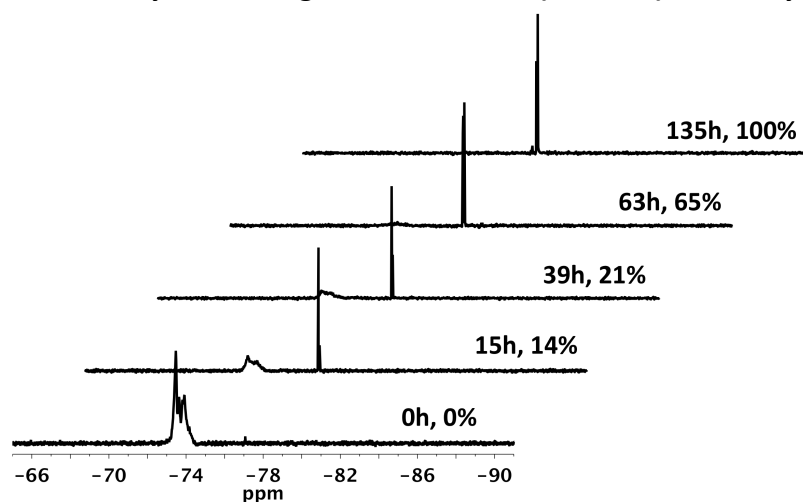


Figure S20:  $^{19}\text{F}$  NMR (376 MHz, acetone- $d_6$ ) P(HFIPMA) P1' with 2-hydroxypropyl amine.

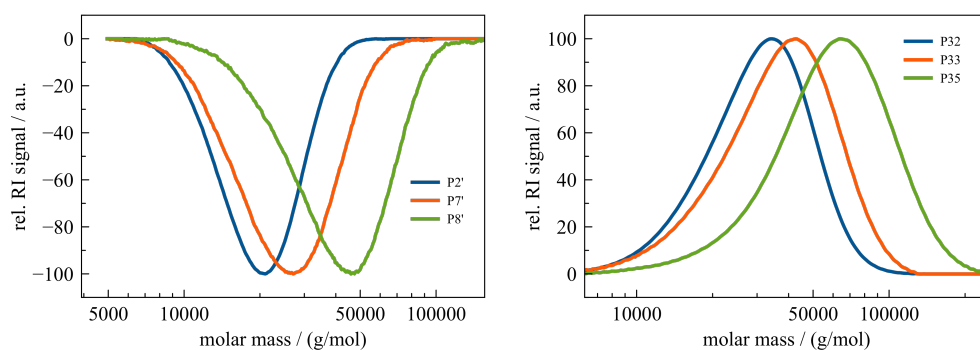


Figure S21: SEC traces of P(HFIPMA) polymers before (left, SEC in THF) and after treatment with 2-hydroxypropyl amine affording P(HPMA) (right, SEC in HFIP).

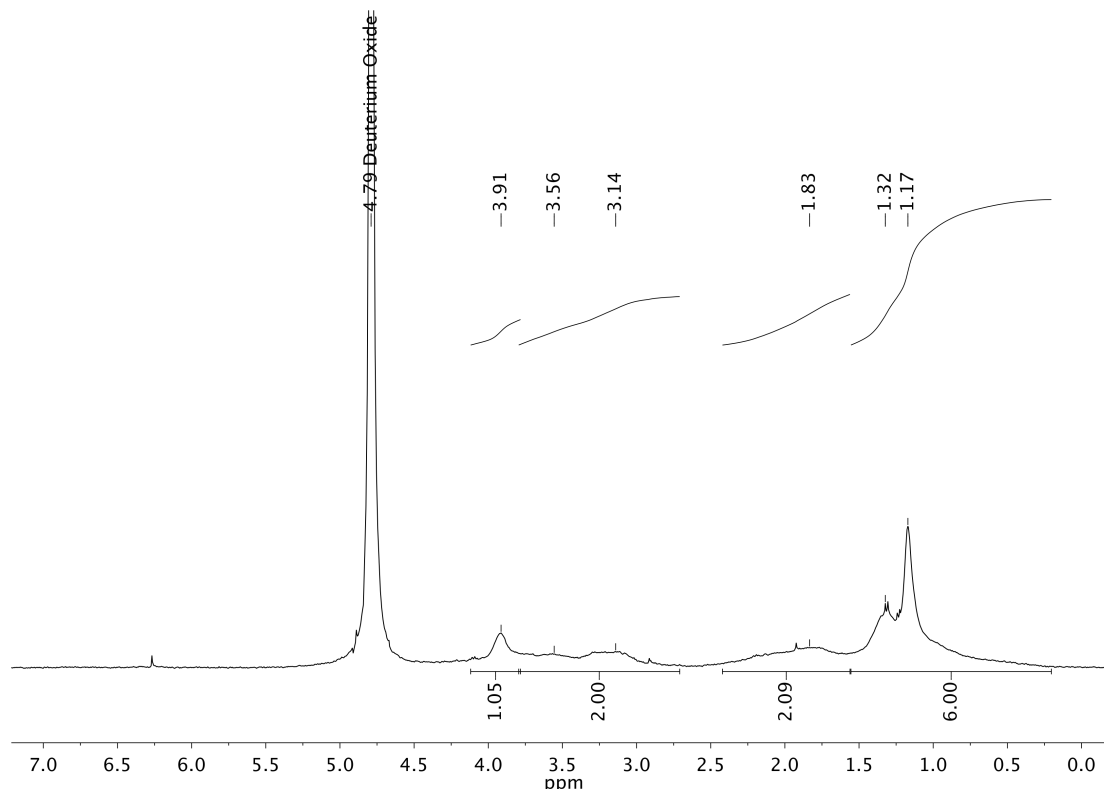


Figure S22:  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ ) of P(HPMA) P31.

### 9. Sequential polymer analogous reaction of P(HFIPMA) with Oregon Green cadaverine and 2-hydroxypropyl amine

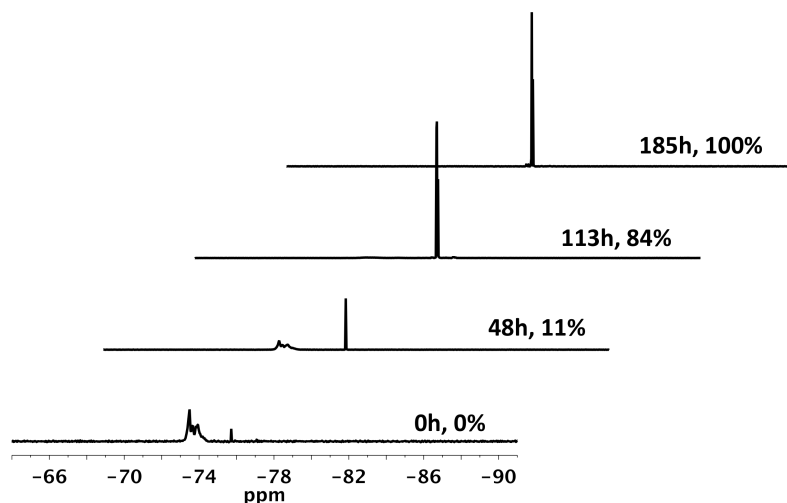


Figure S23:  $^{19}\text{F}$  NMR (376 MHz, acetone- $d_6$ ) P(HFIPMA) P1' with Oregon Green cadaverine and 2-hydroxypropyl amine.

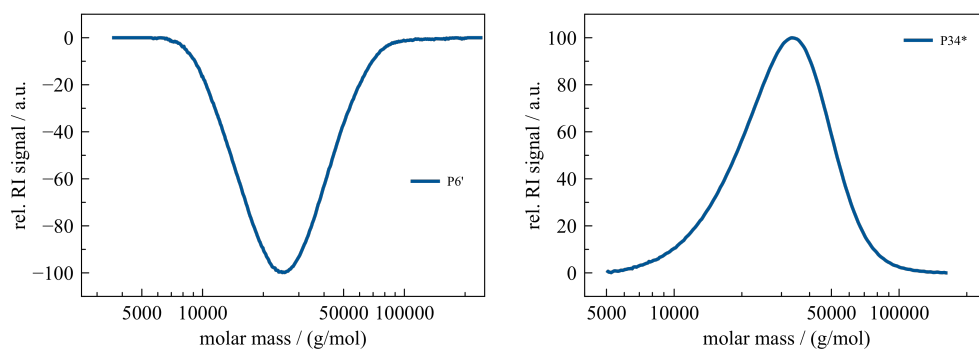


Figure S24: SEC traces of P(HFIPMA) P6' before (left, SEC in THF) and after treatment with Oregon Green cadaverine and 2-hydroxypropyl amine affording Oregon Green labelled P(HPMA) P34\* (right, SEC in HFIP).

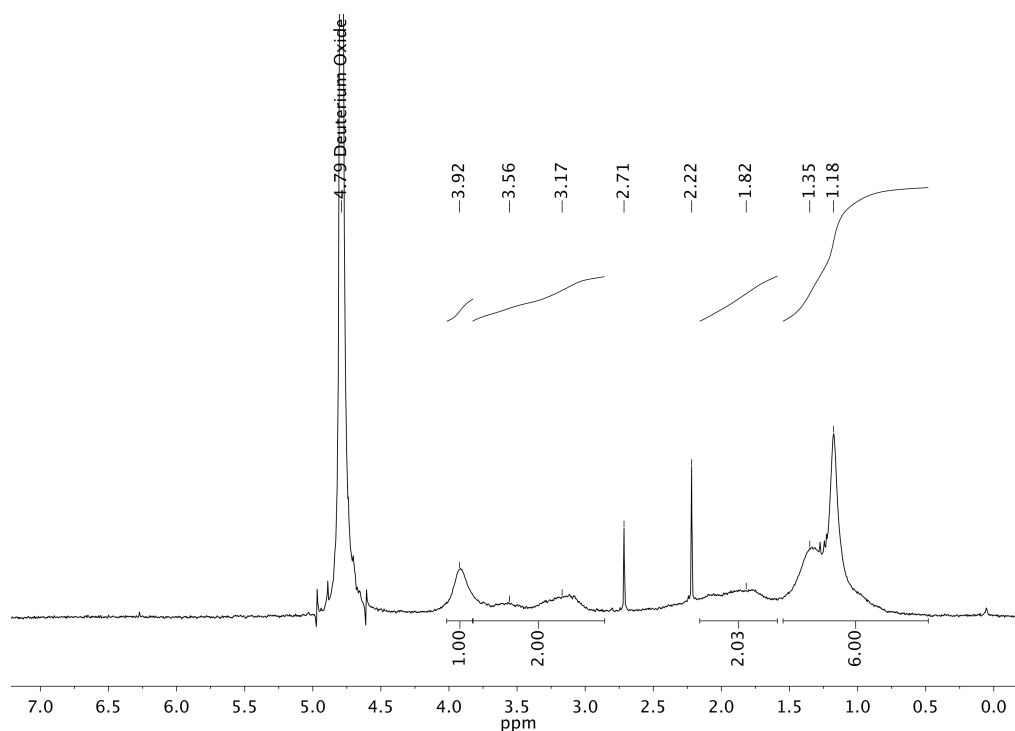


Figure S25:  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ ) of P(HPMA) P34\*.

### 10. Polymer analogous reaction of P(HFIPMA) with 3-(dimethylamino)-1-propylamine

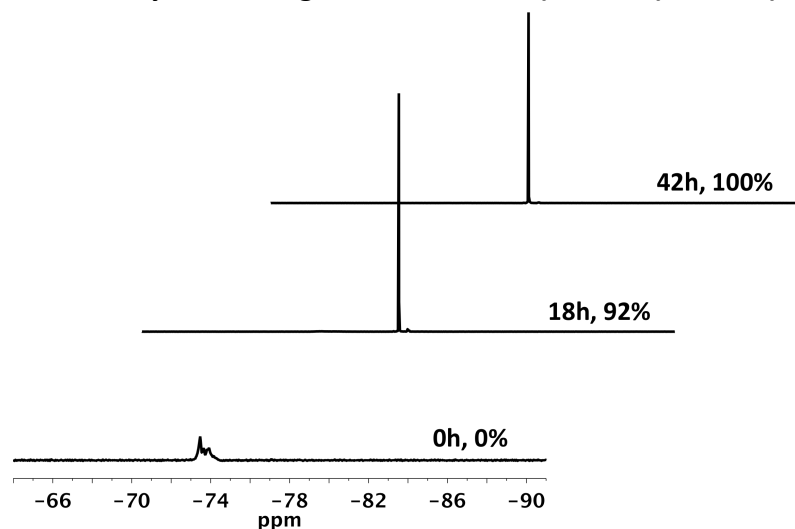


Figure S26:  $^{19}\text{F}$  NMR (376 MHz, acetone- $d_6$ ) P(HFIPMA) P1' with 3-(dimethylamino)-1-propylamine.

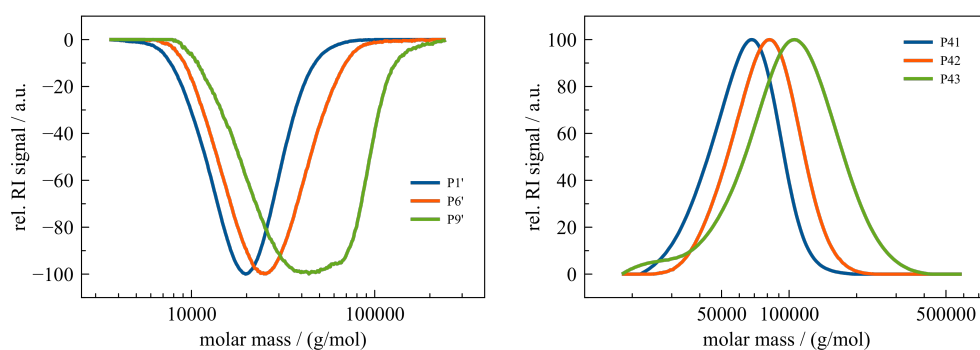


Figure S27: SEC traces of P(HFIPMA) polymers before (left, SEC in THF) and after treatment with 3-(dimethylamino)-1-propylamine affording P(DMAPMAM) (right, SEC in HFIP).

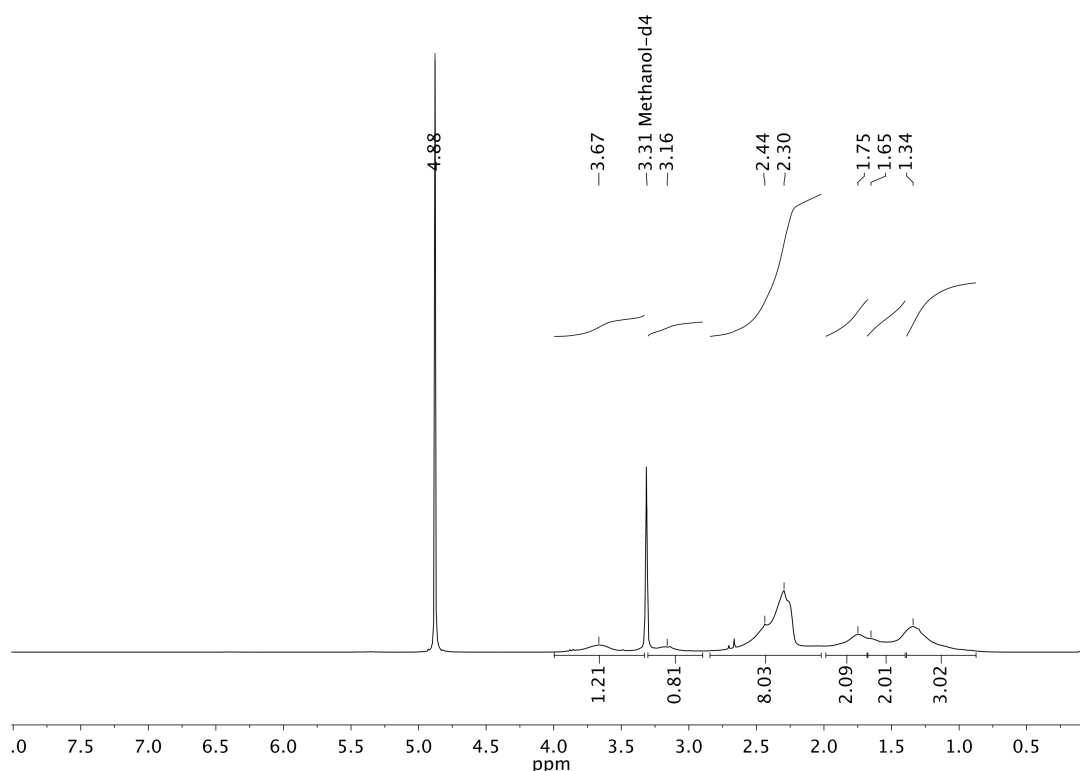


Figure S28:  $^1\text{H}$  NMR (400 MHz, Methanol- $d_4$ ) of P(DMAPMAM) P41.

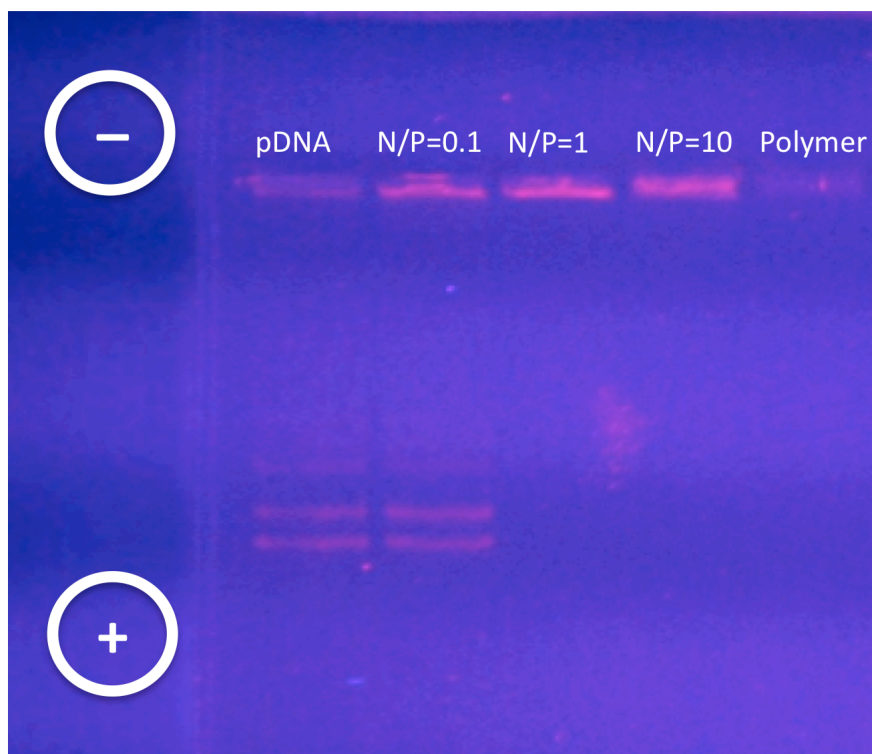
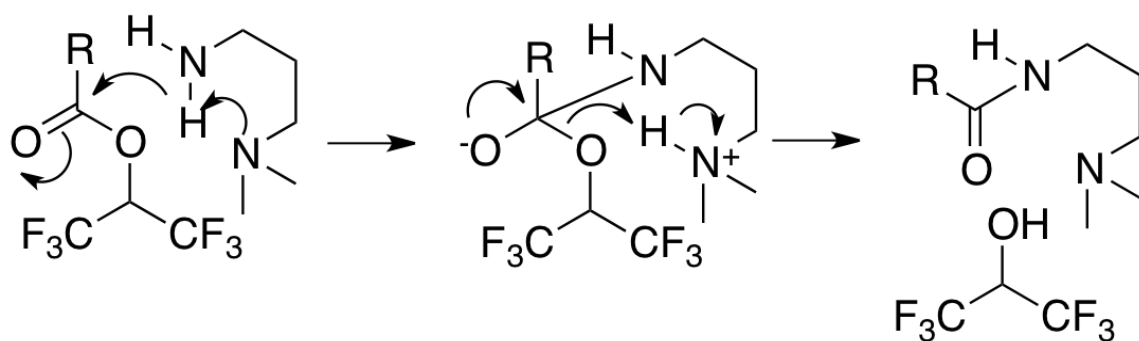


Figure S29: Agarose gel electrophoresis of pDNA complexed with different ratios of P(DMAPMAM) P41.



Scheme S1: Proposed reaction mechanism P(HFIPMA) aminolysis with 3-(dimethylamino)-1-propylamine.

### 11. Polymer analogous reaction of P(HFIPMA)-*b*-P(MEO<sub>3</sub>MA) with 3-(dimethylamino)-1-propylamine

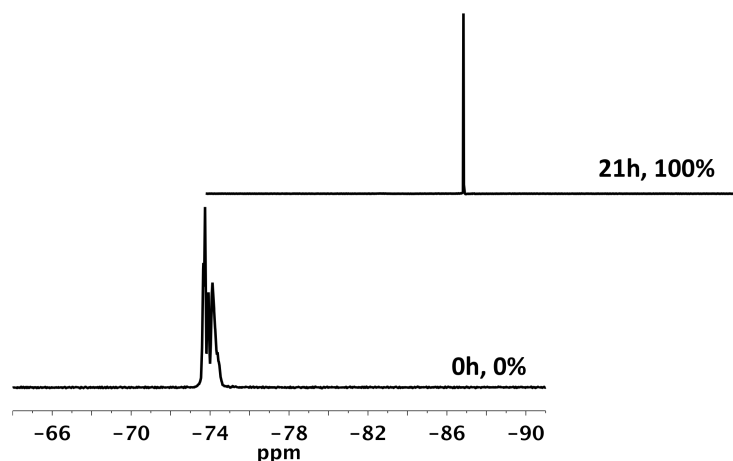


Figure S30: <sup>19</sup>F NMR (376 MHz, acetone-*d*<sub>6</sub>) P(HFIPMA)-*b*-P(MEO<sub>3</sub>MA) P11' with 3-(dimethylamino)-1-propylamine.

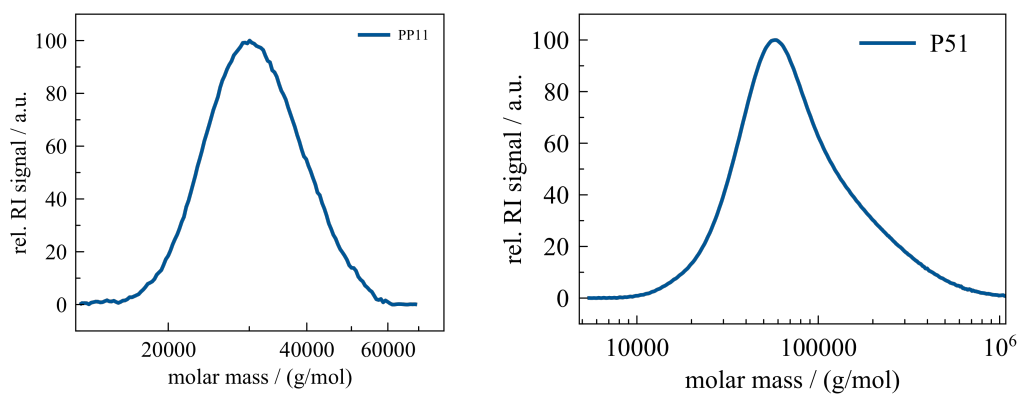


Figure S31: SEC traces of P(HFIPMA)-*b*-P(MEO<sub>3</sub>MA) P11 before (left, SEC in THF) and after treatment with 3-(dimethylamino)-1-propylamine affording P(HFIPMA)-*b*-P(DMAPMAM) P51 (right, SEC in HFIP).

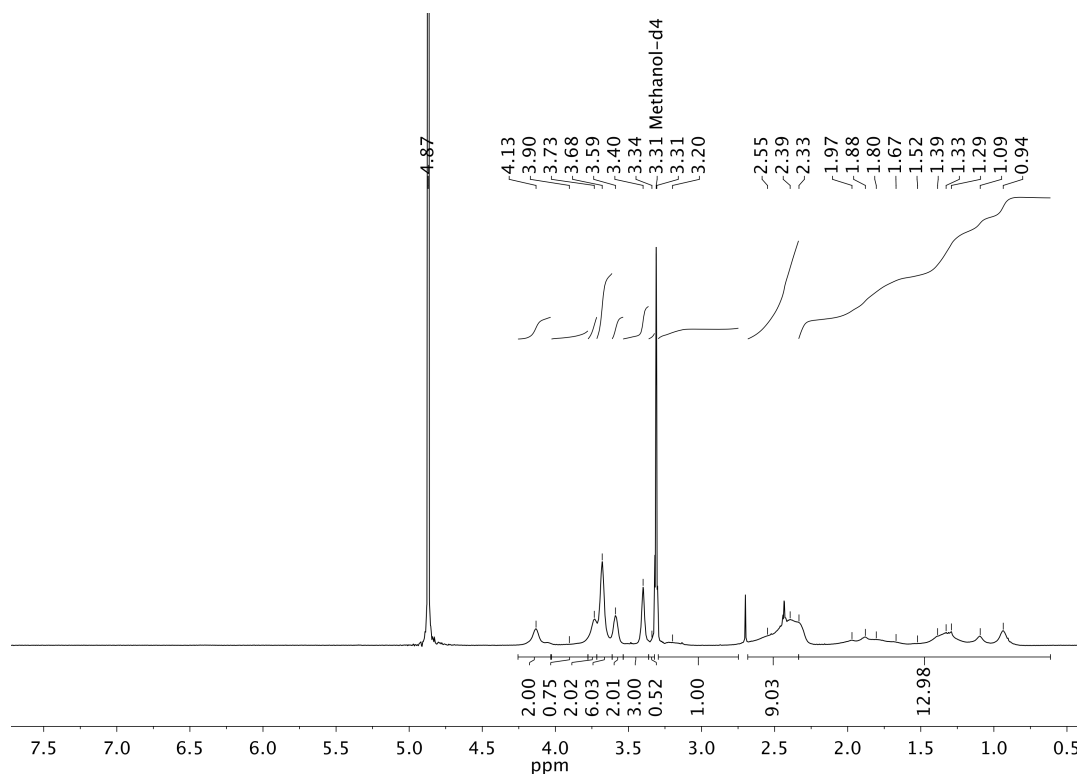


Figure S32: <sup>1</sup>H NMR (400 MHz, Methanol-*d*<sub>4</sub>) of P(HFIPMA)-*b*-P(DMAPMAM) P51.