Supplementary Information

Direct synthesis of fluorinated hyperbranched polyethylenes by chain walking copolymerization

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Contents

1. NMR Spectra

Figure S1. ^{1}H NMR spectrum of the hyperbranched polyethylene obtained in run 1.

The branch density (branches per 1000 carbons) was determined from the integrated intensities of methyl protons in the ^{1}H NMR spectrum according to the following equation:

$$\text{Branches/1000C} = \frac{I(CH3) \times 2}{I(total) \times 3} \times 1000$$

Figure S2. ^{13}C NMR spectrum of the hyperbranched polyethylene obtained from run 1.

Figure S3. ^{1}H NMR spectrum of the polymer obtained from run 2.

Figure S4. ^{1}H NMR spectrum of the polymer obtained from run 3.

The HFIPA comonomer content (mol %) was calculated from the ^{1}H NMR integrals according to the following equation:

$$\text{Comonomer content (mol \%)} = \frac{I(a')}{I(a') + \frac{I(CH + CH2 + CH3) - I(a') * 1}{4}} \times 100\%$$

Figure S5. ^1H-^1H COSY of the polymer obtained from run 3.

Figure S6. DEPT-135 spectrum of the polymer obtained from run 3.

Figure S7. ^{1}H-^{13}C HSQC of the polymer obtained from run 3.

Figure S8. ^{1}H-^{13}C HMBC of the polymer obtained from run 3.

Figure S9. ^{19}F NMR spectra of HFIPA and the polymer obtained from run 3.

Figure S10. ^{1}H NMR spectrum of polymer obtained from run 4.

Figure S11. ^{1}H NMR spectrum of polymer obtained from run 5.

The APFB comonomer content (mol %) was calculated from the ^{1}H NMR integrals according to the following equation:

$$\text{Comonomer content (mol \%)} = \frac{\frac{I(c')/2}{\frac{I(c')}{2} + \frac{I(CH + CH2 + CH3) - 3 * I(c')/2}{4}}} \times 100\%$$

Figure S12. ^{13}C NMR spectrum of the polymer obtained from run 5.

Figure S13. ^{1}H-^{1}H COSY of the polymer obtained from run 5.

Figure S14. DEPT-135 of the polymer obtained from run 5.

Figure S15. ^{1}H-^{13}C HSQC of the polymer obtained from run 5.

Figure S16. ^{1}H-^{13}C HMBC of the polymer obtained from run 5.

Figure S17. ^{19}F NMR spectra of APFB and the polymer obtained from run 5.

Figure S18. ^{1}H NMR spectrum of 13FOAE.

Figure S19. ^{13}C NMR spectrum of 13FOAE.

Figure S20. ^{1}H NMR spectrum of polymer obtained from run 6.

Figure S21. ^{1}H NMR spectrum of polymer obtained from run 7.

The13FOAE comonomer content (mol %) was calculated from the ^{1}H NMR integrals according to the following equation:

$$\text{Comonomer content (mol \%)} = \frac{I(f')/2}{\frac{I(f')}{2} + \frac{I(CH + CH2 + CH3) - 3 * I(f')/2}{4}} \times 100\%$$

Figure S22. ^{1}H-^{1}H COSY of the polymer obtained from run 7.

Figure S23. DEPT-135 of the polymer obtained from run 7.

Figure S24. ^{1}H-^{13}C HSQC of the polymer obtained from run 7.

Figure S25. ^{1}H-^{13}C HMBC of the polymer obtained from run 7.

Figure S26. ^{19}F NMR spectra of 13FOAE and the polymer obtained from run 7.

Figure S27. ^{1}H NMR spectrum of polymer obtained from run 8.

Figure S28. ^{1}H NMR spectrum of polymer obtained from run 9.

Figure S29. ^{13}C NMR spectrum of polymer obtained from run 9.

2. DSC thermograms of the copolymers

Figure S30. DSC thermogram of the polymer obtained from run 1.

Figure S31. DSC thermogram of the polymer obtained from run 2.

Figure S32. DSC thermogram of the polymer obtained from run 3.

Figure S33. DSC thermogram of the polymer obtained from run 4.

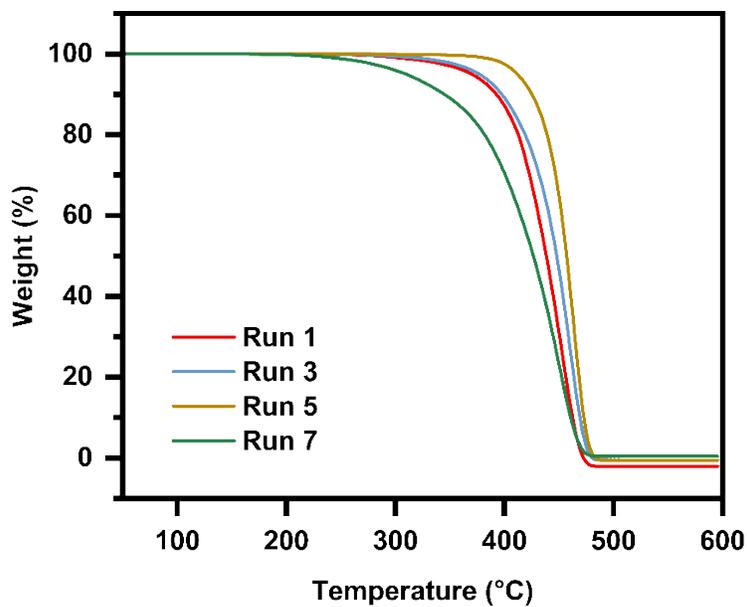**Figure S34.** DSC thermogram of the polymer obtained from run 5.

Figure S35. DSC thermogram of the polymer obtained from run 6.

Figure S36. DSC thermogram of the polymer obtained from run 7.

Figure S37. DSC thermogram of the polymer obtained from run 8.

Figure S38. DSC thermogram of the polymer obtained from run 9.

3. TGA curves

Figure S39. TGA curves of polymer obtained from runs 1, 3, 5 and 7. Measurements were conducted in N_2 at a heating rate of 10 °C/min.

Table S1. TGA data of polymers obtained from runs 1, 3, 5 and 7.

Run	$T_{5\%}$ (°C) [a]	T_{max} (°C) [b]
1	369.9	452.5
3	377.0	460.4
5	411.9	463.6
7	309.5	449.8

[a] Thermal degradation temperature at 5% weight loss, [b] temperature at maximum weight loss rate.
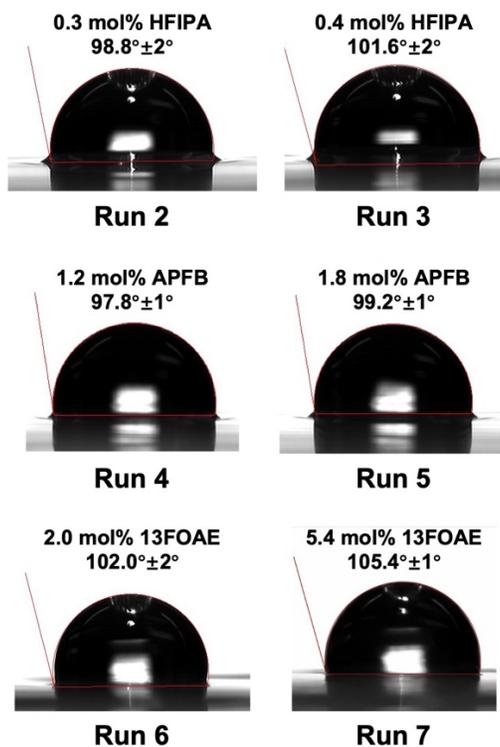
4. WCA

Figure S40. WCA of copolymers.

5. Digital images of representative copolymers

Figure S41. Digital images of representative copolymers obtained from runs 1, 3, 5 and 7.