Electronic Supplementary Information

Aluminum-catalyzed statistical copolymerization of mono-, tri- and penta-fluorophenyl glycidyl ether with ethylene oxide and epichlorohydrin

Fang Guo, Ming Deng, Fan Li, and Shoulong Chen

State Key Laboratory of Fine Chemicals, Department of Polymer Science and Engineering, School of Chemical Engineering, Dalian University of Technology, Dalian 116012, China

Content

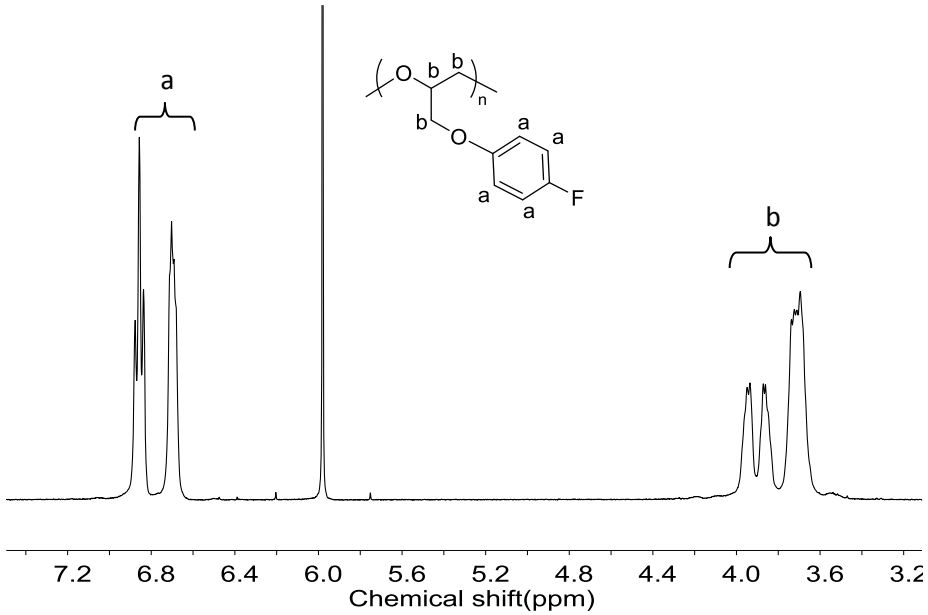


Fig. S1. ^{1}H-NMR spectrum of a MFPGE homopolymer (Table 1, Run 1)

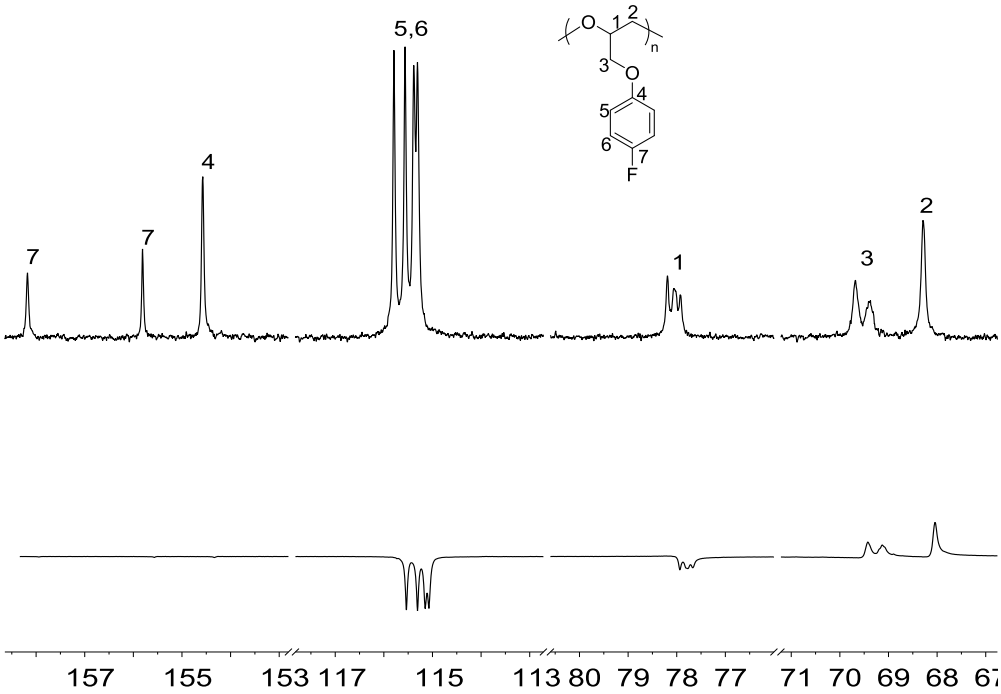


Fig. S2. 135DEPT-^{13}C-NMR spectrum of a MFPGE homopolymer (Table 1, Run 1)

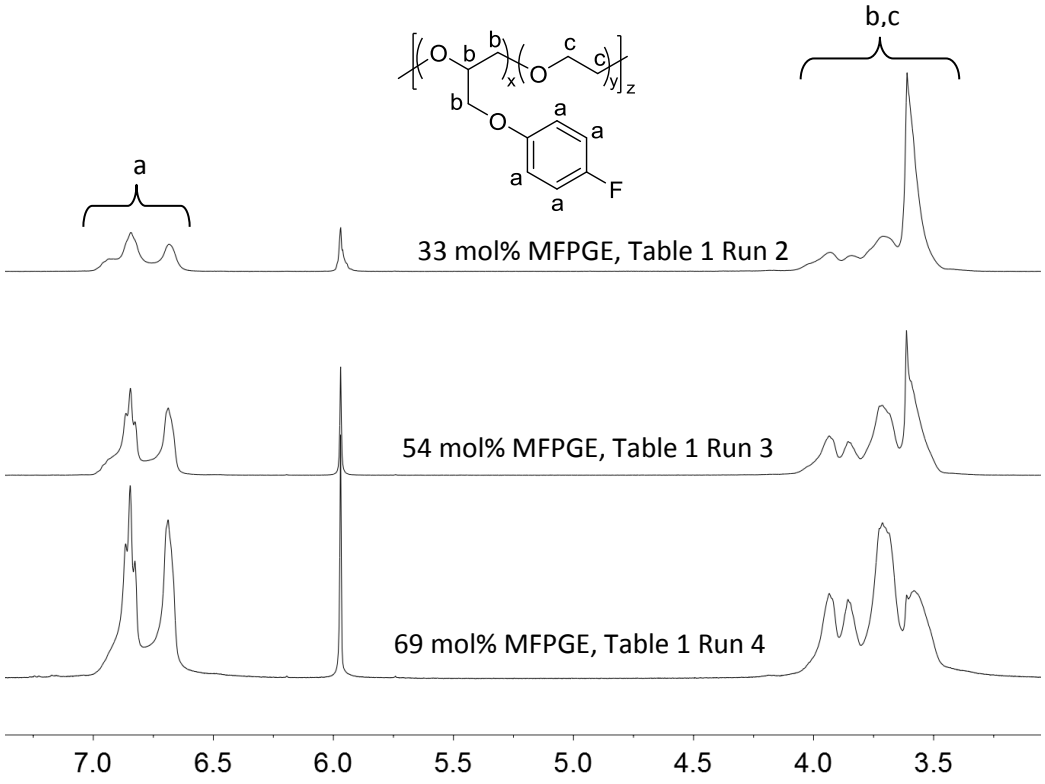


Fig. S3. ^{1}H-NMR spectra of MFPGE-EO statistical copolymers with different MFPGE content

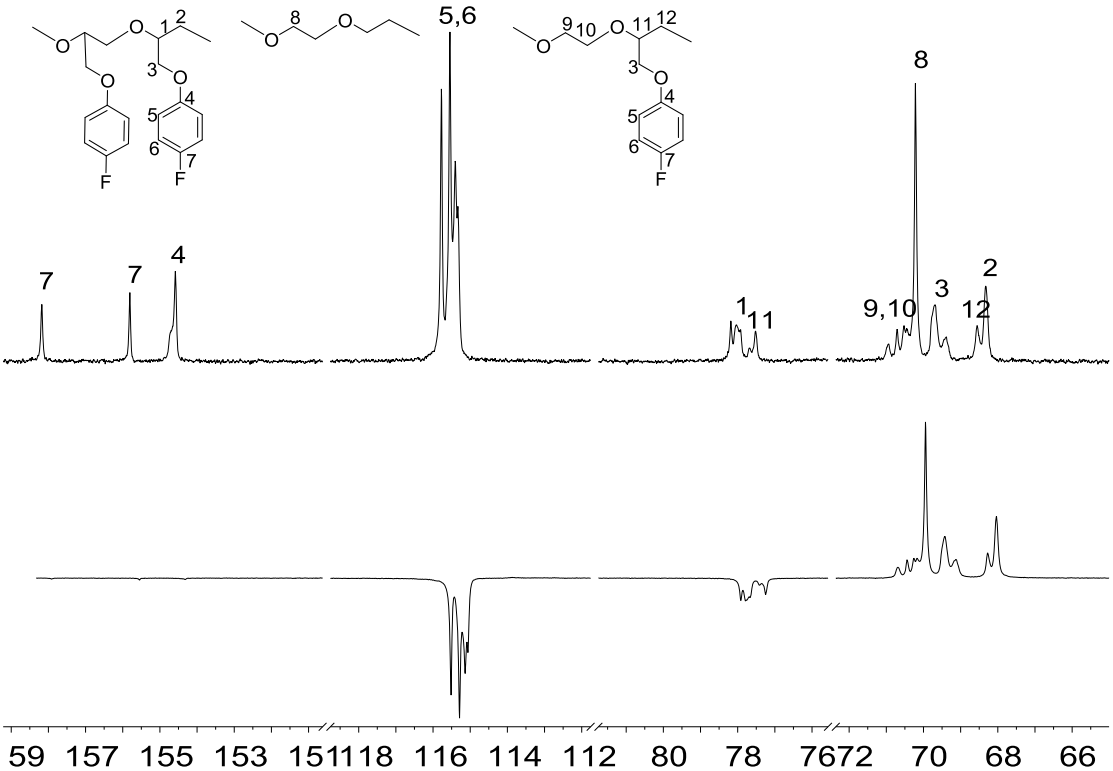


Fig. S4. 135DEPT-^{13}C-NMR spectrum of a MFPGE-EO statistical copolymer with 54 mol% MFPGE (Table 1, Run 3)

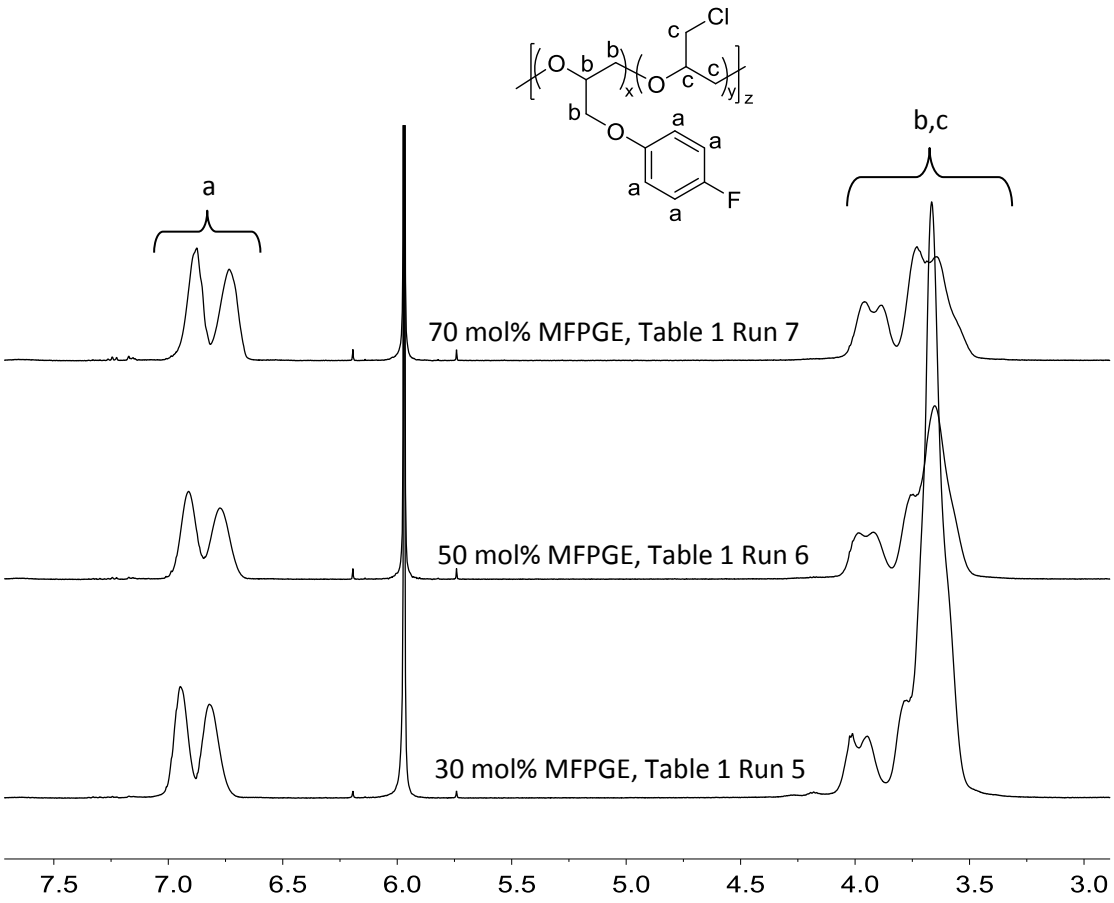


Fig. S5. ^{1}H-NMR spectra of MFPGE-ECH statistical copolymers with different MFPGE content

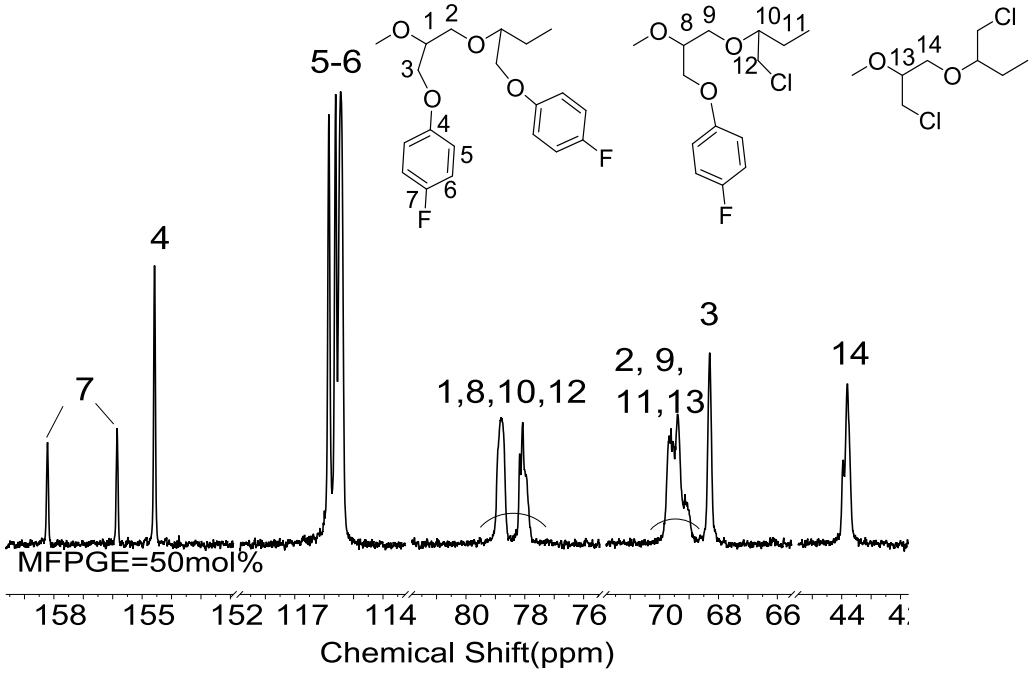


Fig. S6. ^{13}C-NMR spectrum of a MFPGE-ECH statistical copolymer with 50 mol% MFPGE (Table 1, Run 6)

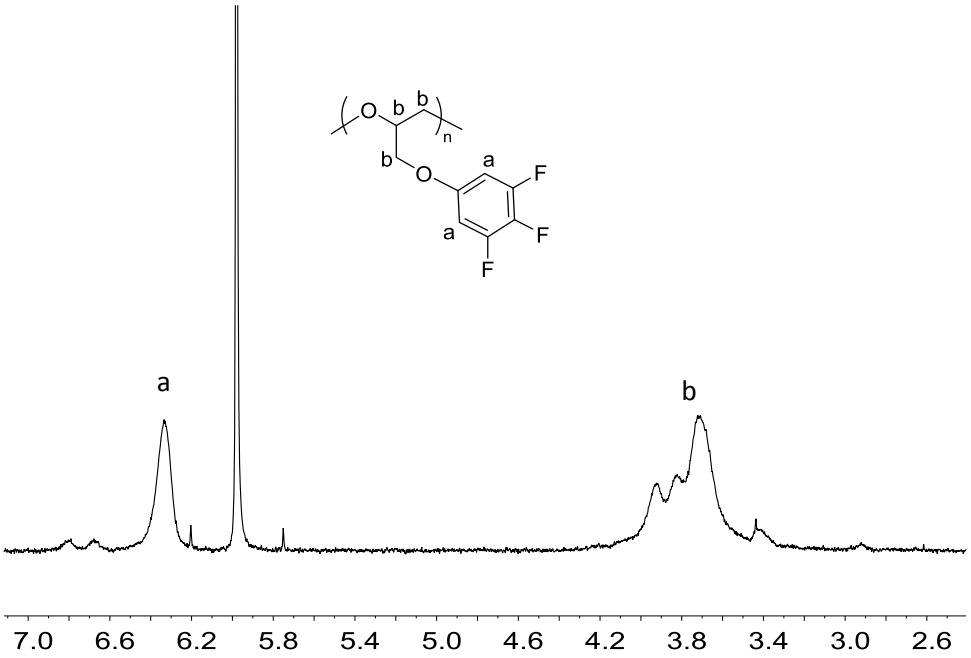


Fig. S7. ^{1}H-NMR spectrum of a TFPGE homopolymer (Table 1, Run 8)

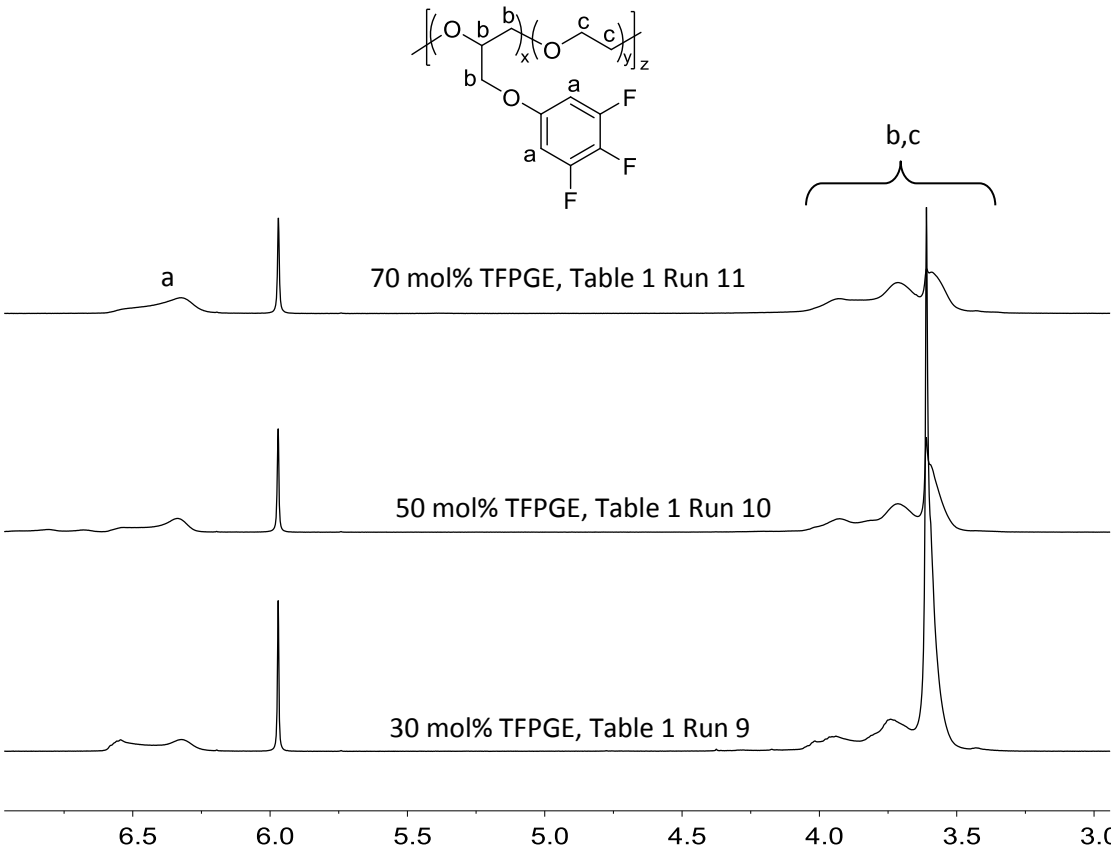


Fig. S8. ^{1}H-NMR spectra of TFPGE-EO statistical copolymers with different TFPGE content

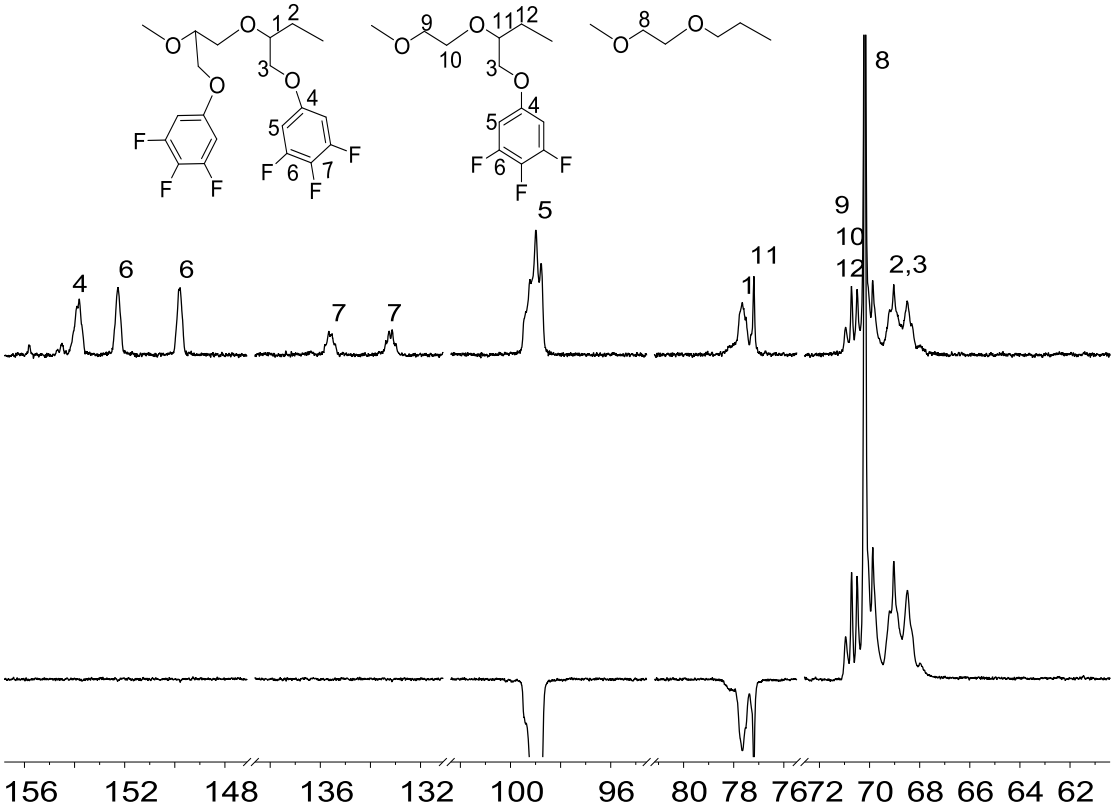


Fig. S9. 135DEPT-^{13}C-NMR spectrum of a TFPGE-EO statistical copolymer with 50 mol% TFPGE (Table 1, Run 10)

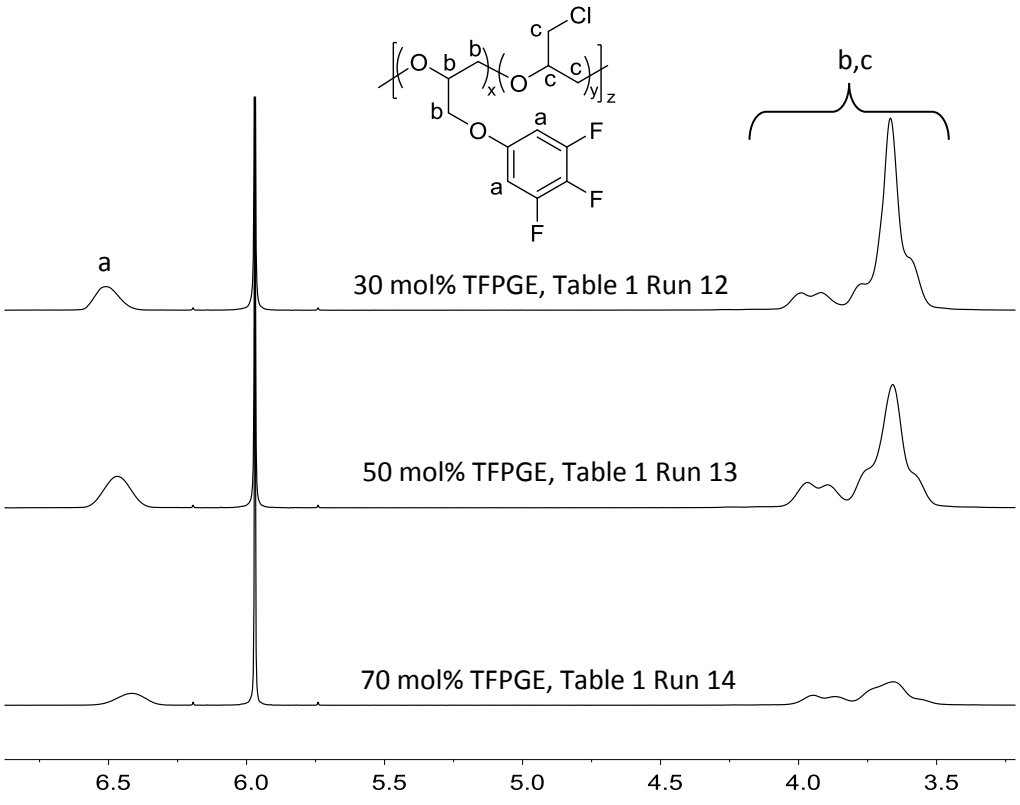


Fig. S10. ^{1}H-NMR spectra of TFPGE-ECH statistical copolymers with different TFPGE content

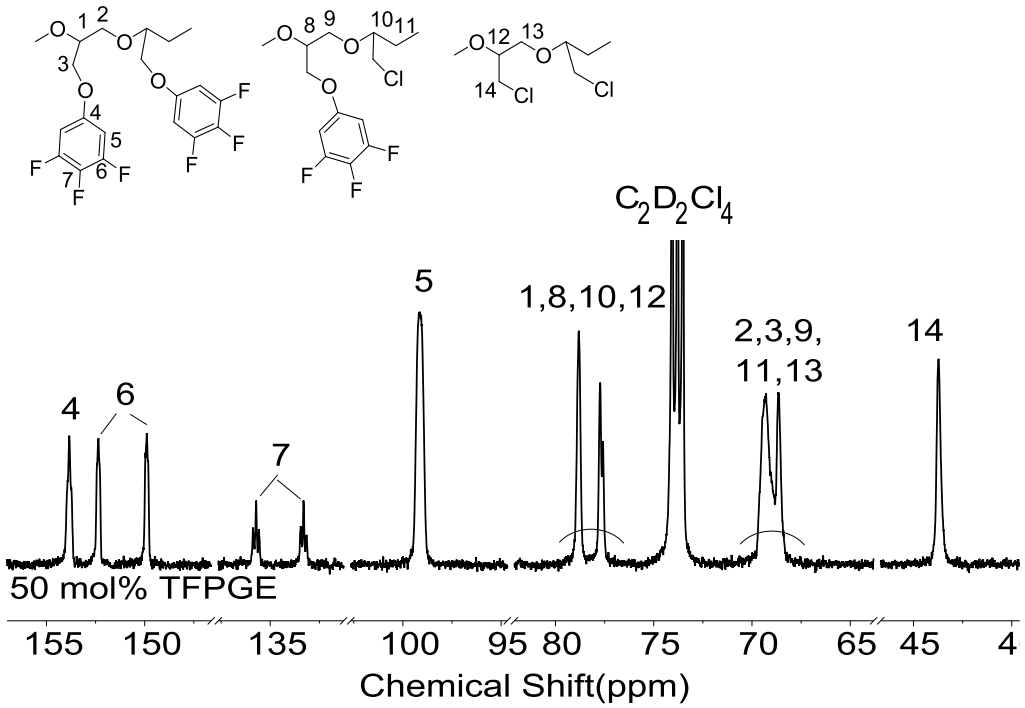


Fig. S11. ^{13}C-NMR spectrum of a TFPGE-ECH statistical copolymer with 50 mol% TFPGE (Table 1, Run 13)

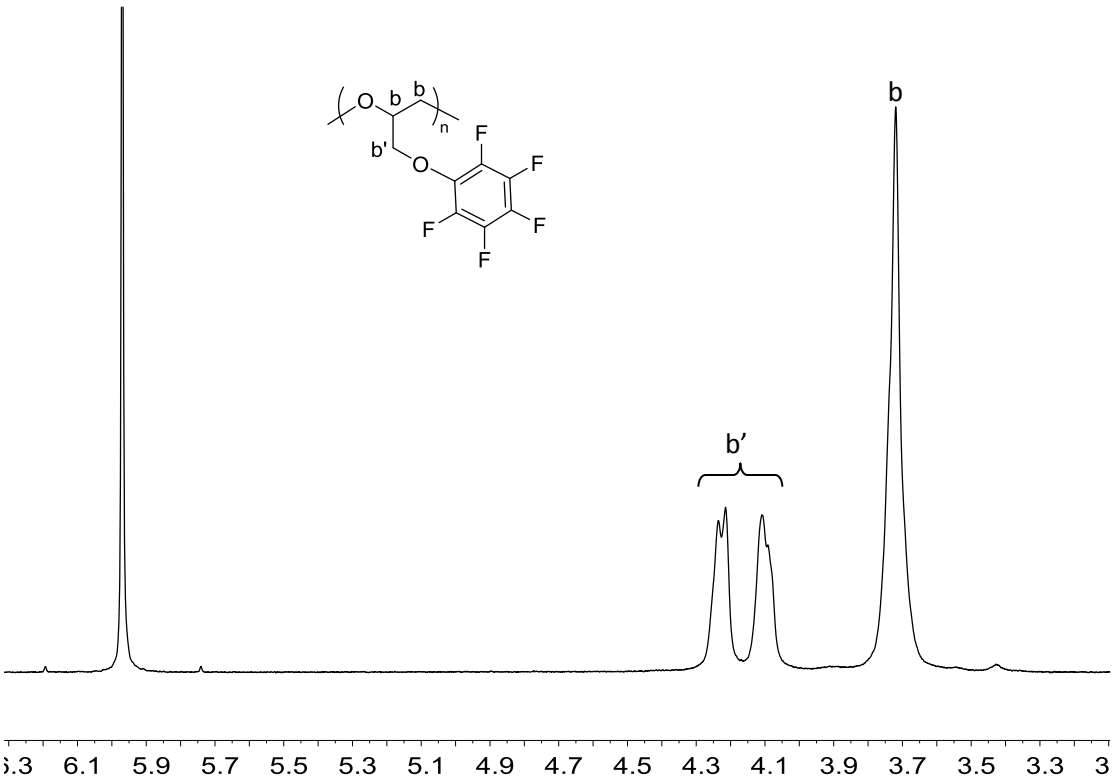


Fig. S12. ^{1}H-NMR spectrum of a PFPGE homopolymer (Table 1, Run 15)

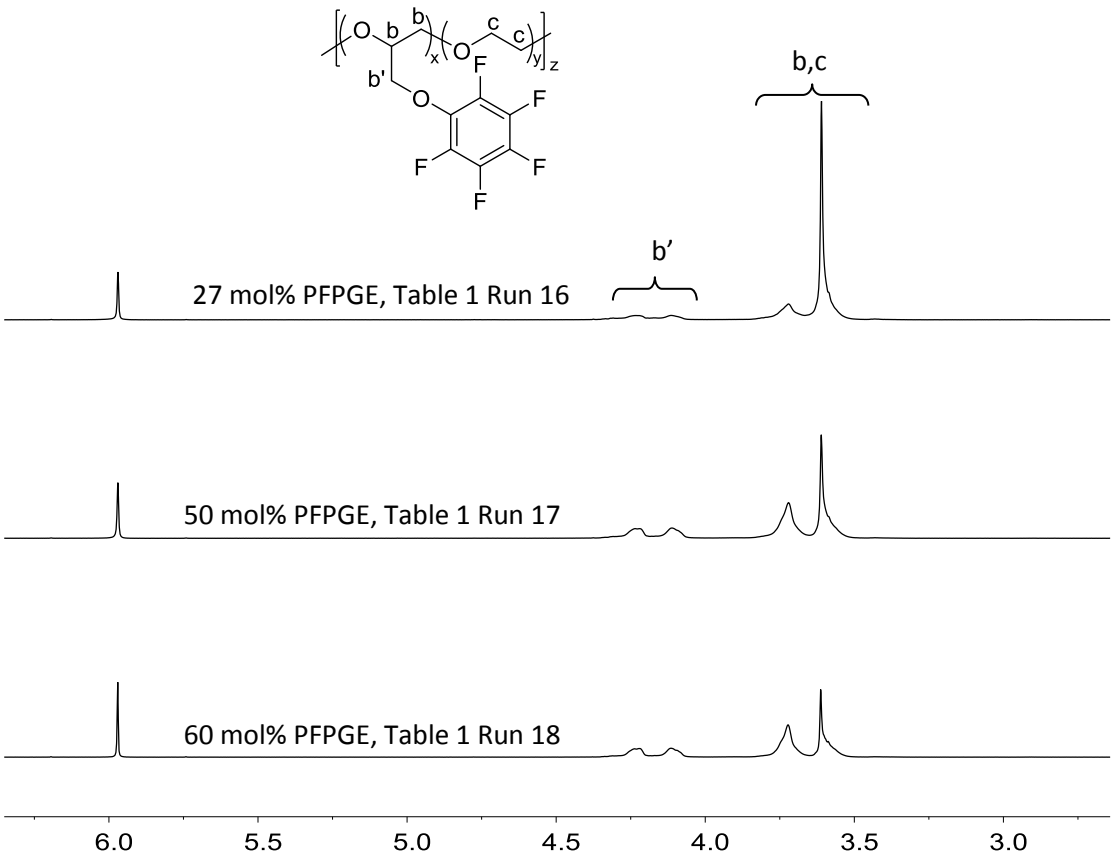


Fig. S13. ^{1}H-NMR spectra of PFPGE-EO statistical copolymers with different PFPGE content

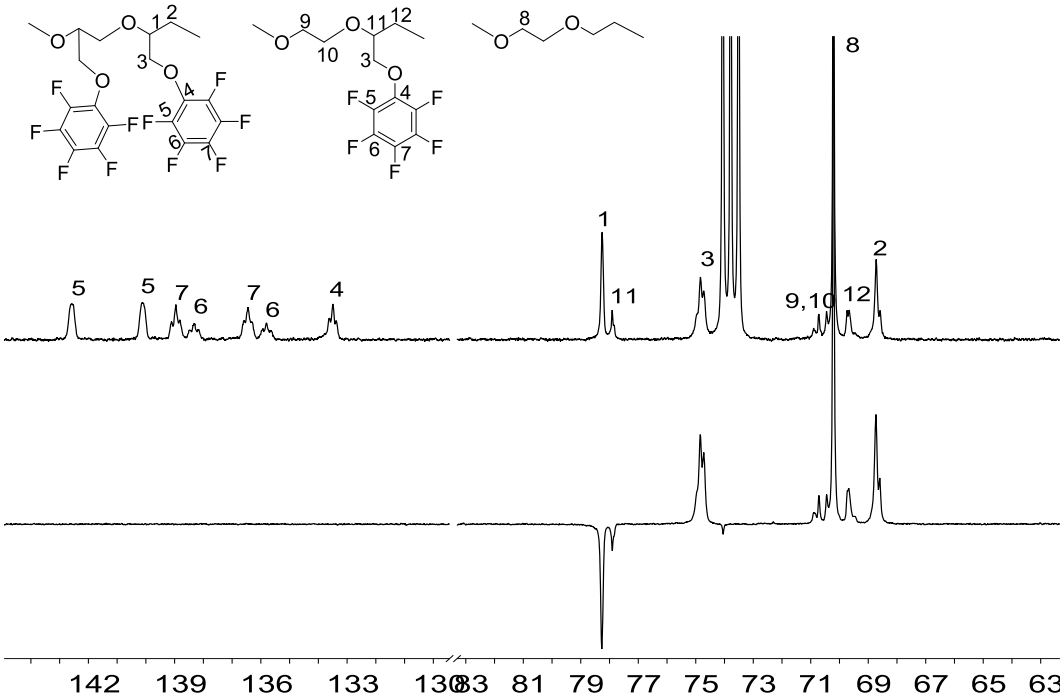


Fig. S14. 135DEPT-^{13}C-NMR spectrum of a PFPGE-EO statistical copolymer with 50 mol% PFPGE (Table 1, Run 17)

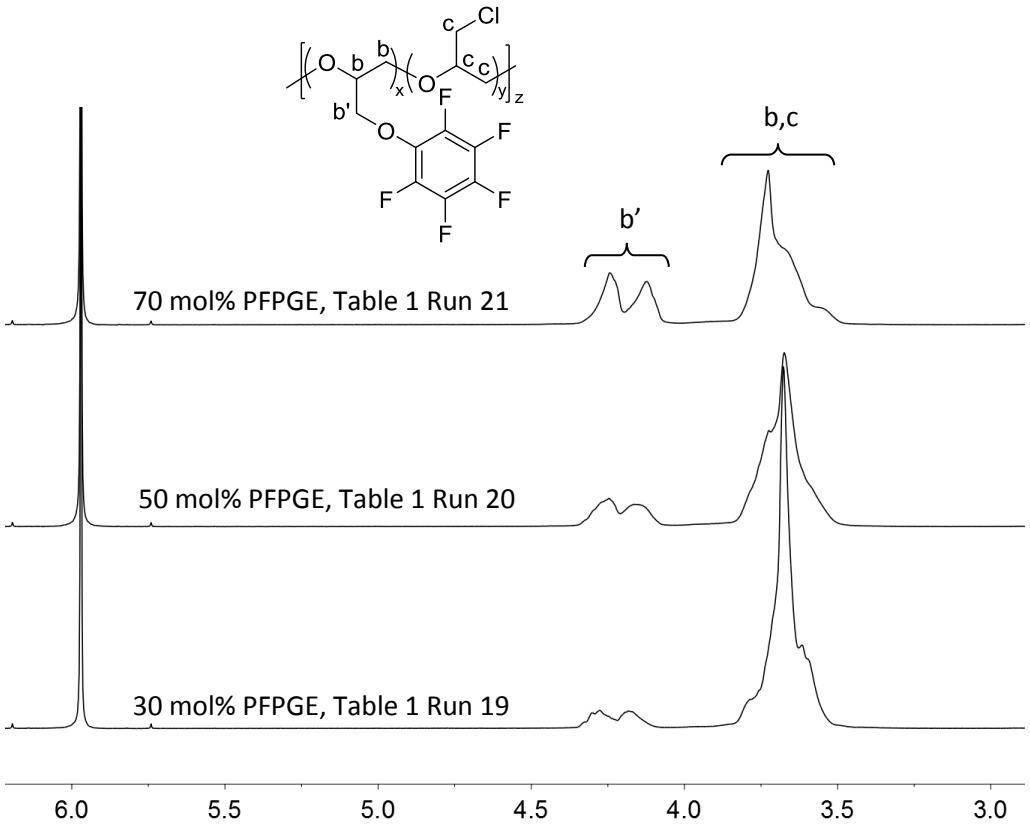


Fig. S15. ^{1}H-NMR spectra of PFPGE-ECH statistical copolymers with different PFPGE content

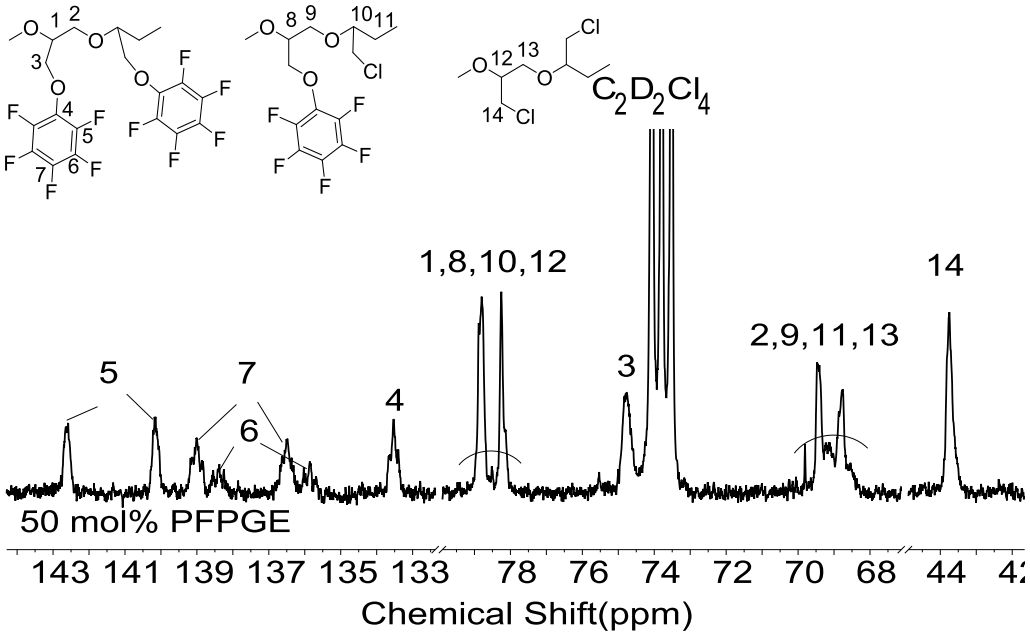


Fig. S16. ^{13}C-NMR spectrum of a PFPGE-ECH statistical copolymer with 50 mol% PFPGE (Table 1, Run 20)

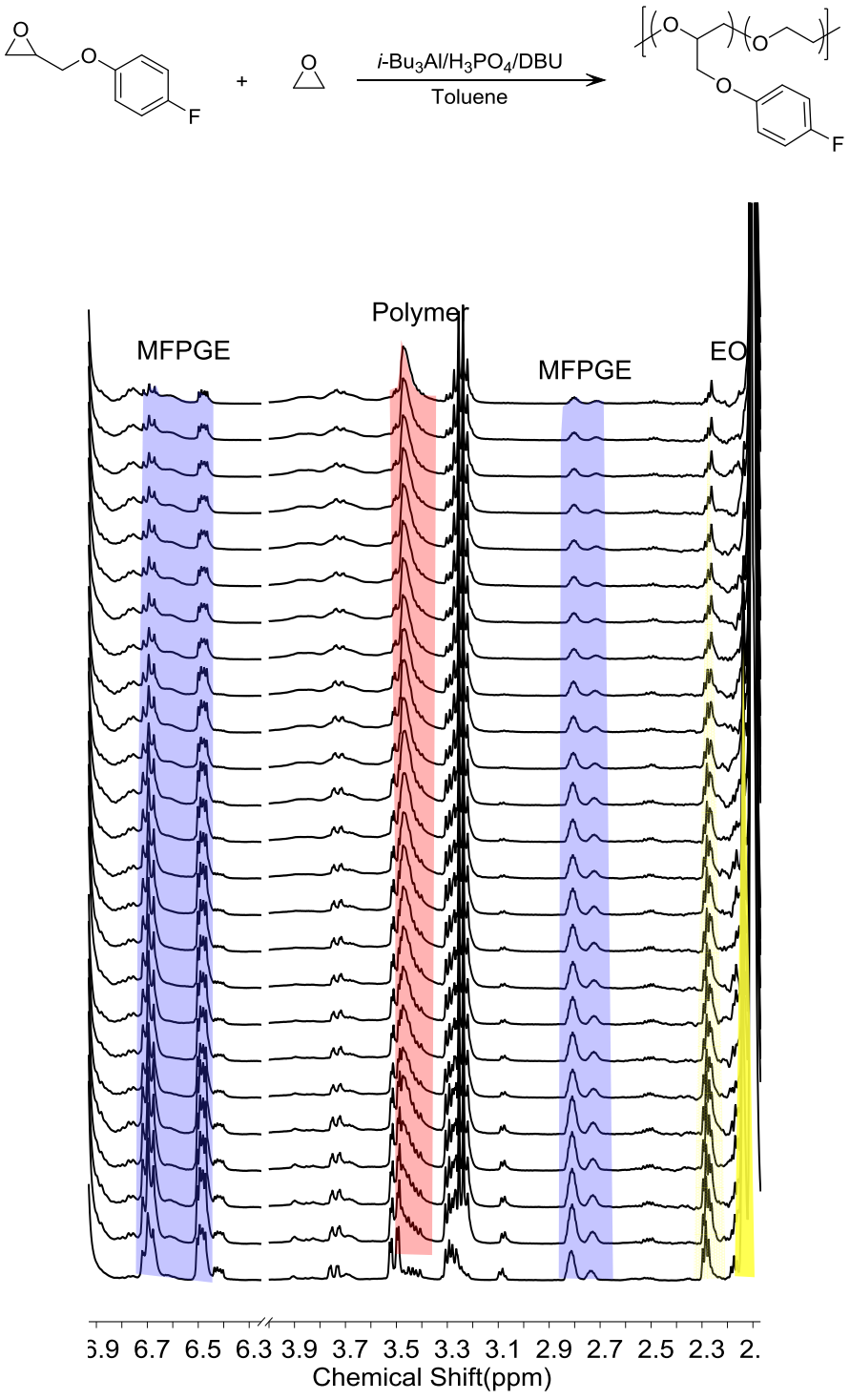


Fig. S17. ^{1}H-NMR spectra of kinetic experiment of MFPGE/EO copolymerization (MFPGE monomer was shaded in blue, EO monomer was shaded in yellow, the copolymer was shaded in red)

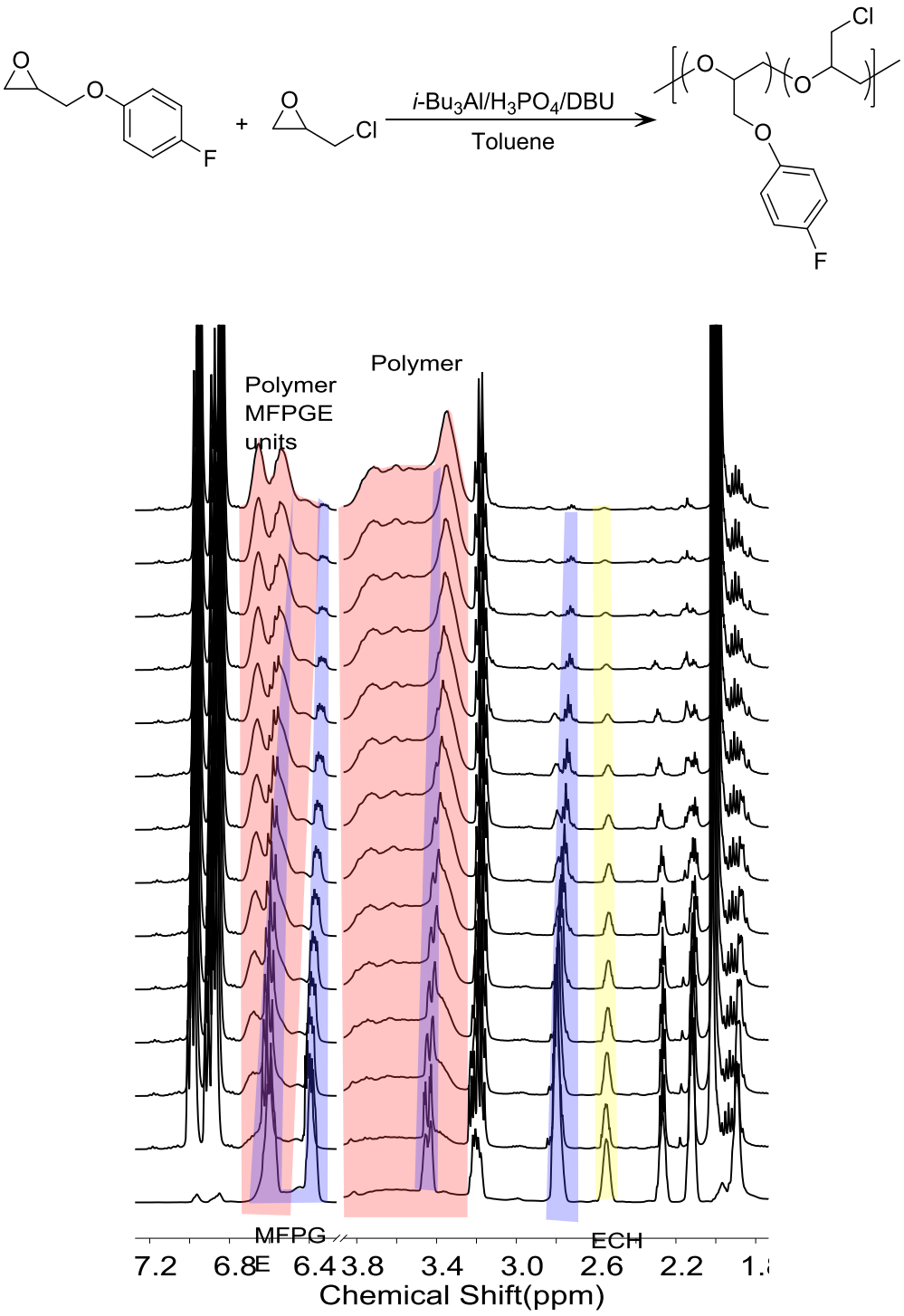
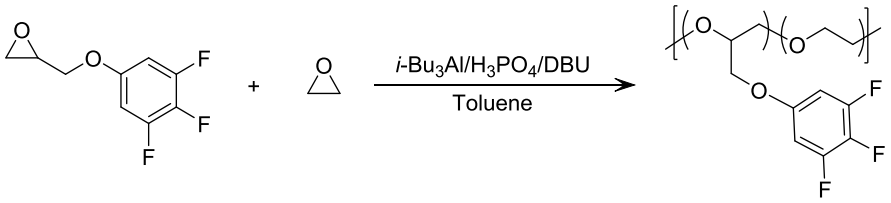


Fig. S18. ^{1}H-NMR spectra of kinetic experiment of MFPGE/ECH copolymerization (MFPGE monomer was shaded in blue, ECH monomer was shaded in yellow, the copolymer was shaded in red)



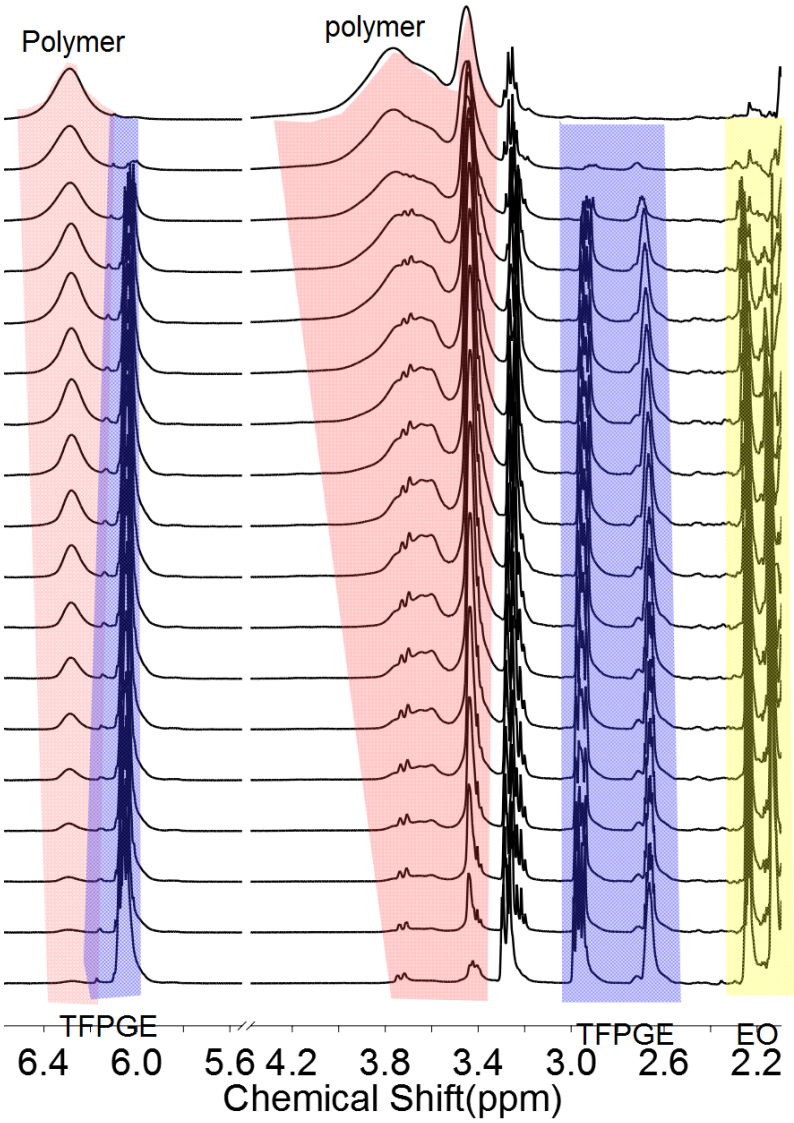


Fig. S19. ^{1}H-NMR spectra of kinetic experiment of TFPGE/EO copolymerization (TFPGE monomer was shaded in blue, EO monomer was shaded in yellow, the copolymer was shaded in red)

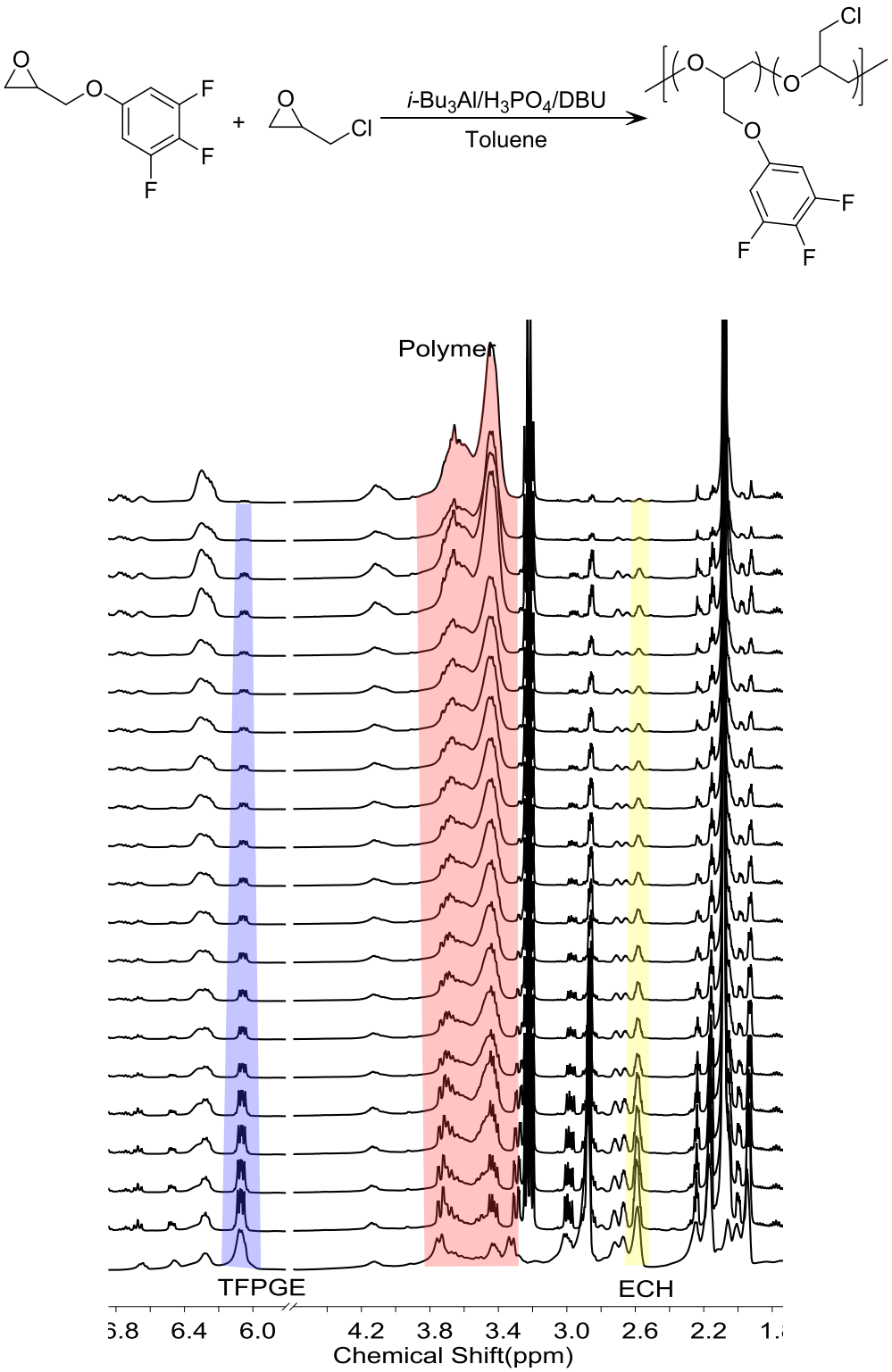


Fig. S20. ^{1}H-NMR spectra of kinetic experiment of TFPGE/ECH copolymerization (TFPGE monomer was shaded in blue, ECH monomer was shaded in yellow, the copolymer was shaded in red)

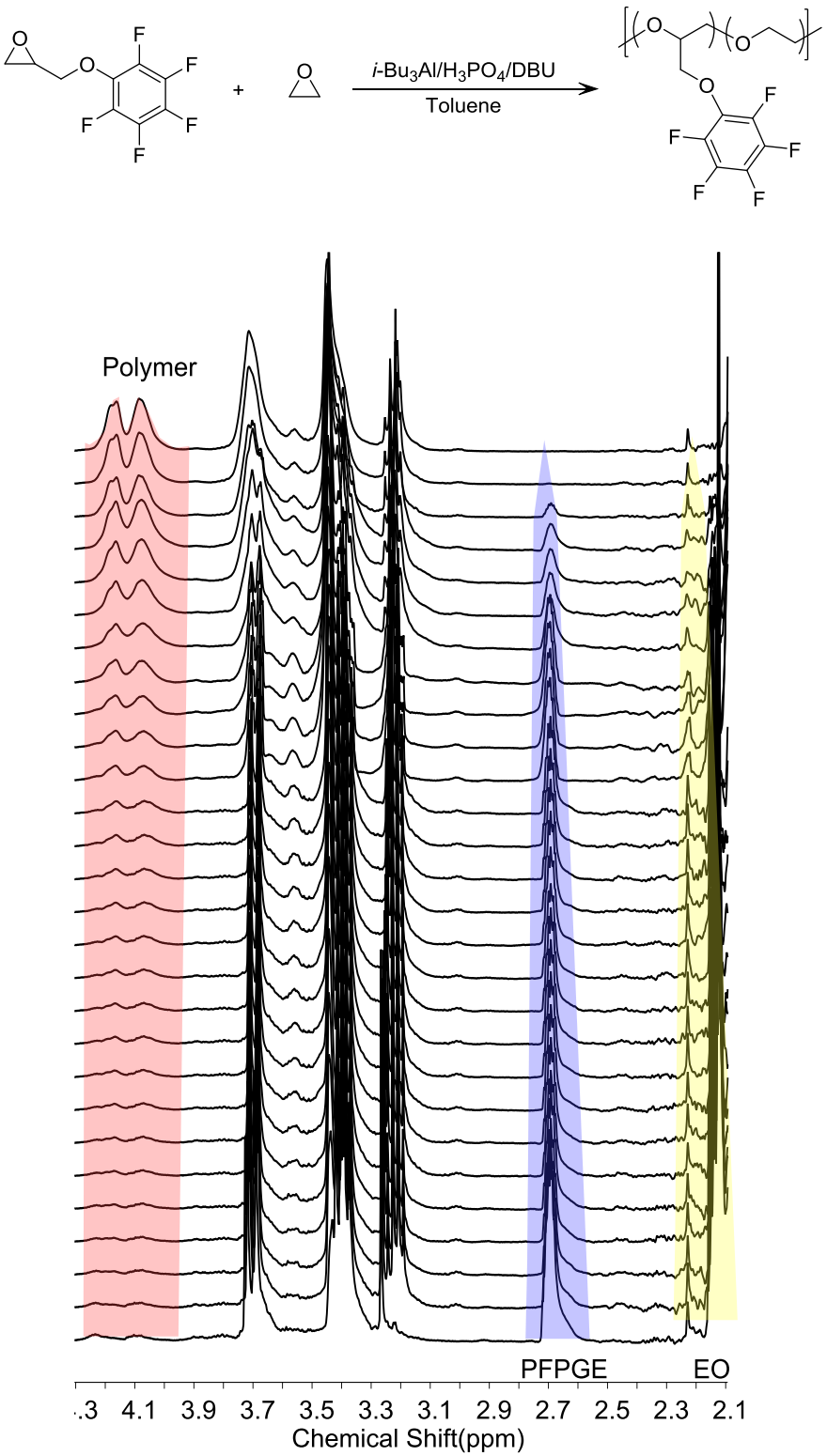


Fig. S21. ^{1}H-NMR spectra of kinetic experiment of PFPGE/EO copolymerization (PFPGE monomer was shaded in blue, EO monomer was shaded in yellow, the copolymer was shaded in red)

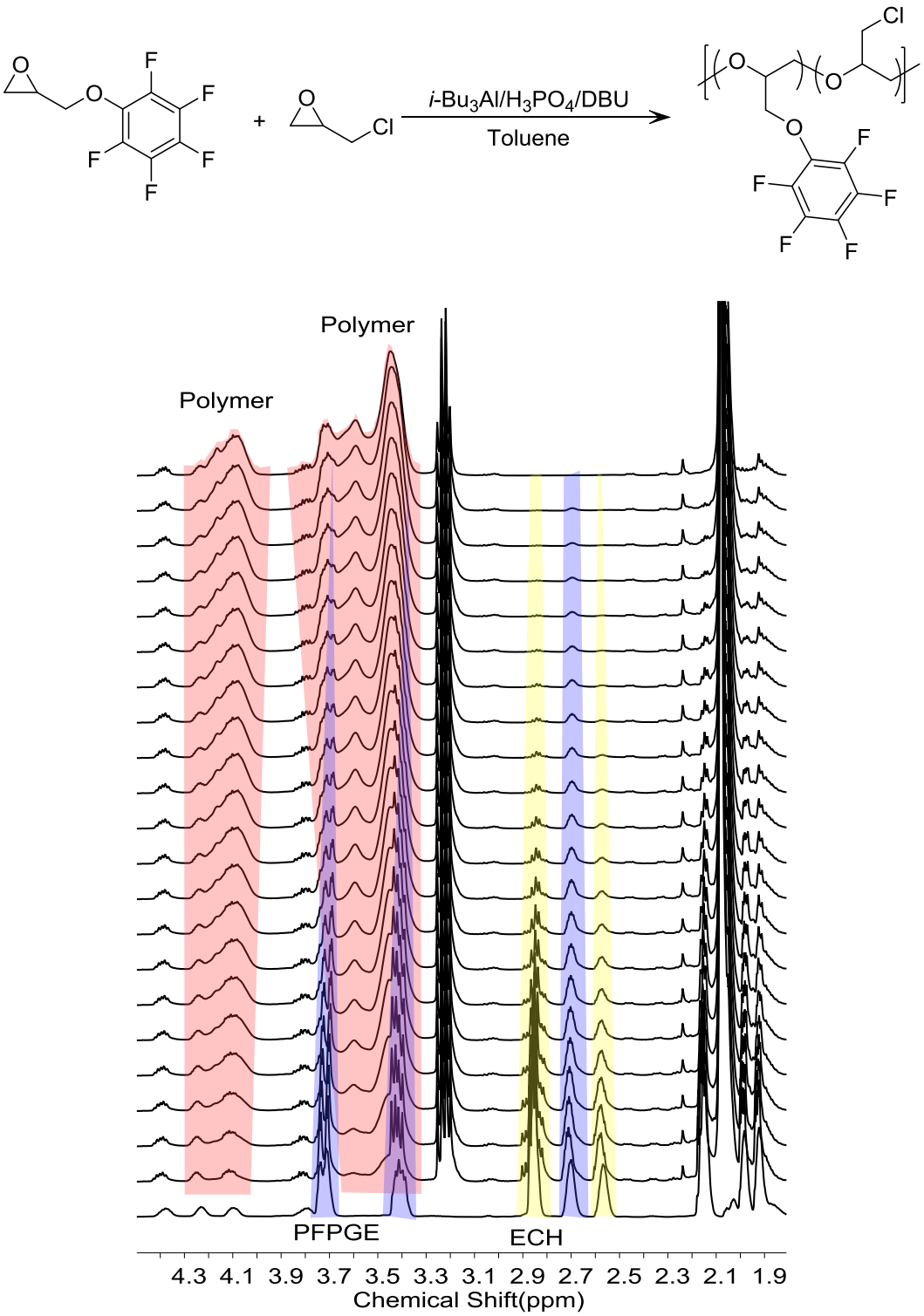


Fig. S22. ^{1}H-NMR spectra of kinetic experiment of PFPGE/ECH copolymerization (PFPGE monomer was shaded in blue, ECH monomer was shaded in yellow, the copolymer was shaded in red)

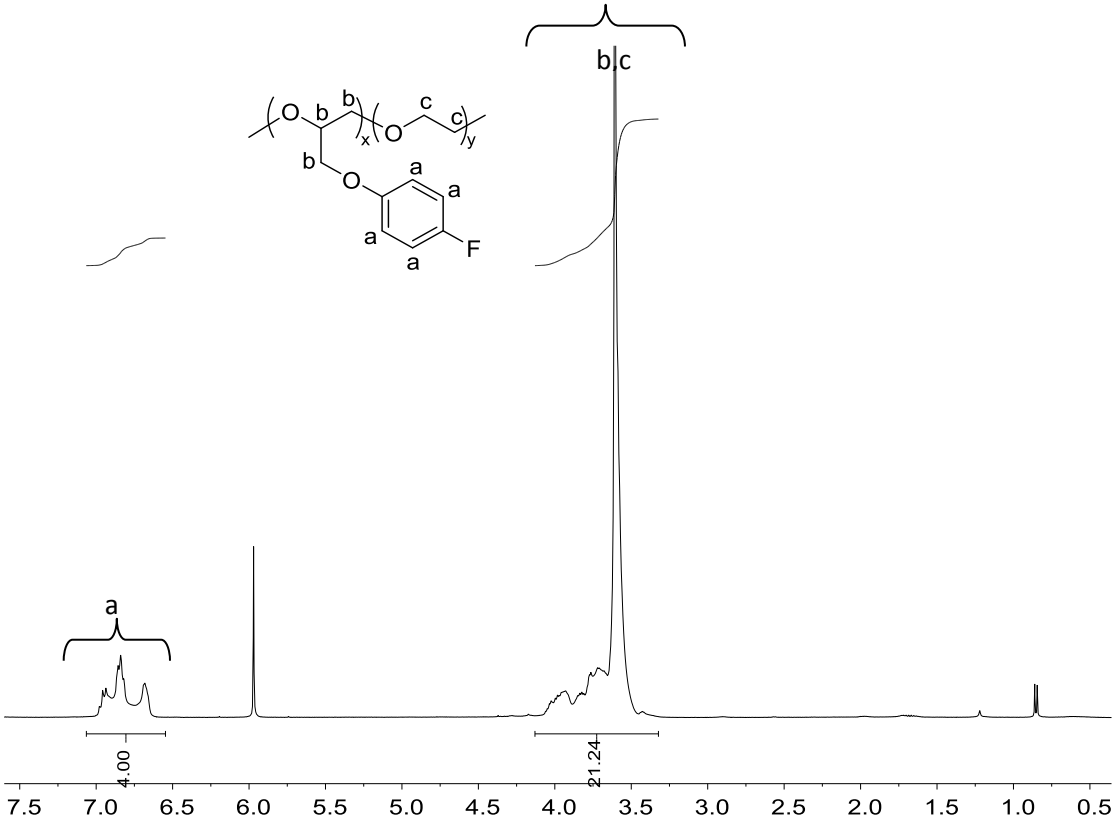


Fig. S23. [1]H-NMR spectrum of a MFPGE-EO block copolymer with 20 mol% MFPGE (Table 2, Run 3)

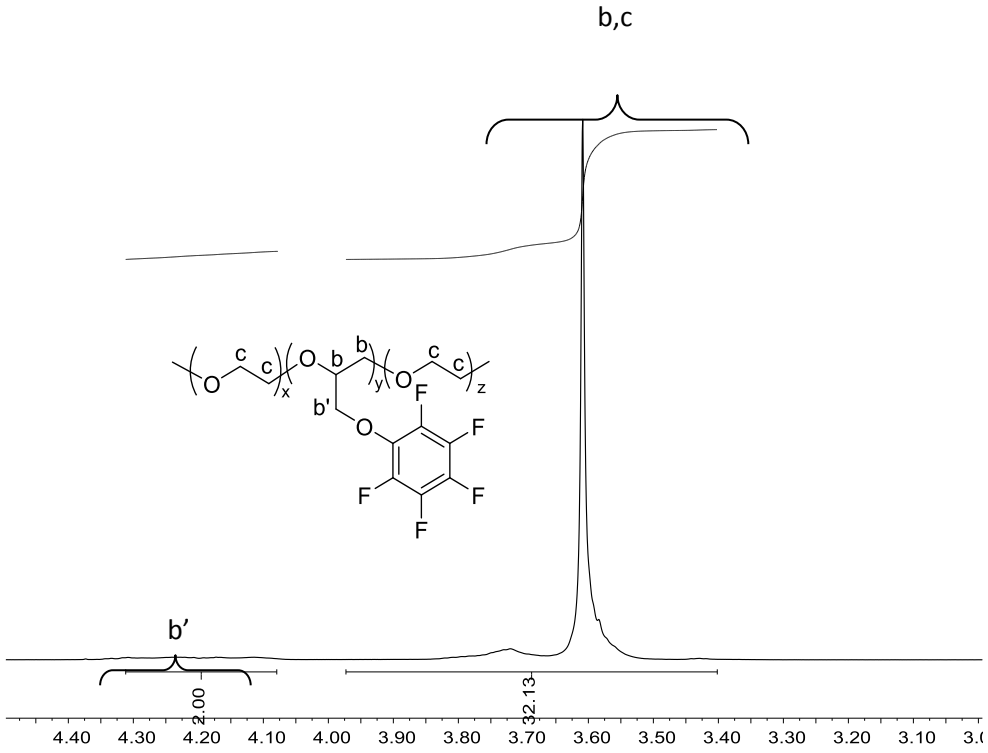


Fig. S24. [1]H-NMR spectrum of a EO-PFPGE-EO block terpolymer with 12 mol% PFPGE (Table 2, Run 4)

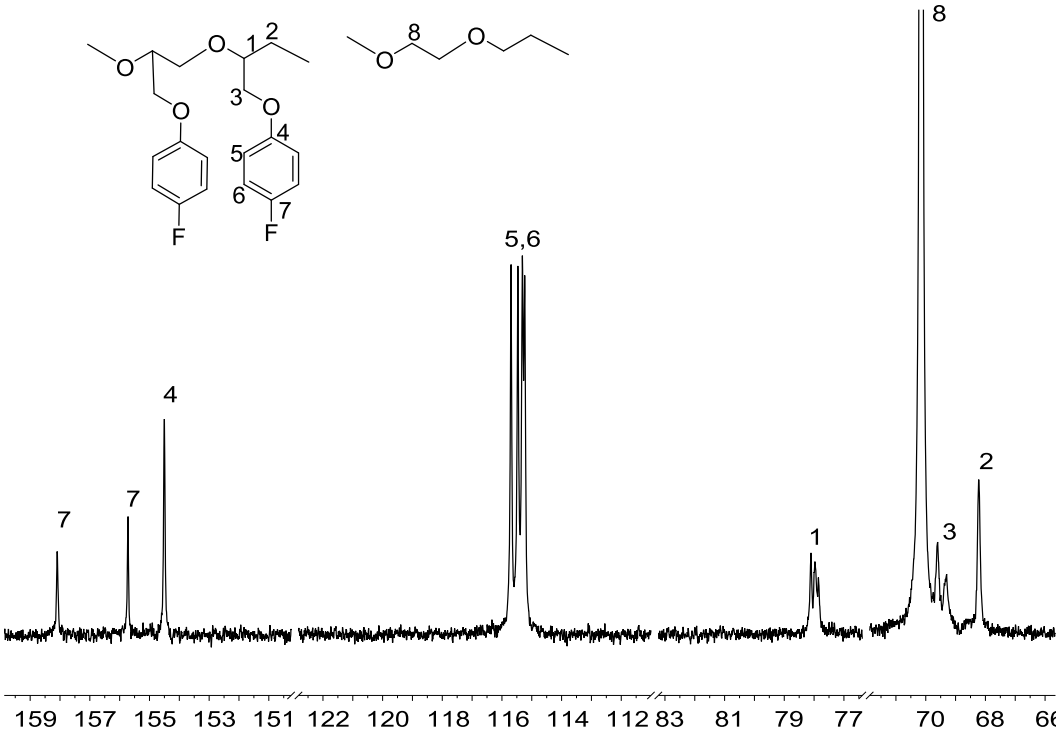


Fig. S25. ^{13}C-NMR spectrum of a EO-MFPGE-EO block terpolymer with 11 mol% MFPGE (Table 2, Run 6)

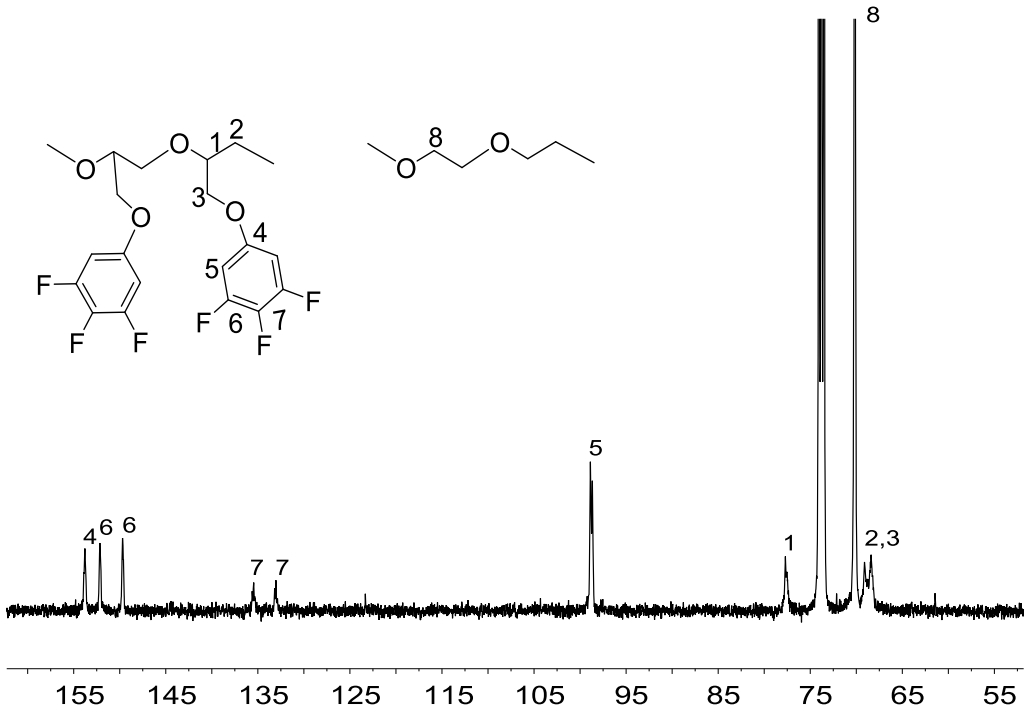


Fig. S26. ^{13}C-NMR spectrum of a EO-TFPGE-EO block terpolymer with 11 mol% TFPGE (Table 2, Run 5)

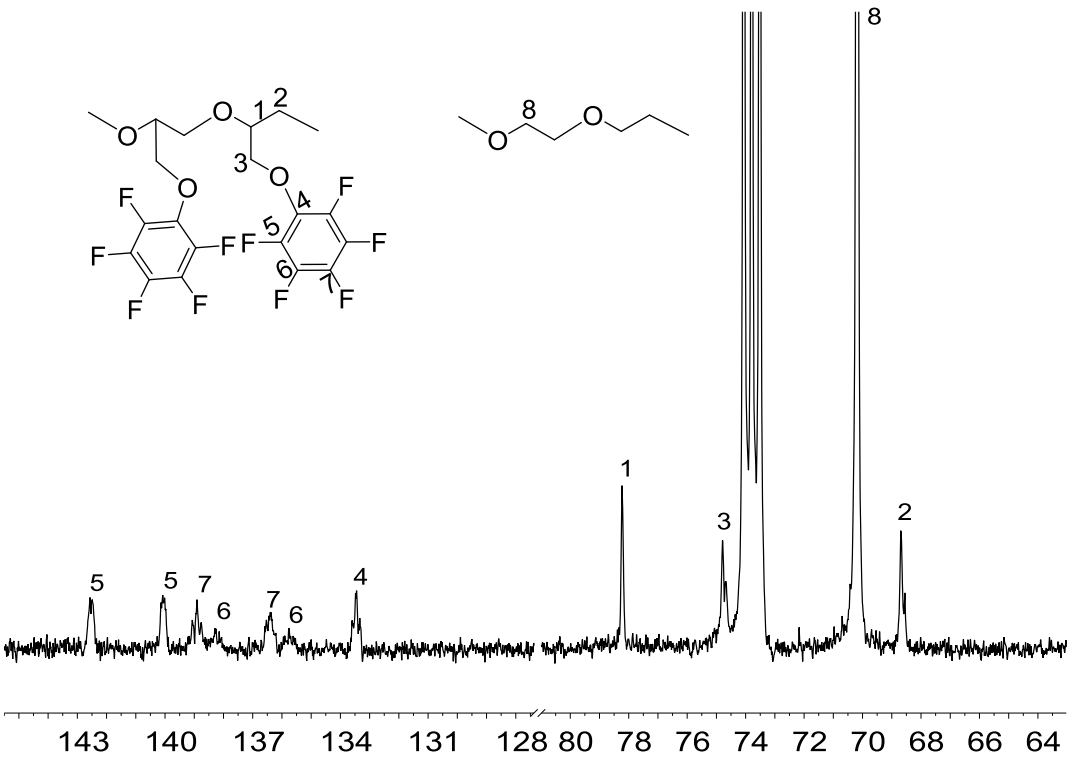


Fig. S27. ^{13}C-NMR spectra of a EO-PFPGE-EO block terpolymer with 11 mol% PFPGE (Table 2, Run 4)

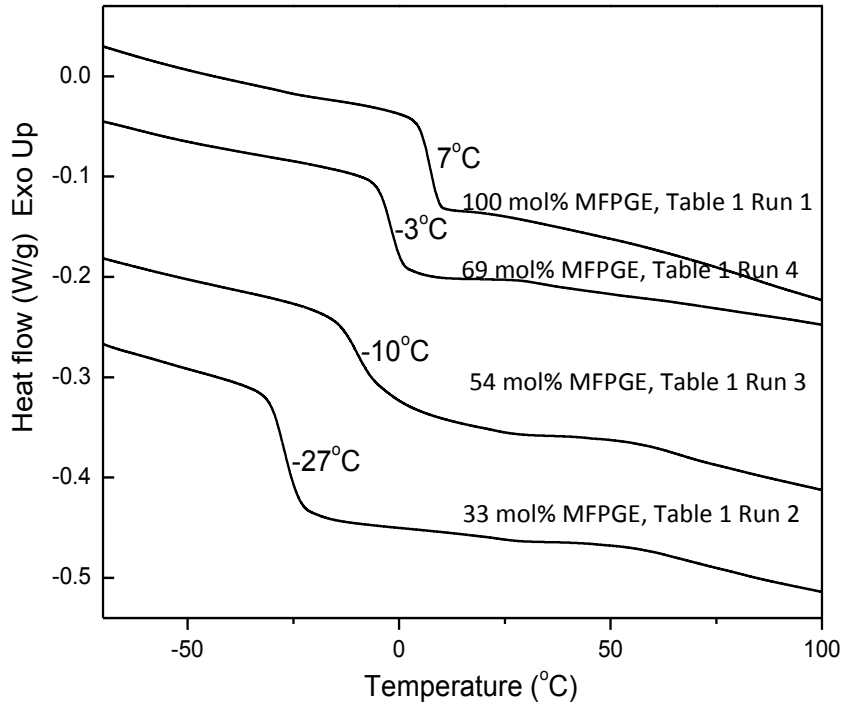


Fig. S28. DSC curves of MFPGE-EO statistical copolymers with different compositions

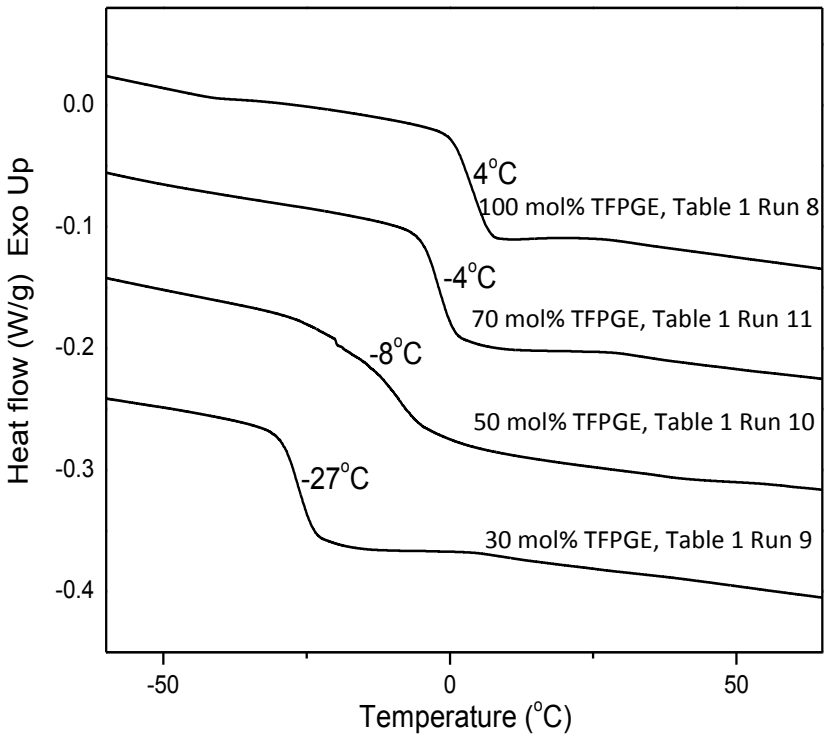


Fig. S29. DSC curves of TFPGE-EO statistical copolymers with different compositions

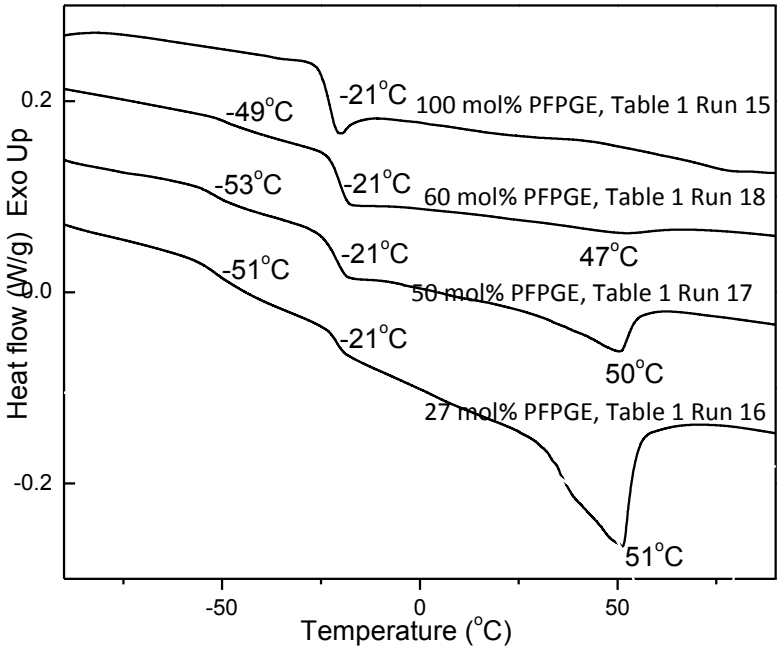


Fig. S30. DSC curves of PFPGE-EO statistical copolymers with different compositions

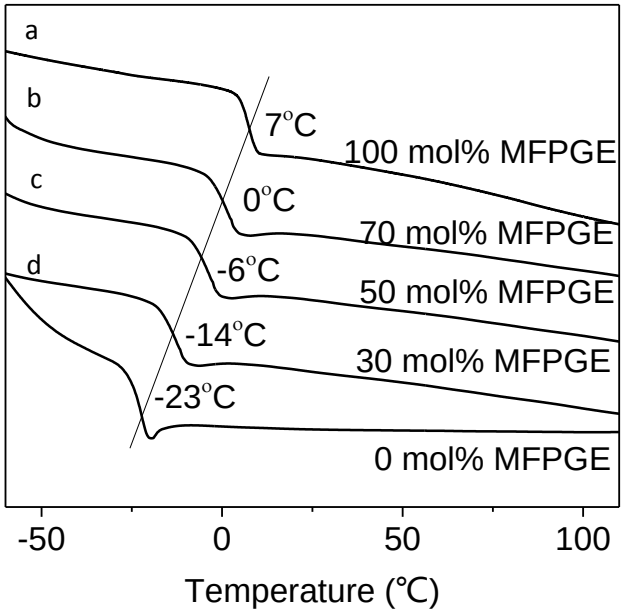


Fig. S31. DSC curves of MFPGE-ECH statistical copolymers with different compositions (a: Table 1, Run 1; b: Table 1, Run 7; c: Table 1, Run 6; d: Table 1, Run 5)

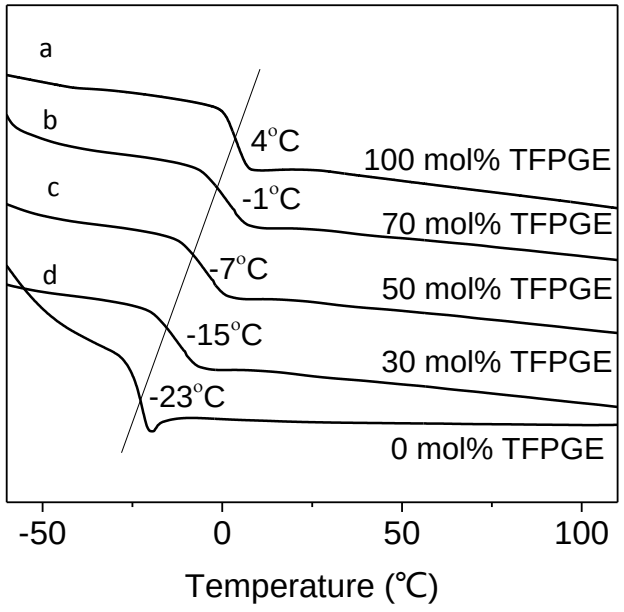


Fig. S32. DSC curves of TFPGE-ECH statistical copolymers with different compositions (a: Table 1, Run 8; b: Table 1, Run 14; c: Table 1, Run 13; d: Table 1, Run 12)

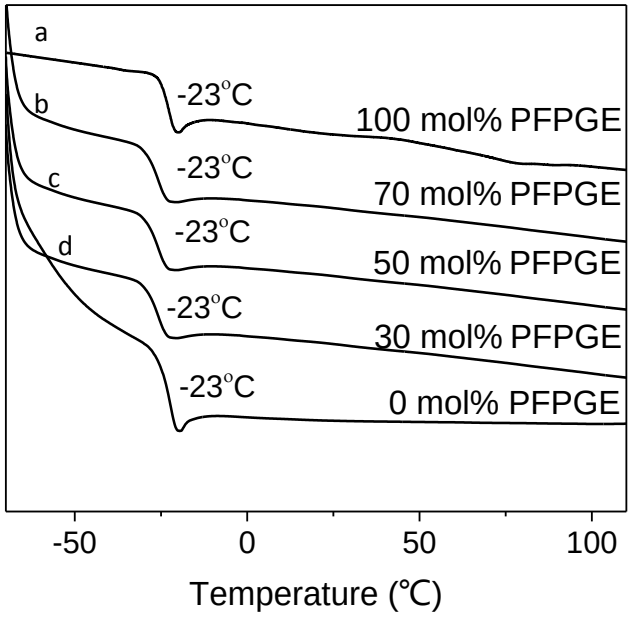


Fig. S33. DSC curves of PFPGE-ECH statistical copolymers with different compositions (a: Table 1, Run 15; b: Table 1, Run 21; c: Table 1, Run 20; d: Table 1, Run 19)

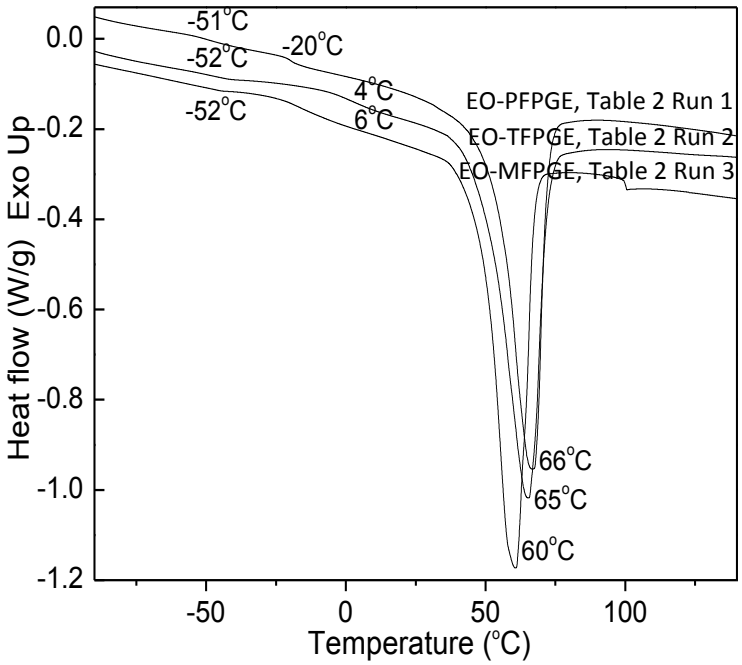


Fig. S34. DSC curves of MFPGE-EO, TFPGE-EO, and PFPGE-EO block copolymers

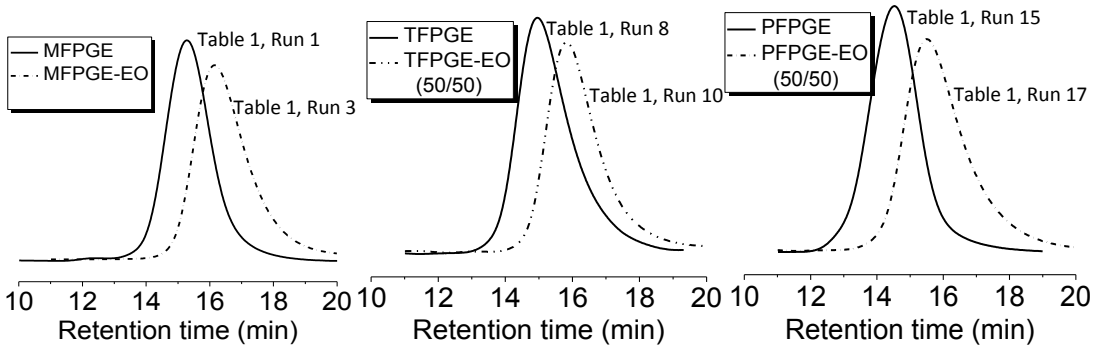


Fig. S35. GPC traces of MFPGE-EO, TFPGE-EO, TFPGE-EO statistical copolymers

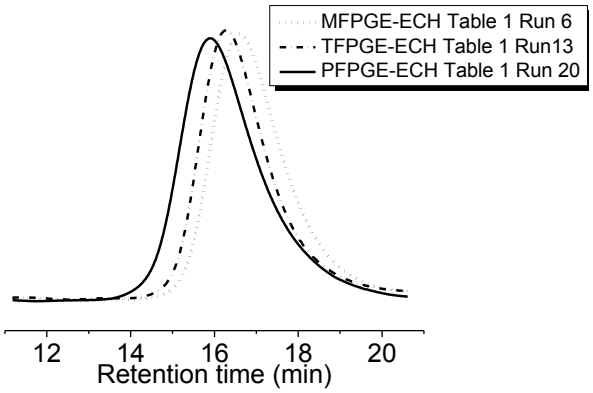


Fig. S36. GPC traces of MFPGE-ECH, TFPGE-ECH, TFPGE-ECH statistical copolymers

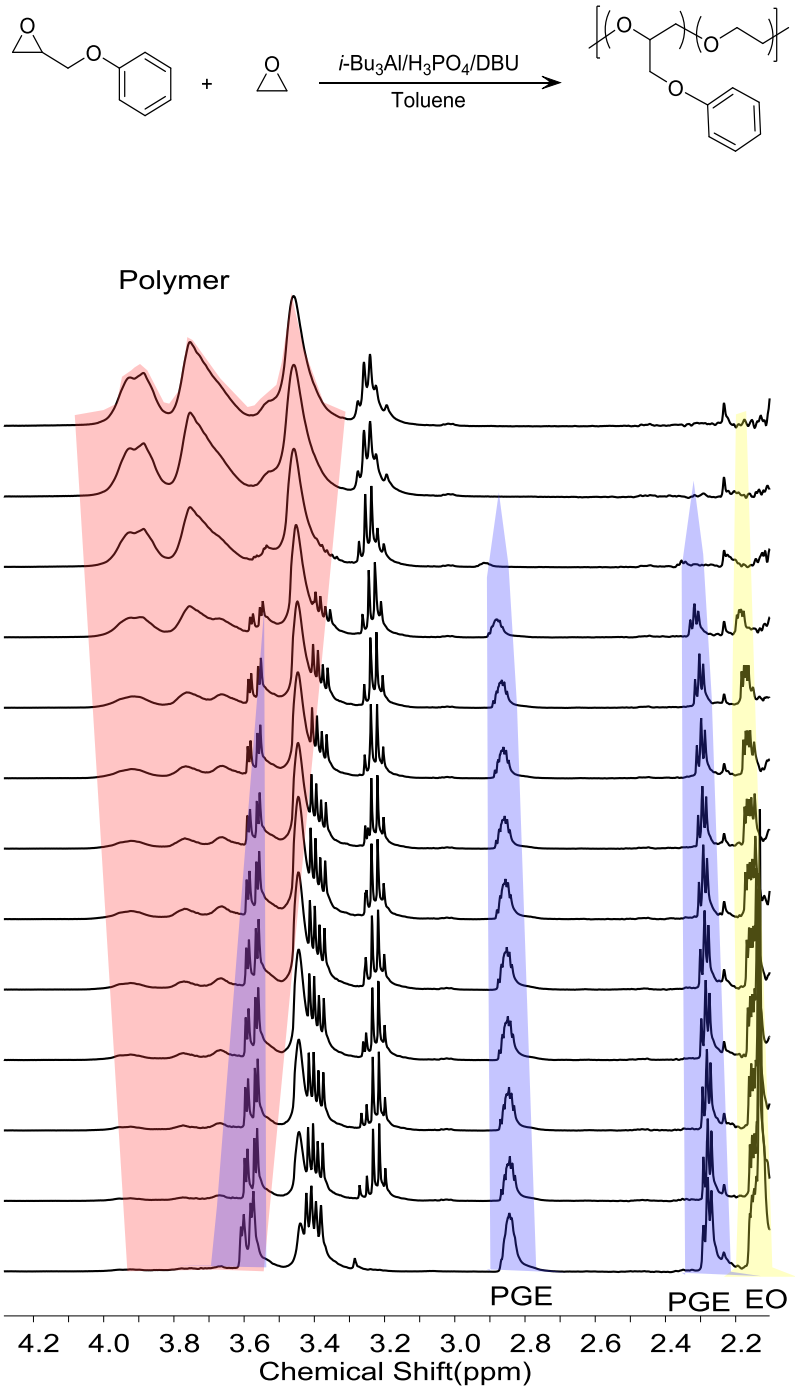


Fig. S37. ^{1}H-NMR spectra of kinetic experiment of PGE/EO copolymerization (PGE monomer was shaded in blue, EO monomer was shaded in yellow, the copolymer was shaded in red)

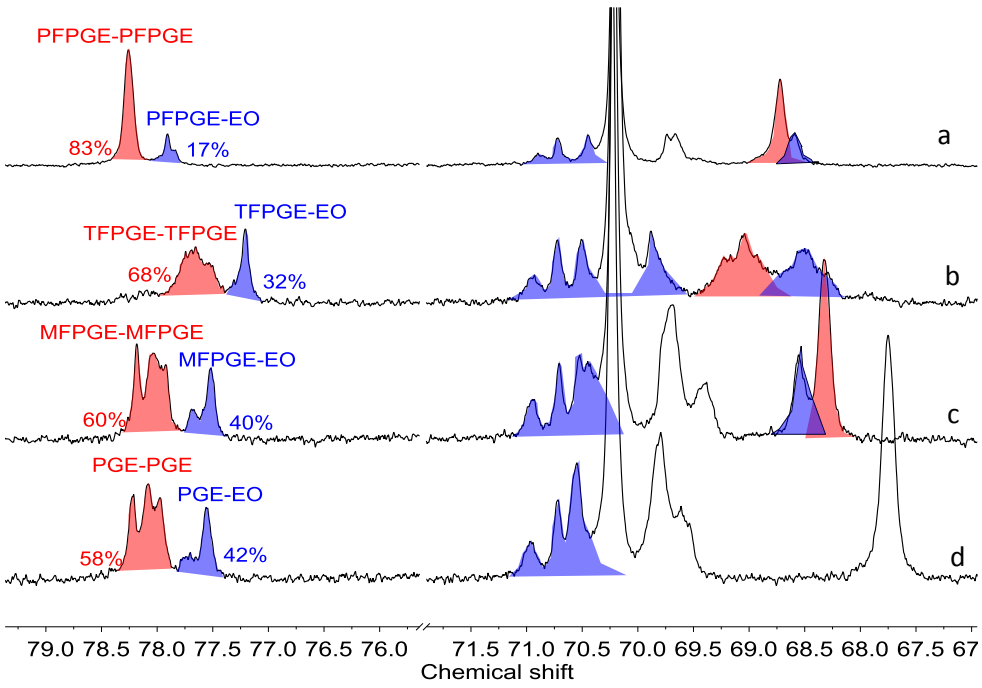


Fig. S38. Comparisons of ^{13}C-NMR spectra of PFPGE-EO (a: Table 1, Run 17), TFPGE-EO (b: Table 1, Run 10), MFPGE-EO (c: Table 1, Run 3) and PGE-EO (d: Table S1, Run 2) copolymers with 50 mol% EO (joint signals in blue shadow, self-self signals in red shadow)

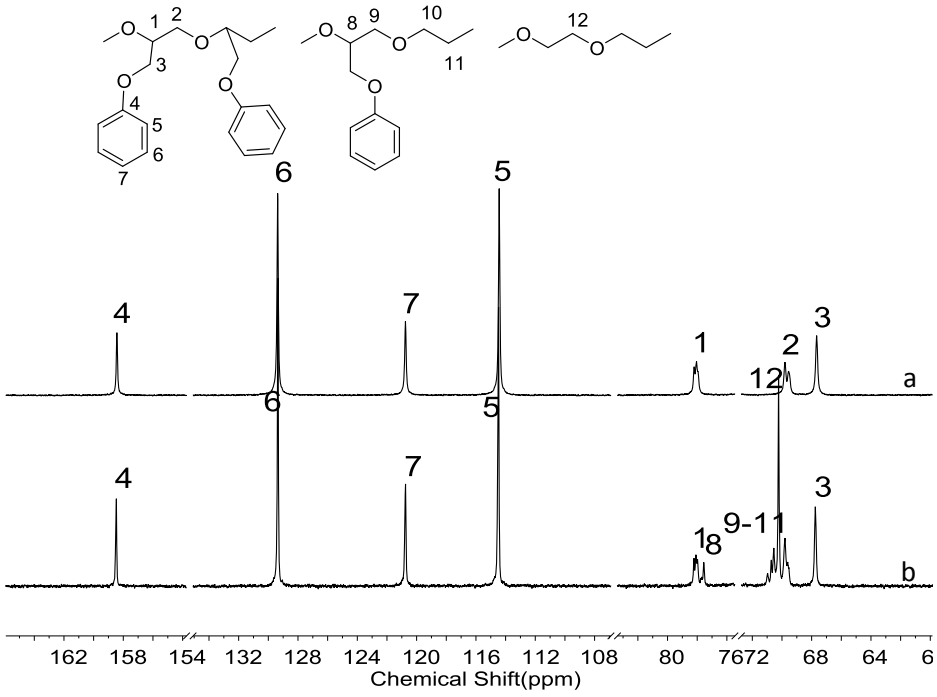


Fig. S39. ^{13}C-NMR spectra of PGE homopolymer (a: Table S1, Run 1) and PGE-EO copolymer with 50 mol% MFPGE (b: Table S1, Run 2)

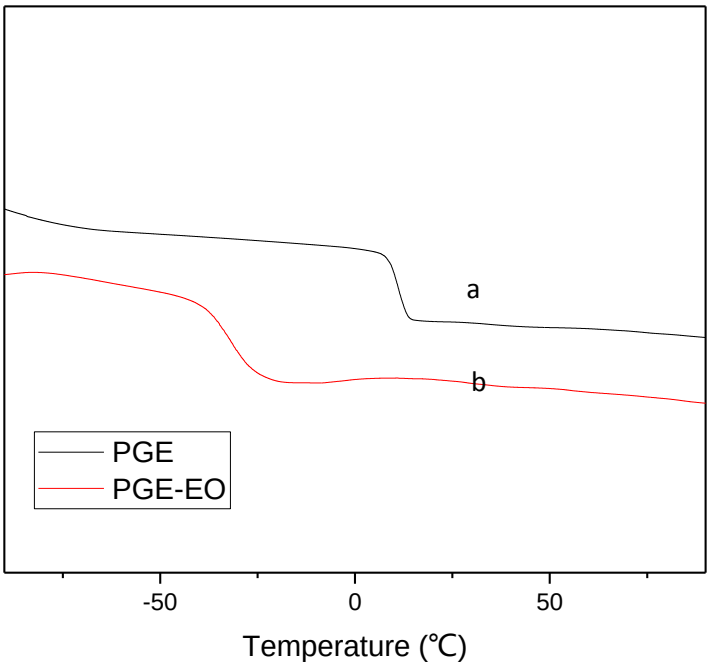
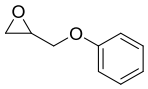


Fig. S40. DSC curves of PGE homopolymer (a: Table S1, Run 1) and PGE-EO copolymer with 50 mol% MFPGE (b: Table S1, Run 2).

Table S1 Simultaneous copolymerization of phenyl glycidyl ether (PGE) with EO by *i*-Bu_3Al/H_3PO_4/DBU[a]

Run	PGE	comonomer	f_{PGE}[b] mol%	Yield (%)	F_{PGE}[c] mol%	M_n[d] (×10⁴)	M_w/M_n[d]	T_g[e] (°C)
1		–	100	100	100	14.1	1.42	11
2			50	99	50	9.1	1.37	-32

[a] Reaction condition: *i*-Bu_3Al/H_3PO_4/DBU molar ratio, 1/0.33/0.25; *i*-Bu_3Al, 0.25 mmol; monomer (2 mol/L in toluene)/*i*-Bu_3Al=40 ; 25 °C; 30 min. [b] Initial mole fraction of PGE. [c] Final cumulative mole fraction composition of copolymer measured by ^{1}H-NMR spectroscopy. [d] Determined by GPC in 1,2,4-trichlorobenzene at 150 °C against polystyrene standard. [e] Determined by DSC.