Supporting information

Syndio- and *cis*-1,4 Dually Selective Copolymerization of Polar Fluorostyrene and Butadiene using Rare-earth Metal Catalysts

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Legends

Figure S1. ^{1}H NMR spectrum of poly(*p*-fluorostyrene-butadiene) obtained by complex **2a** (Table 1, entry 3) (500MHz, $CDCl_3$, 25^{o}C).
Figure S2. ^{1}H NMR spectrum of poly(*p*-fluorostyrene-butadiene) obtained by complex **2a** (Table 1, entry 5) (500MHz, $CDCl_3$, 25^{o}C).
Figure S3. ^{1}H NMR spectrum of poly(*p*-fluorostyrene-butadiene) obtained by complex **2a** (Table 1, entry 6) (500MHz, $CDCl_3$, 25^{o}C).
Figure S4. ^{1}H NMR spectrum of poly(*p*-fluorostyrene-butadiene) obtained by complex **2a** (Table 1, entry 7) (500MHz, $CDCl_3$, 25^{o}C).
Figure S5. ^{1}H NMR spectrum of poly(*p*-fluorostyrene-butadiene) obtained by complex **2a** (Table 1, entry 8) (500MHz, $CDCl_3$, 25^{o}C).
Figure S6. ^{1}H NMR spectrum of poly(*p*-fluorostyrene-butadiene) obtained by complex **2b** (Table 1, entry 9) (500MHz, $CDCl_3$, 25^{o}C).
Figure S7. ^{1}H NMR spectrum of poly(*p*-fluorostyrene-butadiene) obtained by complex **2b** (Table 1, entry 10) (500MHz, $CDCl_3$, 25^{o}C).
Figure S8. ^{1}H NMR spectrum of poly(*p*-fluorostyrene-butadiene) obtained by complex **2b** (Table 1, entry 11) (500MHz, $CDCl_3$, 25^{o}C).
Figure S9. ^{1}H NMR spectrum of poly(*p*-fluorostyrene-butadiene) obtained by complex **2b** (Table 1, entry 12) (500MHz, $CDCl_3$, 25^{o}C).
Figure S10. ^{13}C NMR spectrum of poly(*p*-fluorostyrene-butadiene) obtained by complex **2a** (Table 1, entry 3) (125MHz, $CDCl_3$, 25^{o}C).
Figure S11. ^{13}C NMR spectrum of poly(*p*-fluorostyrene-butadiene) obtained by complex **2a** (Table 1, entry 5) (125MHz, $CDCl_3$, 25^{o}C).
Figure S12. ^{13}C NMR spectrum of poly(*p*-fluorostyrene-butadiene) obtained by complex **2a** (Table 1, entry 6) (125MHz, $CDCl_3$, 25^{o}C).
Figure S13. ^{13}C NMR spectrum of poly(*p*-fluorostyrene-butadiene) obtained by complex **2a** (Table 1, entry 7) (125MHz, $CDCl_3$, 25^{o}C).
Figure S14. ^{13}C NMR spectrum of poly(*p*-fluorostyrene-butadiene) obtained by complex **2b** (Table 1, entry 8) (125MHz, $CDCl_3$, 25^{o}C).
Figure S15. ^{13}C NMR spectrum of poly(*p*-fluorostyrene-butadiene) obtained by complex **2b**

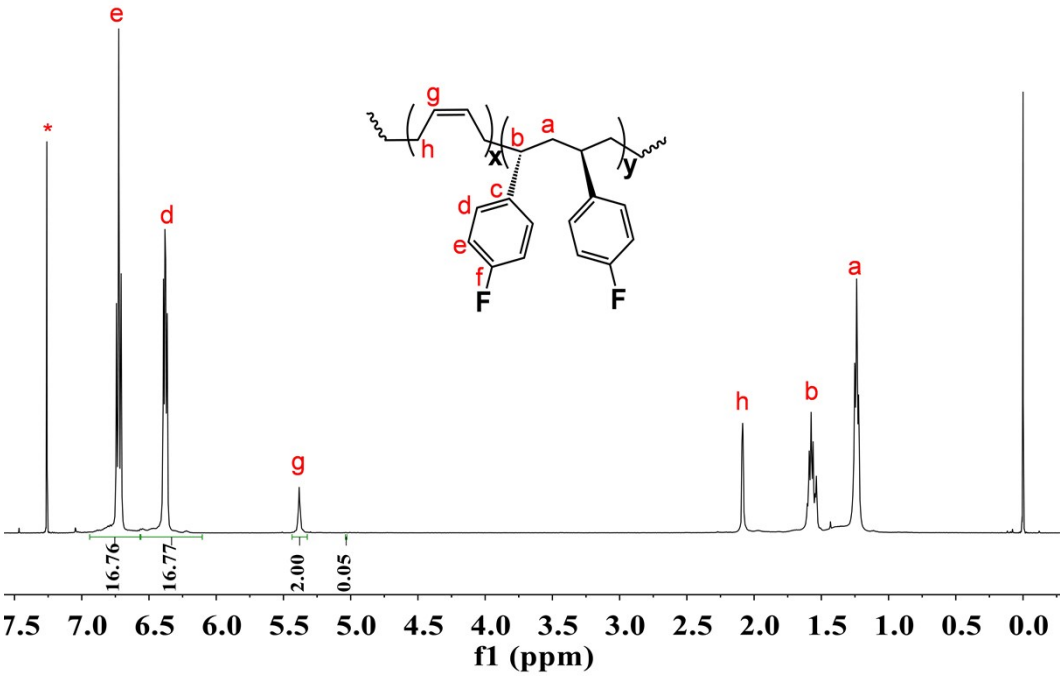


Figure S1. ^{1}H NMR spectrum of poly(*p*-fluorostyrene-butadiene) obtained by complex **2a** (Table 1, entry 3) (500MHz, $CDCl_3$, 25^{o}C).

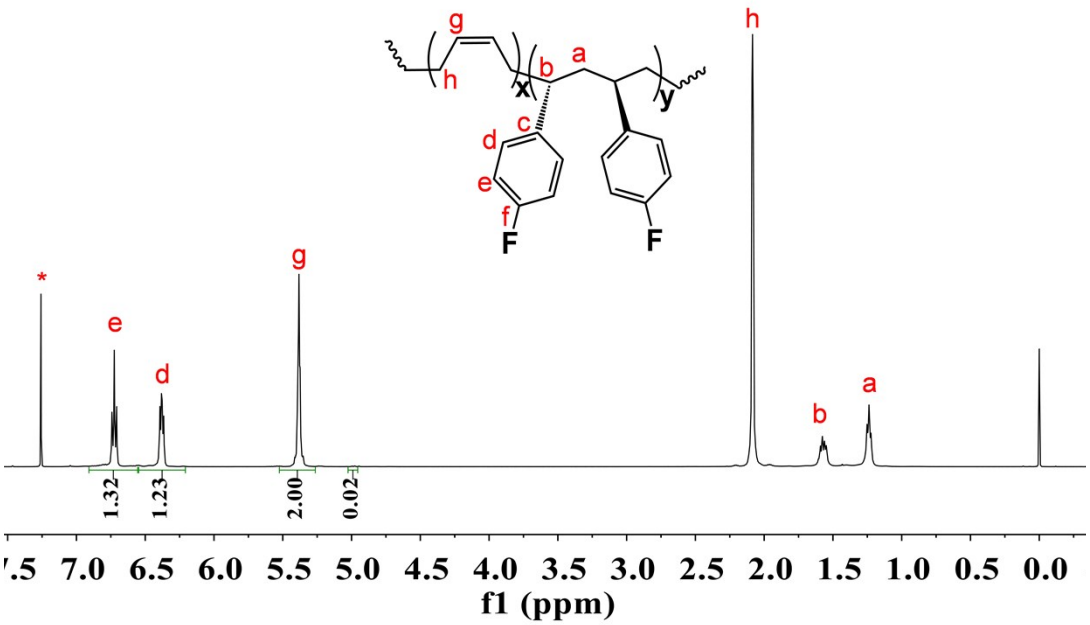


Figure S2. ^{1}H NMR spectrum of poly(*p*-fluorostyrene-butadiene) obtained by complex **2a** (Table 1, entry 5) (500MHz, $CDCl_3$, 25^{o}C).

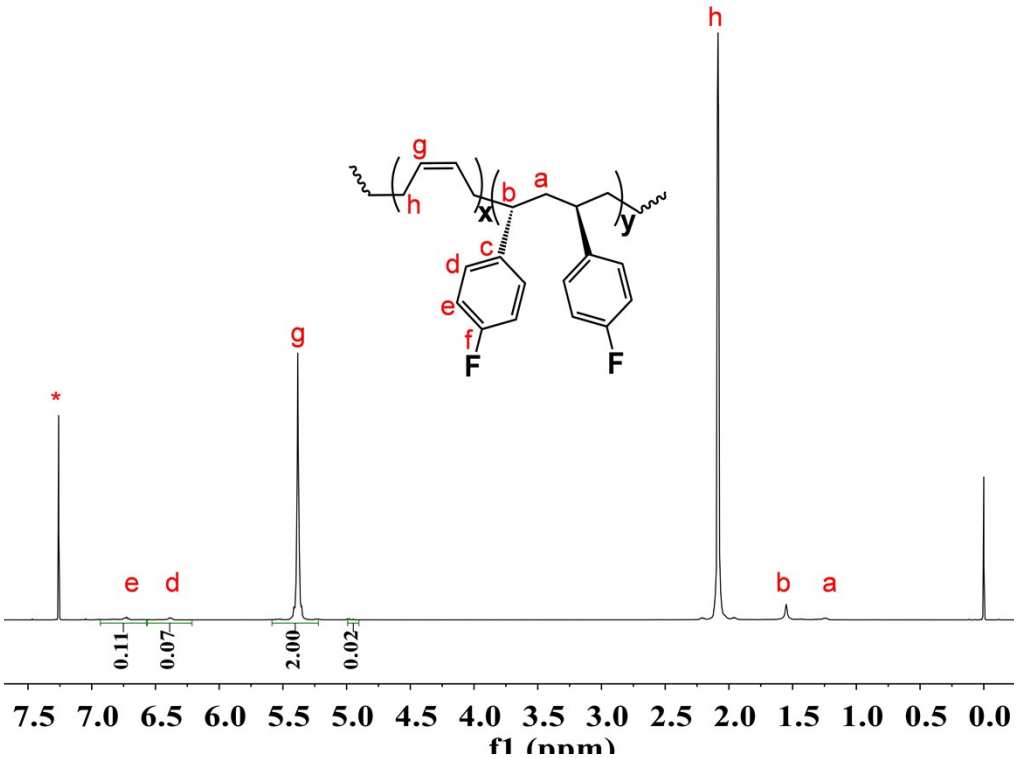


Figure S3. ^{1}H NMR spectrum of poly(*p*-fluorostyrene-butadiene) obtained by complex **2a** (Table 1, entry 6) (500MHz, $CDCl_3$, 25^{o}C).

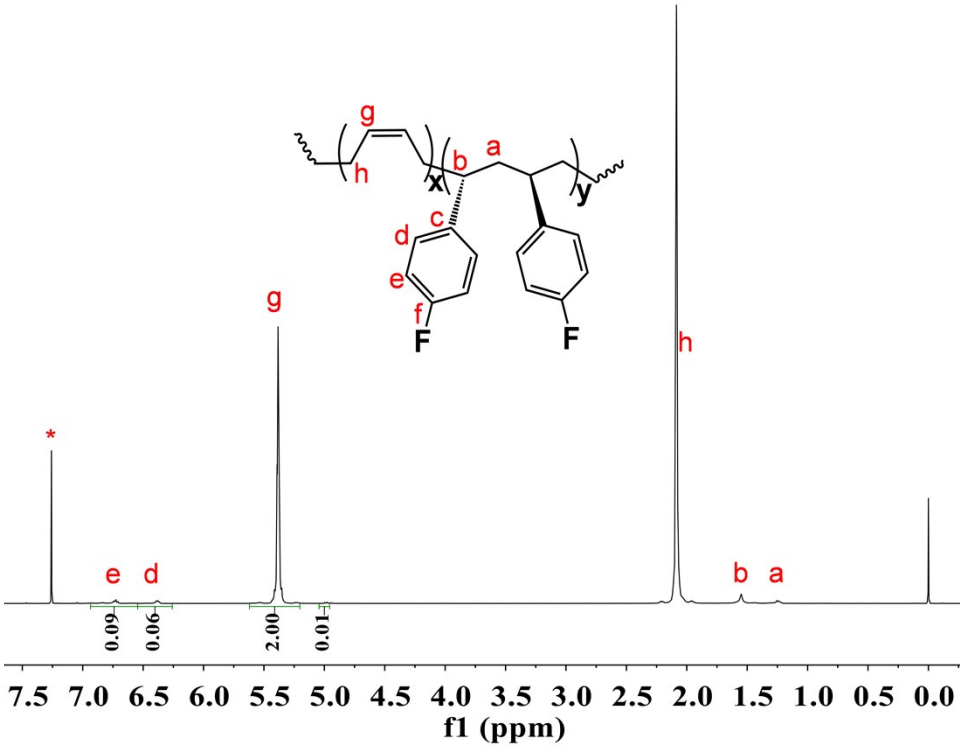


Figure S4. ^{1}H NMR spectrum of poly(*p*-fluorostyrene-butadiene) obtained by complex **2a** (Table 1, entry 7) (500MHz, $CDCl_3$, 25^{o}C).

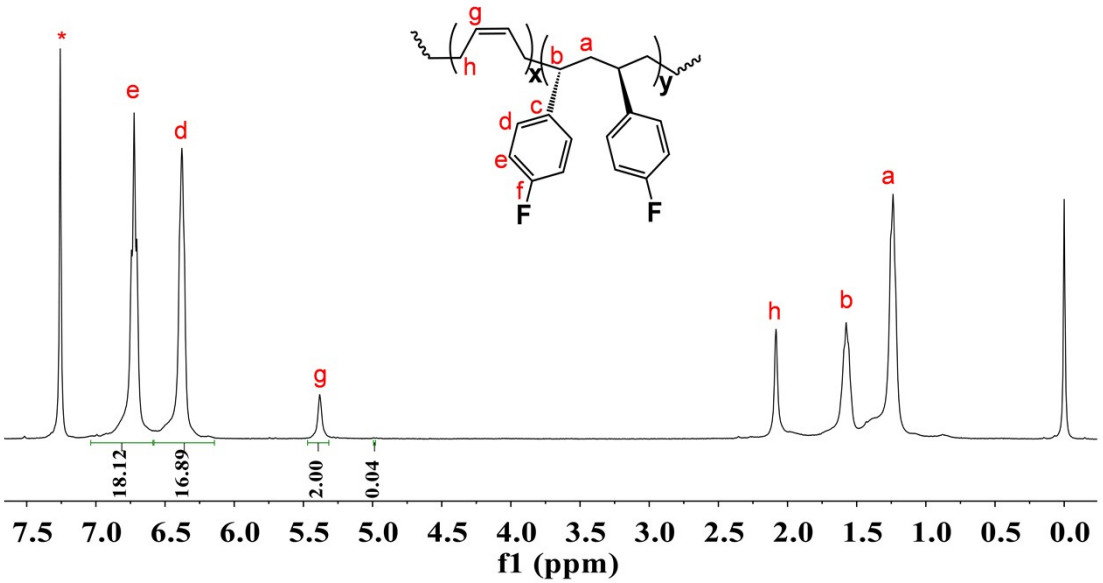


Figure S5. ^{1}H NMR spectrum of poly(*p*-fluorostyrene-butadiene) obtained by complex **2a** (Table 1, entry 8) (500MHz, $CDCl_3$, 25^{o}C).

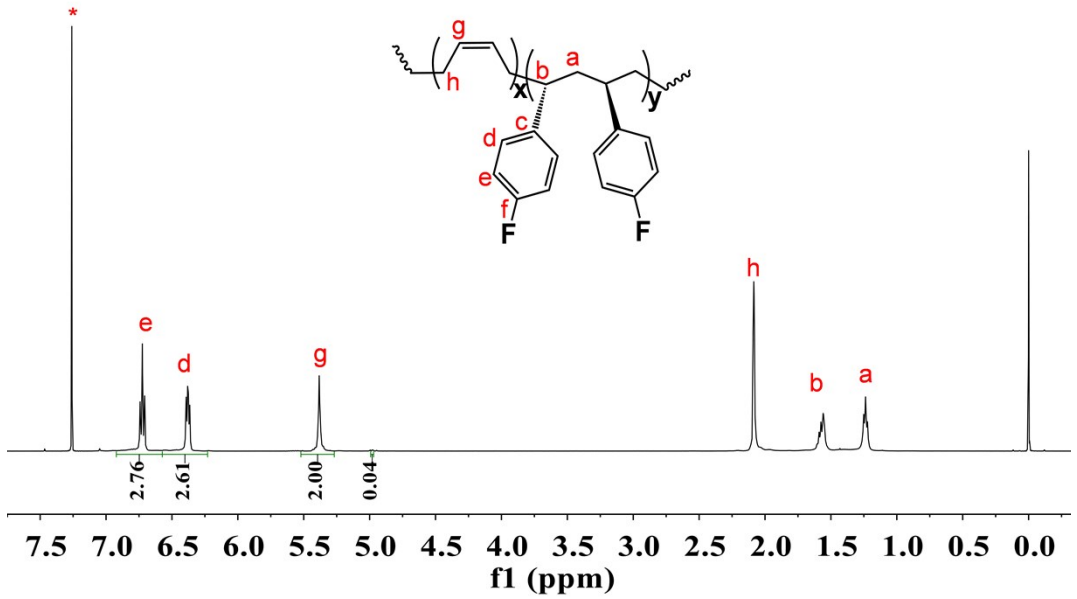


Figure S6. ^{1}H NMR spectrum of poly(*p*-fluorostyrene-butadiene) obtained by complex **2b** (Table 1, entry 9) (500MHz, $CDCl_3$, 25^{o}C).

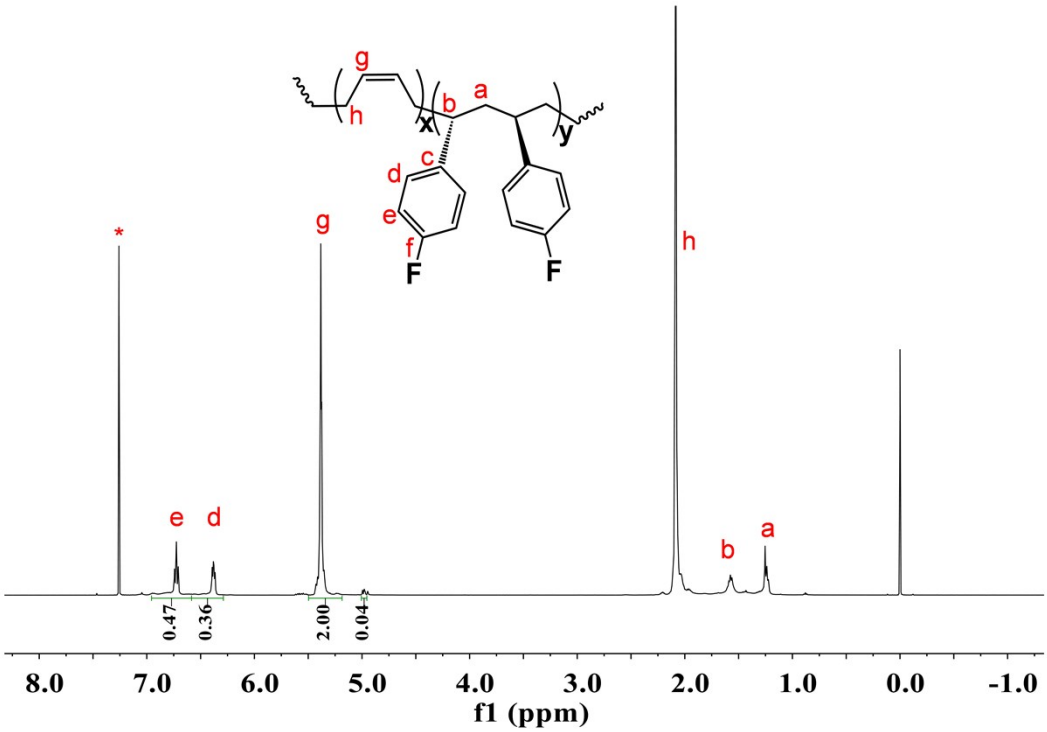


Figure S7. ^{1}H NMR spectrum of poly(*p*-fluorostyrene-butadiene) obtained by complex **2b** (Table 1, entry 10) (500MHz, $CDCl_3$, 25^{o}C).

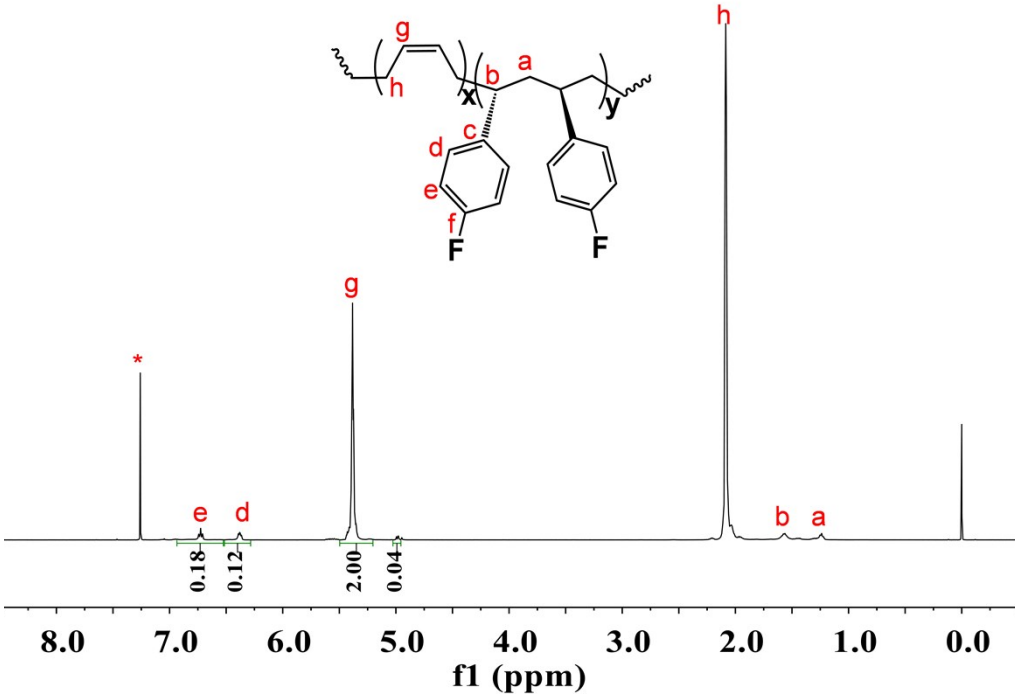


Figure S8. ^{1}H NMR spectrum of poly(*p*-fluorostyrene-butadiene) obtained by complex **2b** (Table 1, entry 11) (500MHz, $CDCl_3$, 25^{o}C).

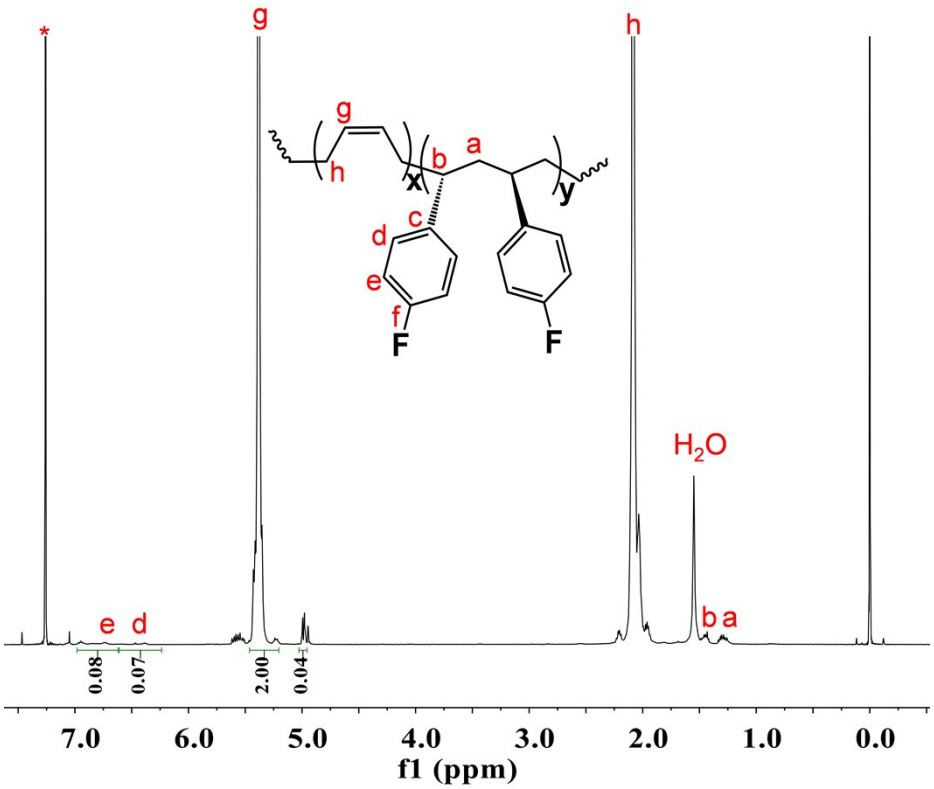


Figure S9. ^{1}H NMR spectrum of poly(*p*-fluorostyrene-butadiene) obtained by complex **2b** (Table 1, entry 12) (500MHz, $CDCl_3$, 25^{o}C).

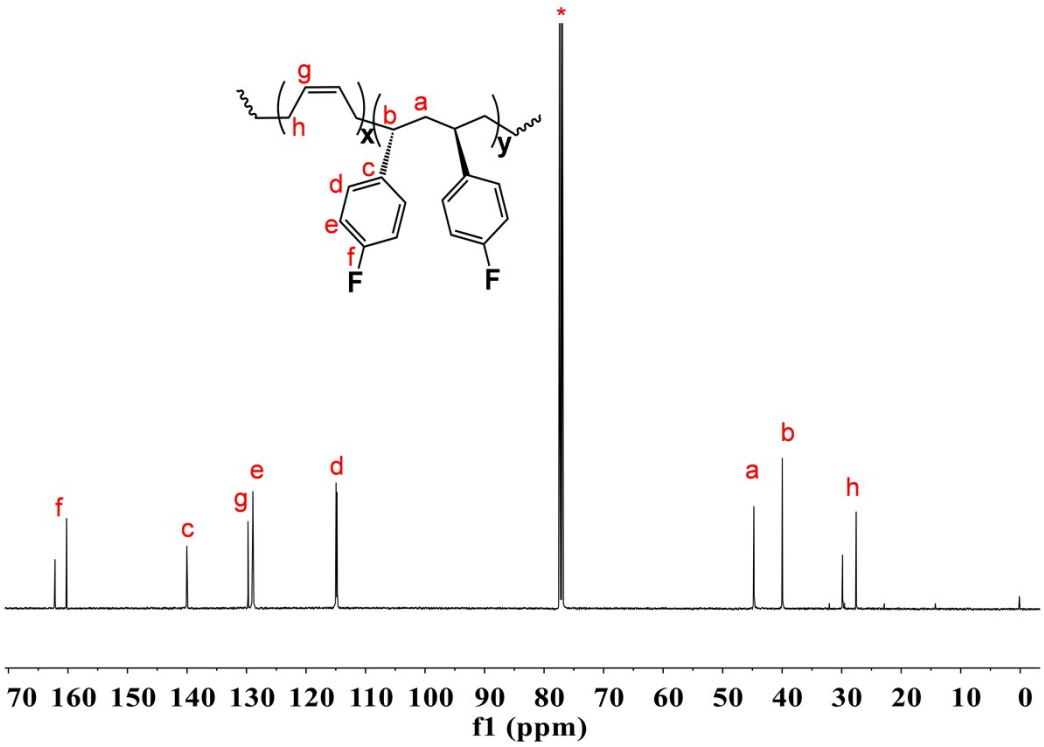


Figure S10. ^{13}C NMR spectrum of poly(*p*-fluorostyrene-butadiene) obtained by complex **2a** (Table 1, entry 3) (125MHz, $CDCl_3$, 25^{o}C).

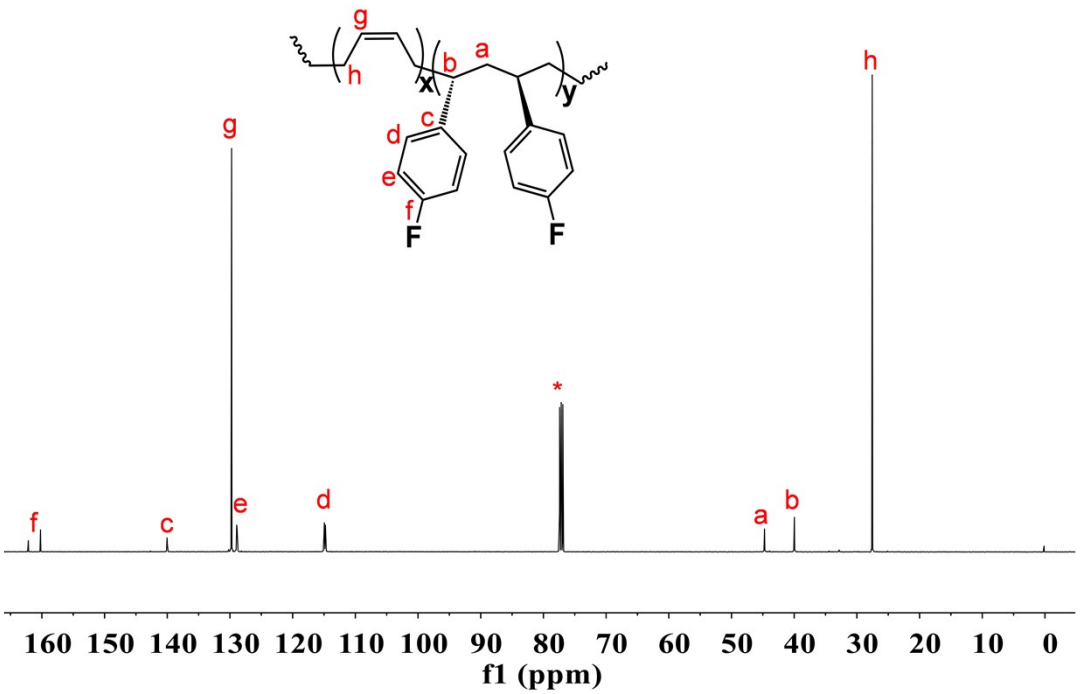


Figure S11. ^{13}C NMR spectrum of poly(*p*-fluorostyrene-butadiene) obtained by complex **2a** (Table 1, entry 5) (125MHz, $CDCl_3$, 25°C).

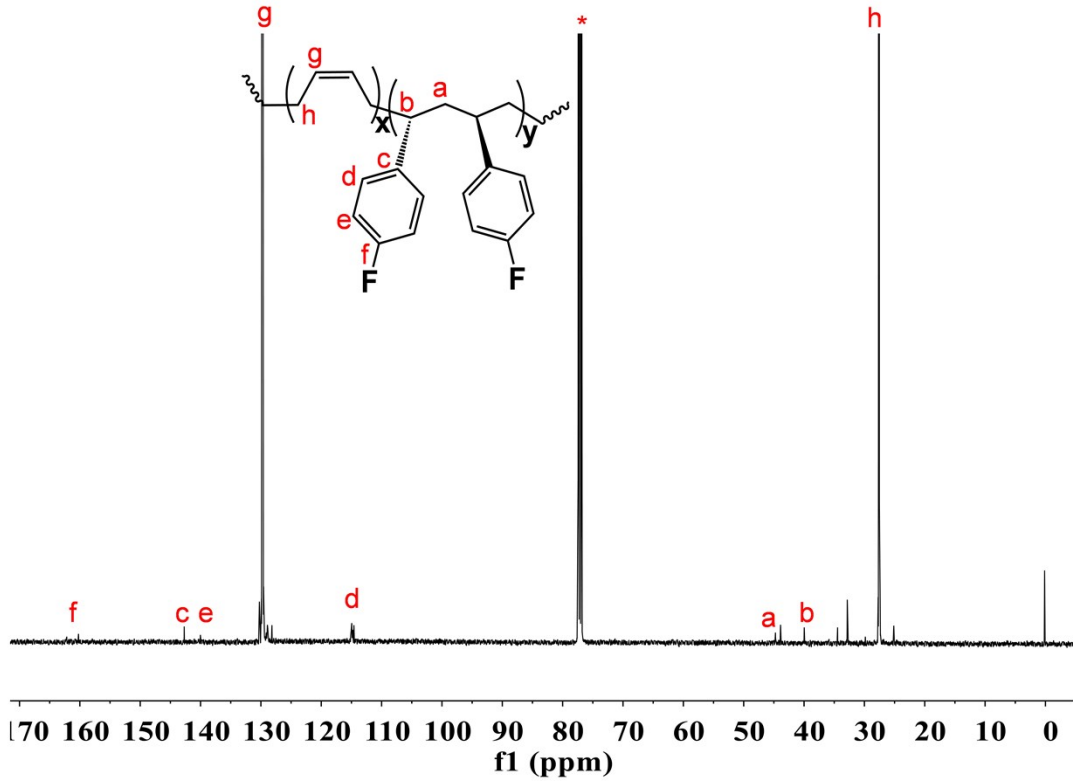


Figure S12. ^{13}C NMR spectrum of poly(*p*-fluorostyrene-butadiene) obtained by complex **2a** (Table 1, entry 6) (125MHz, $CDCl_3$, 25°C).

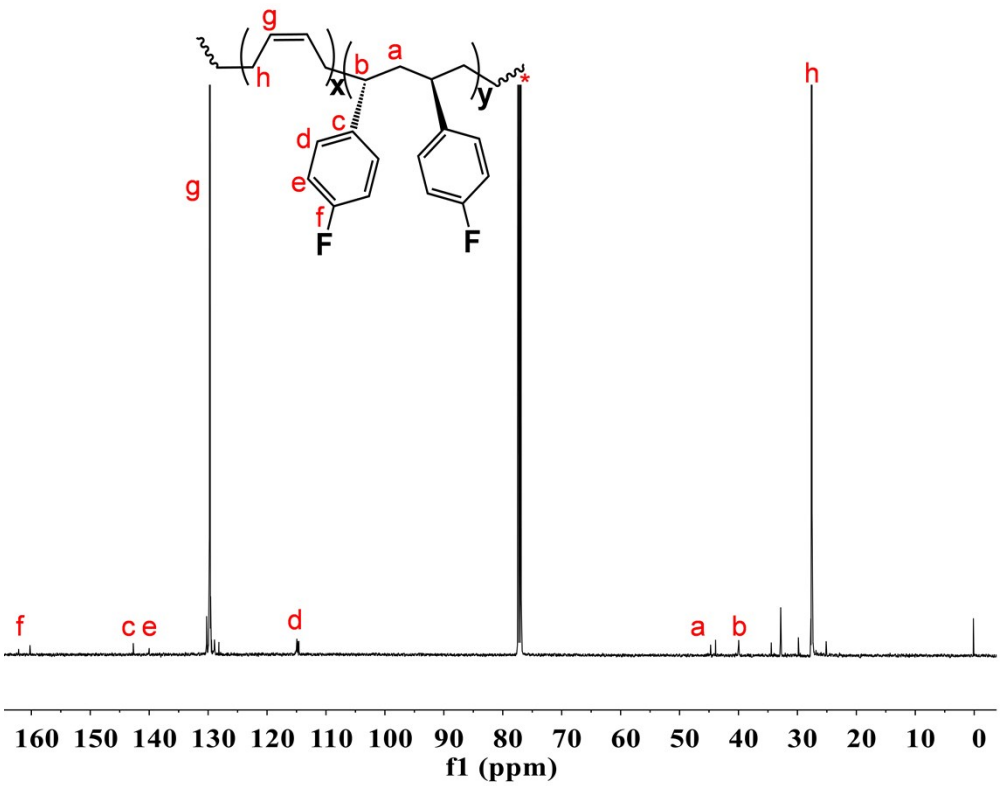


Figure S13. ^{13}C NMR spectrum of poly(*p*-fluorostyrene-butadiene) obtained by complex **2a** (Table 1, entry 7) (125MHz, $CDCl_3$, 25°C).

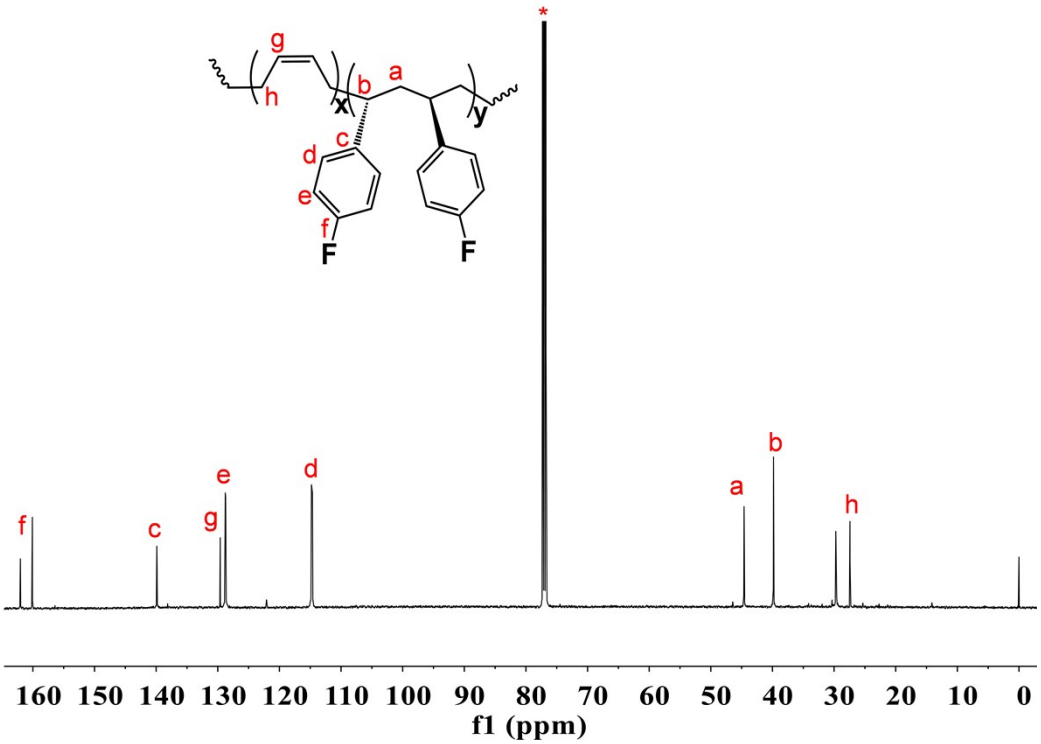


Figure S14. ^{13}C NMR spectrum of poly(*p*-fluorostyrene-butadiene) obtained by complex **2b** (Table 1, entry 8) (125MHz, $CDCl_3$, 25°C).

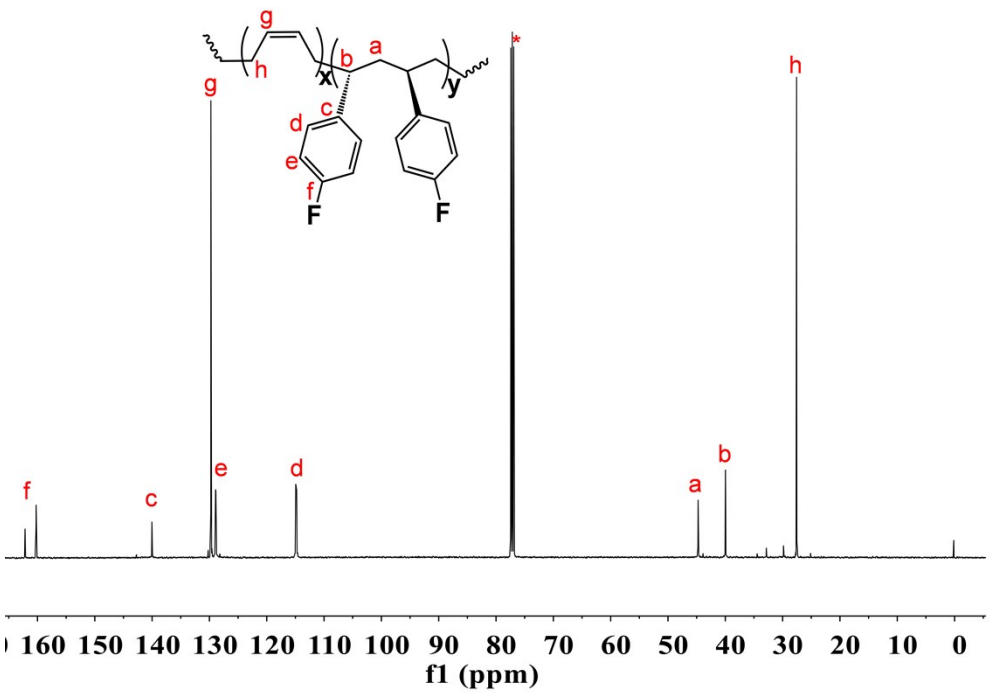


Figure S15. ^{13}C NMR spectrum of poly(*p*-fluorostyrene-butadiene) obtained by complex **2b** (Table 1, entry 9) (125MHz, $CDCl_3$, 25°C).

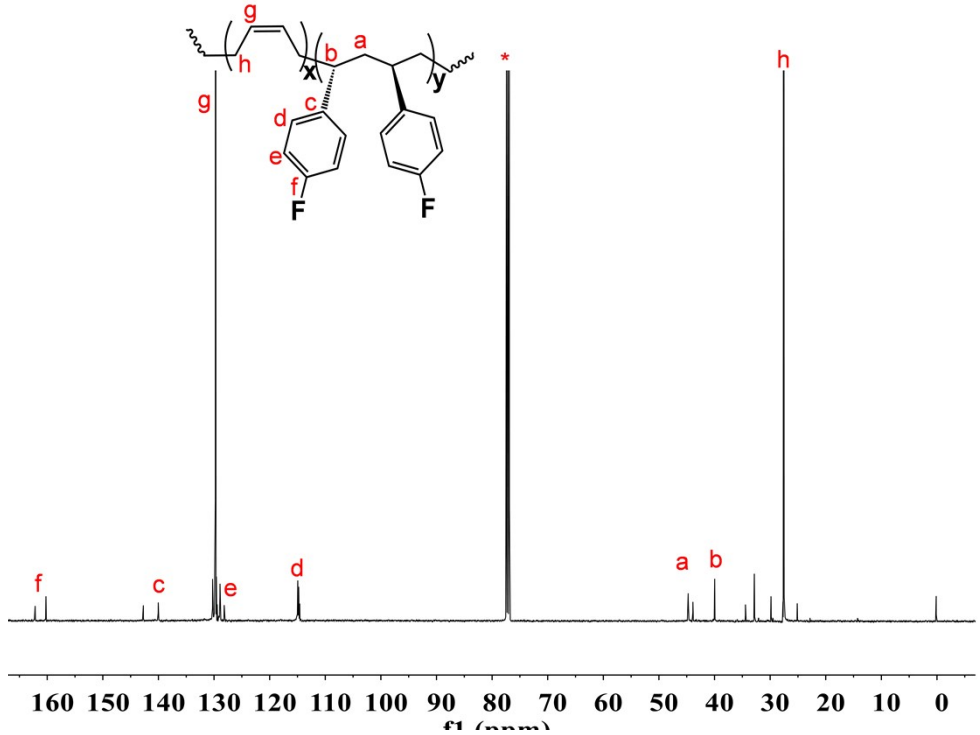


Figure S16. ^{13}C NMR spectrum of poly(*p*-fluorostyrene-butadiene) obtained by complex **2b** (Table 1, entry 10) (125MHz, $CDCl_3$, 25°C).

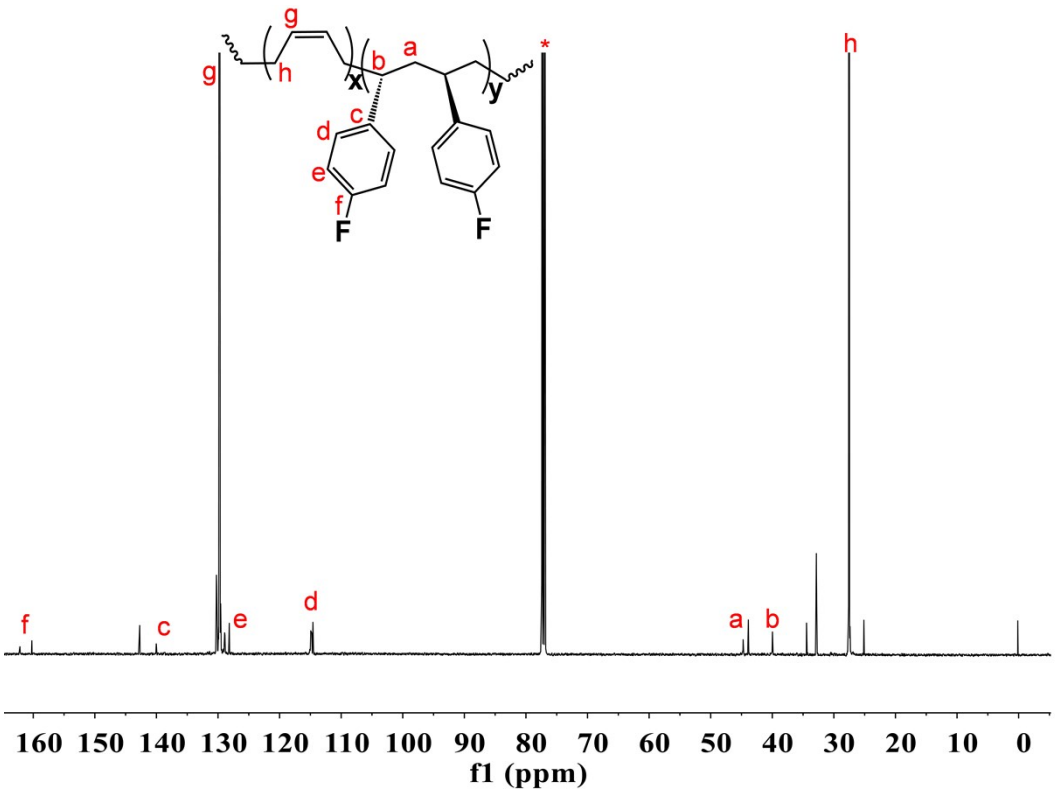


Figure S17. ^{13}C NMR spectrum of poly(*p*-fluorostyrene-butadiene) obtained by complex **2b** (Table 1, entry 11) (125MHz, $CDCl_3$, 25°C).

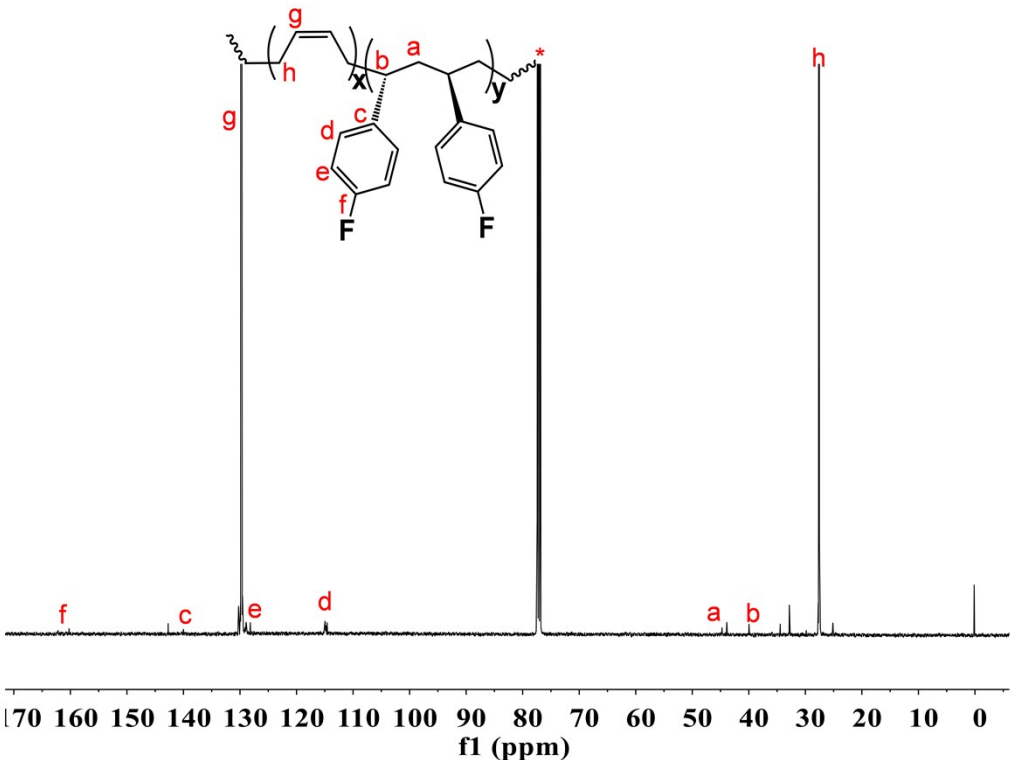


Figure S18. ^{13}C NMR spectrum of poly(*p*-fluorostyrene-butadiene) obtained by complex **2b** (Table 1, entry 12) (125MHz, $CDCl_3$, 25°C).

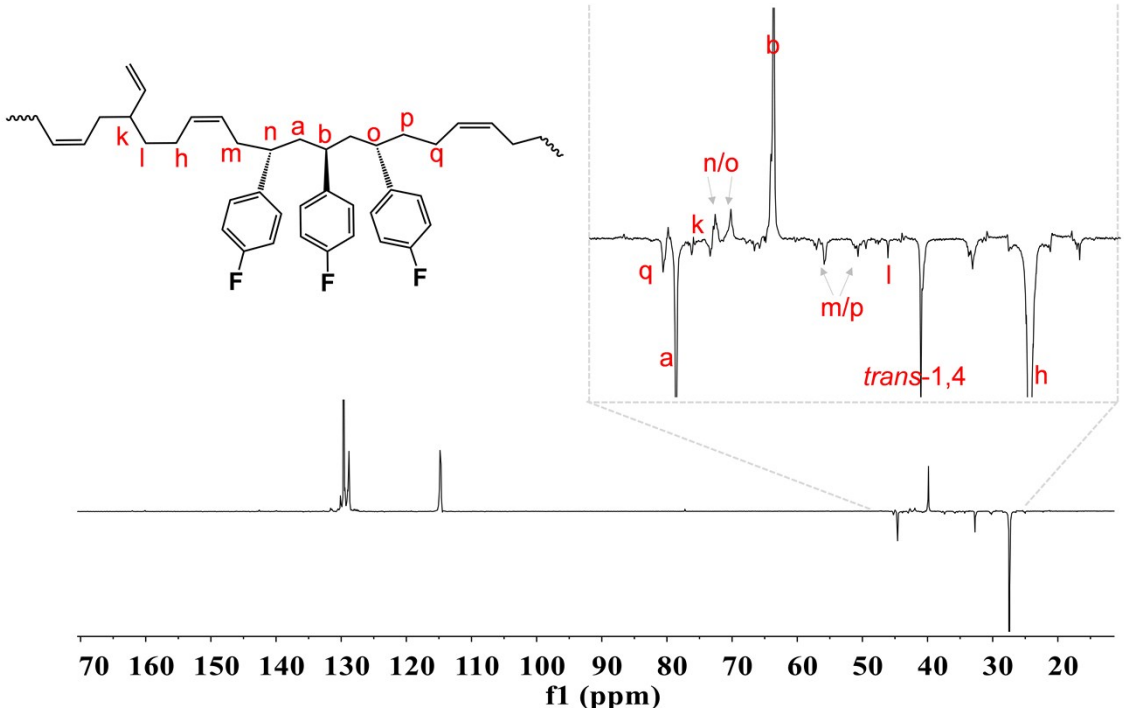


Figure S19. DEPT (distortionless enhancement by polarization transfer) 135 spectrum of multi-block poly(*p*FS-BD). (125MHz, $CDCl_3$, 25°C).

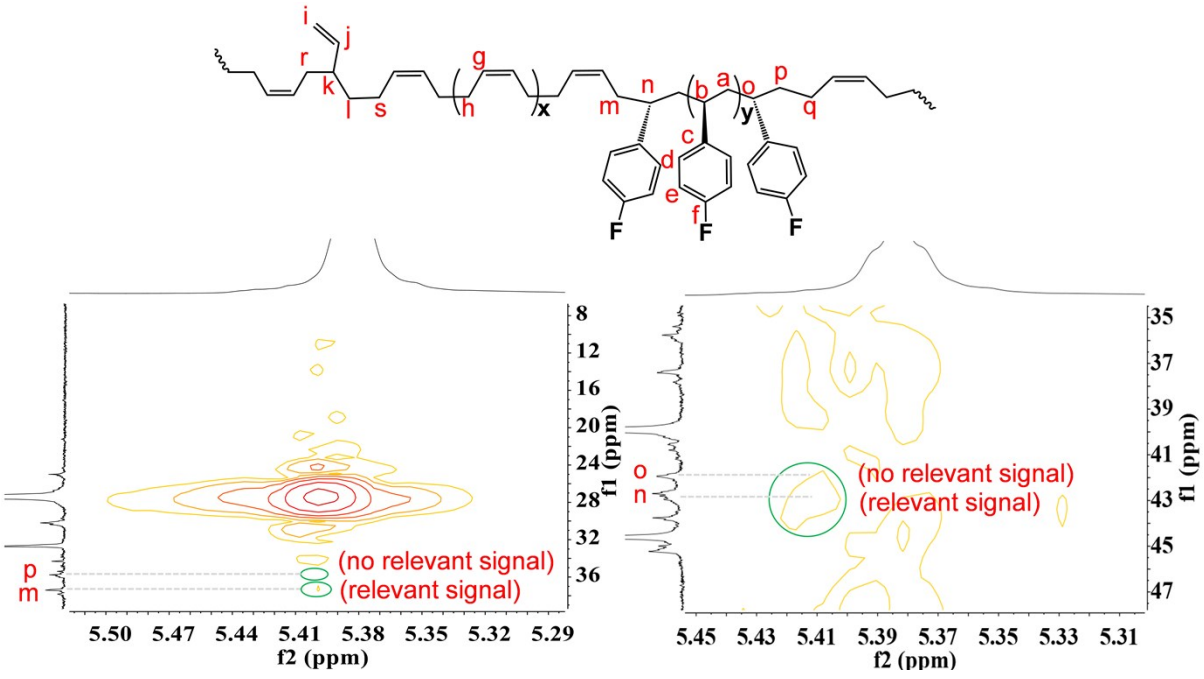


Figure S20. HMBC (^{1}H detected heteronuclear multiple bond correlation) spectrum of multi-block poly(*p*FS-BD). (125MHz, $CDCl_3$, 25°C).

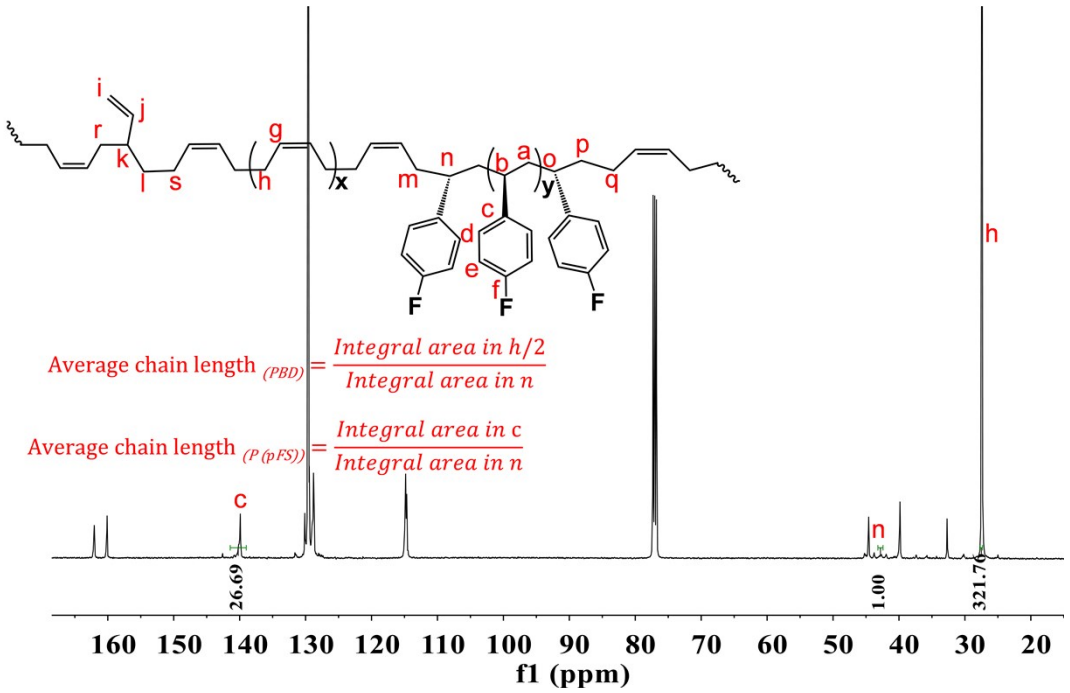


Figure S21. Quantitative ^{13}C NMR spectrum of multi-block poly(*p*FS-BD). (125MHz, $CDCl_3$, 25°C).

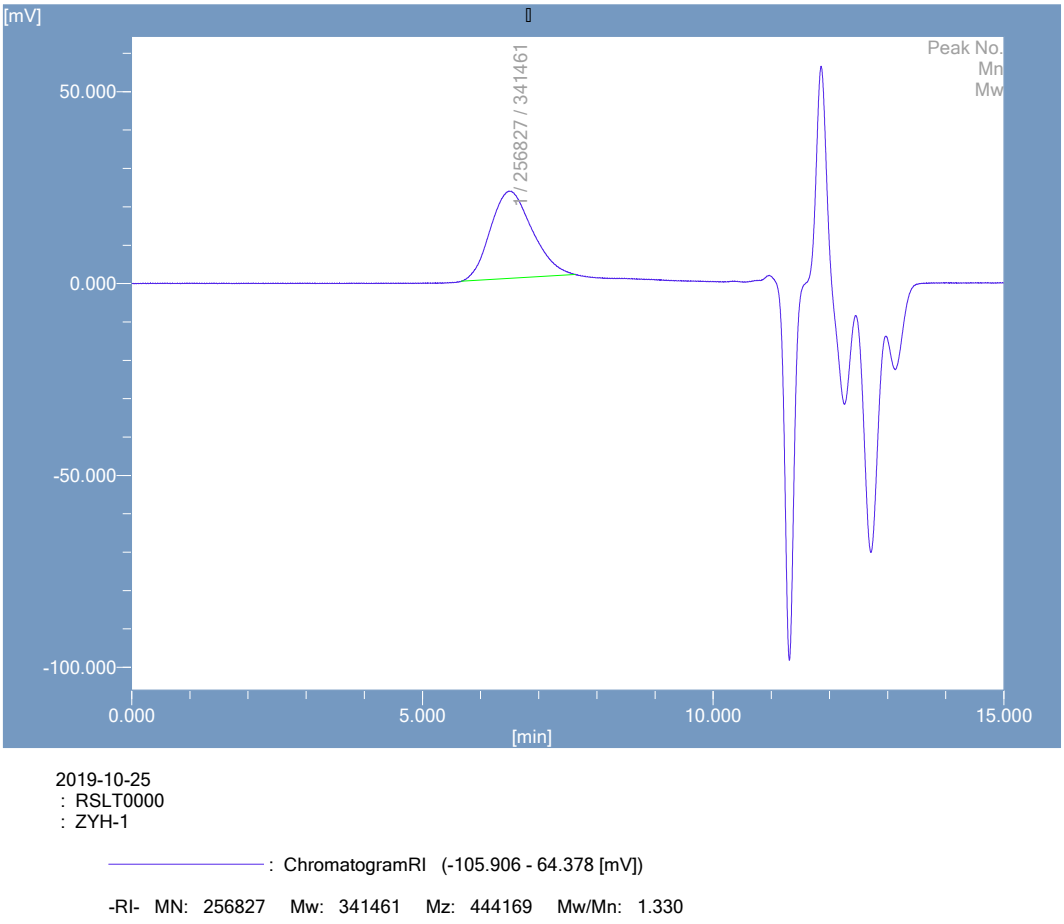
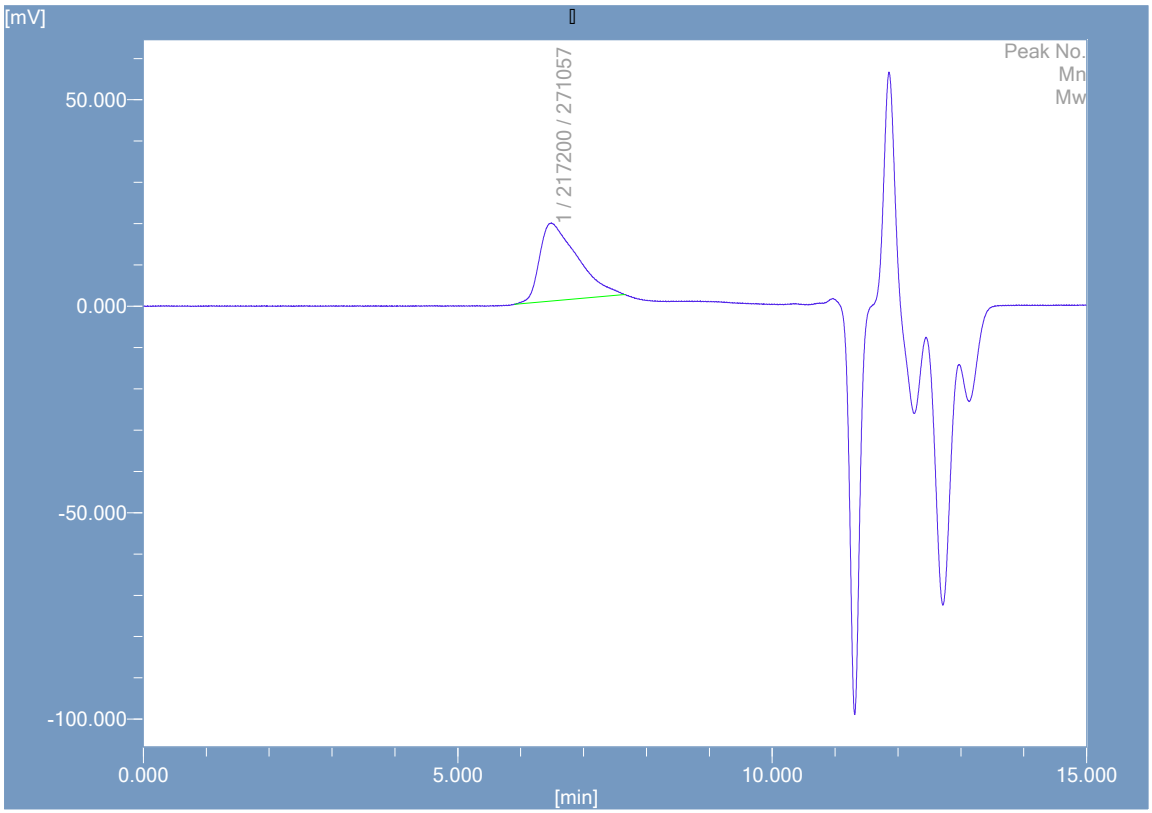


Figure S22. GPC curve of poly(*p*-fluorostyrene-butadiene) obtained by complex **2a** (Table 1, entry 3).



2019-10-25
: RSLT0001
: ZYH-2

: ChromatogramRI (-106.673 - 64.497 [mV])

-RI- MN: 217200 Mw: 271057 Mz: 322956 Mw/Mn: 1.248

Figure S23. GPC curve of poly(*p*-fluorostyrene-butadiene) obtained by complex **2a** (Table 1, entry 4).

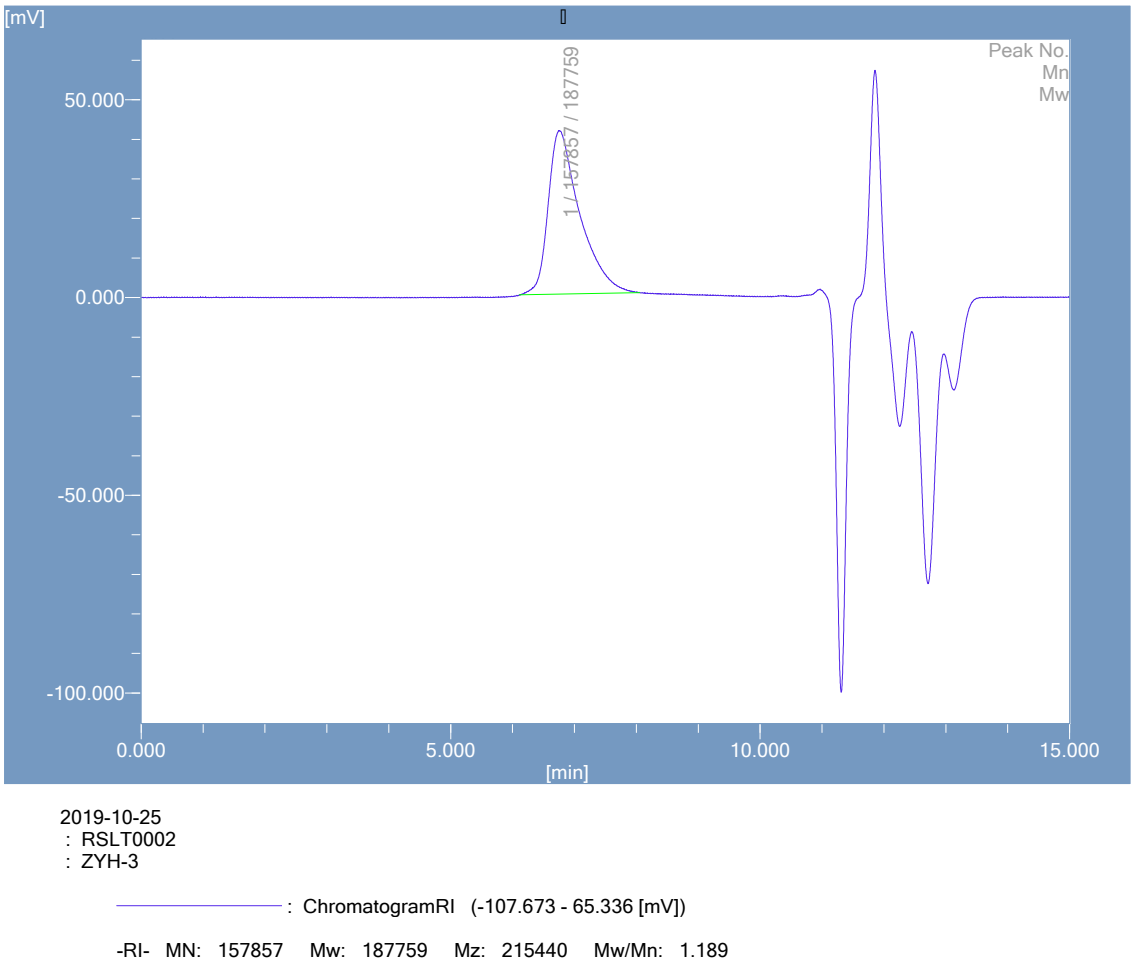
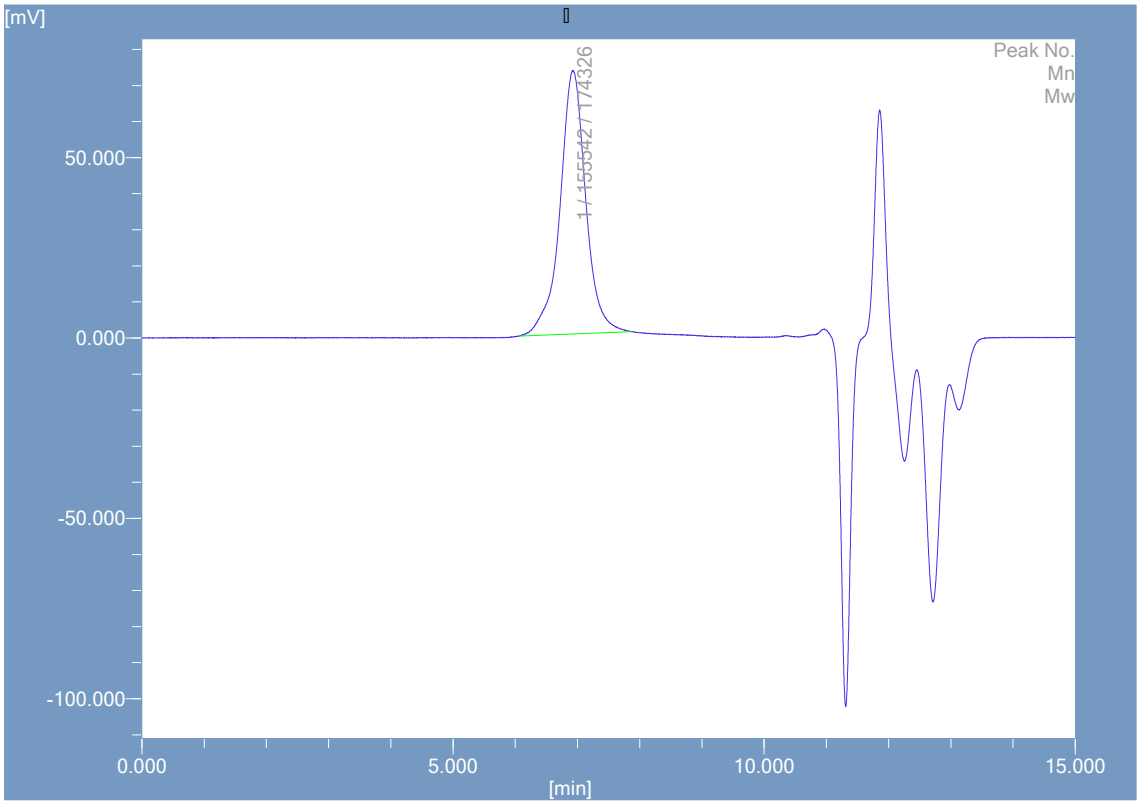


Figure S24. GPC curve of poly(*p*-fluorostyrene-butadiene) obtained by complex **2a** (Table 1, entry 5).

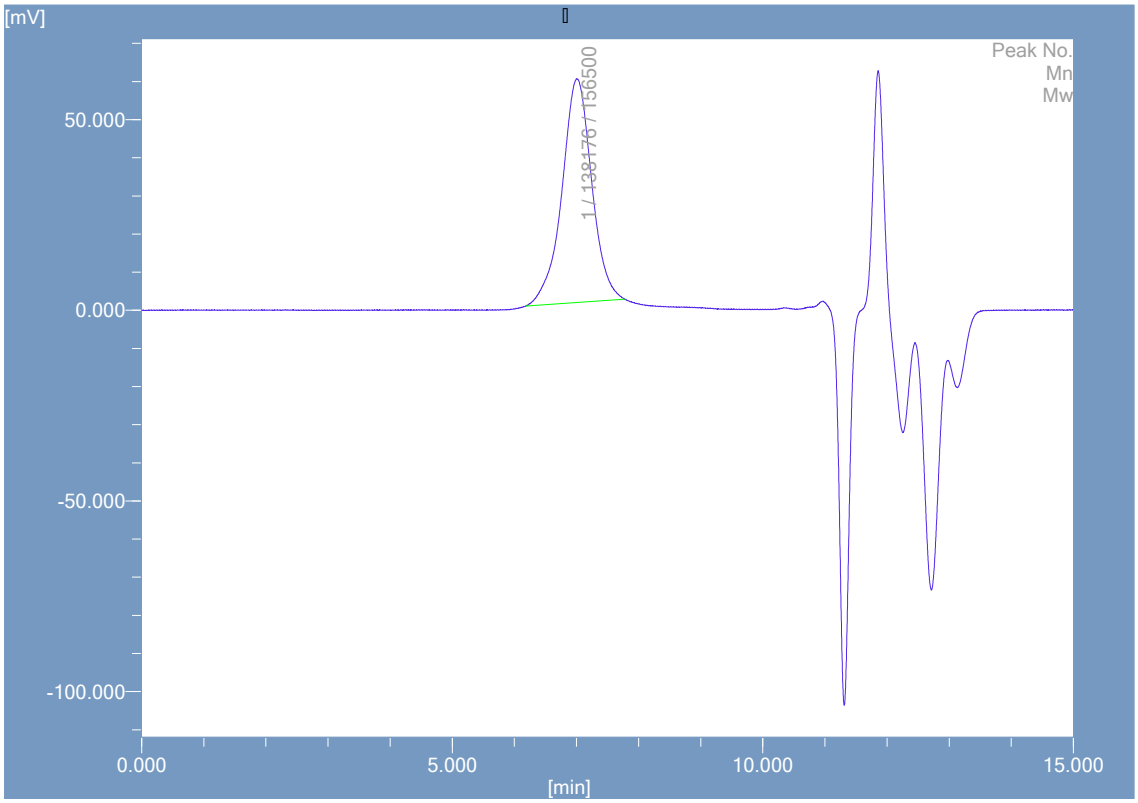


2019-10-25
: RSLT0003
: ZYH-4

: ChromatogramRI (-110.943 - 82.911 [mV])

-RI- MN: 155542 Mw: 174326 Mz: 197582 Mw/Mn: 1.121

Figure S25. GPC curve of poly(*p*-fluorostyrene-butadiene) obtained by complex **2a** (Table 1, entry 6).

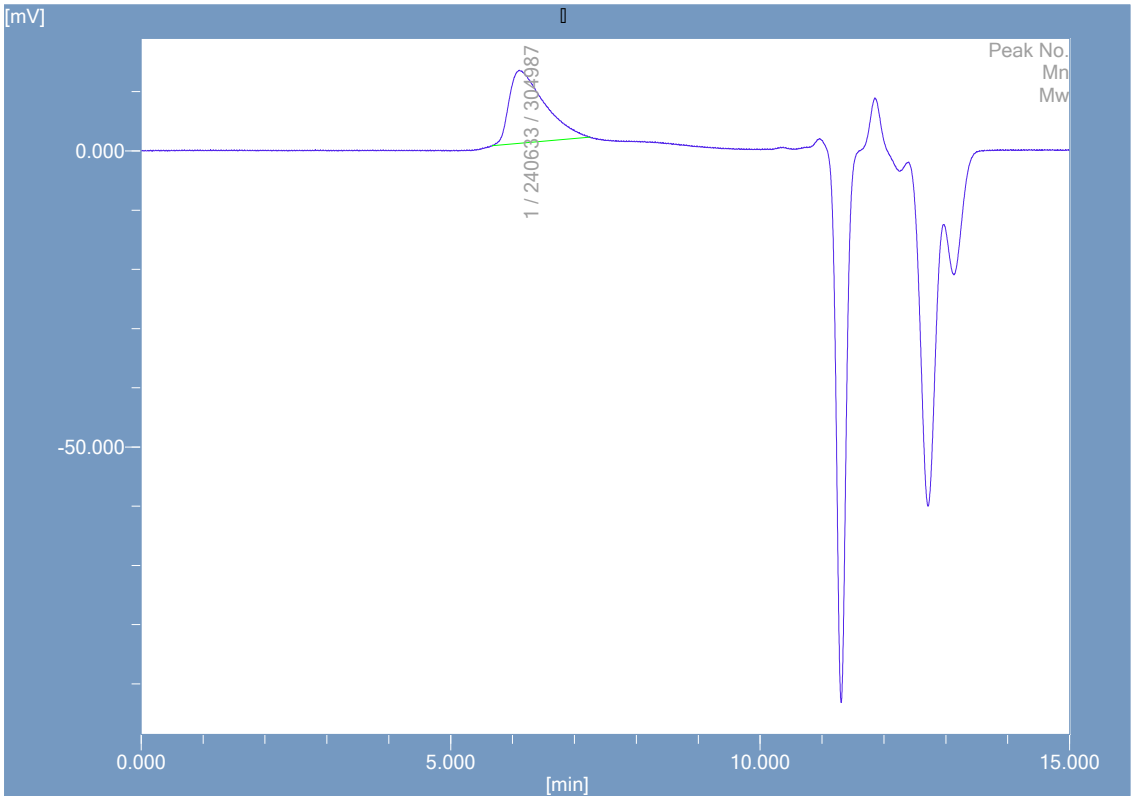


2019-10-25
: RSLT0004
: ZYH-5

: ChromatogramRI (-111.912 - 71.188 [mV])

-RI- MN: 138176 Mw: 156500 Mz: 179279 Mw/Mn: 1.133

Figure S26. GPC curve of poly(*p*-fluorostyrene-butadiene) obtained by complex **2a** (Table 1, entry 7).

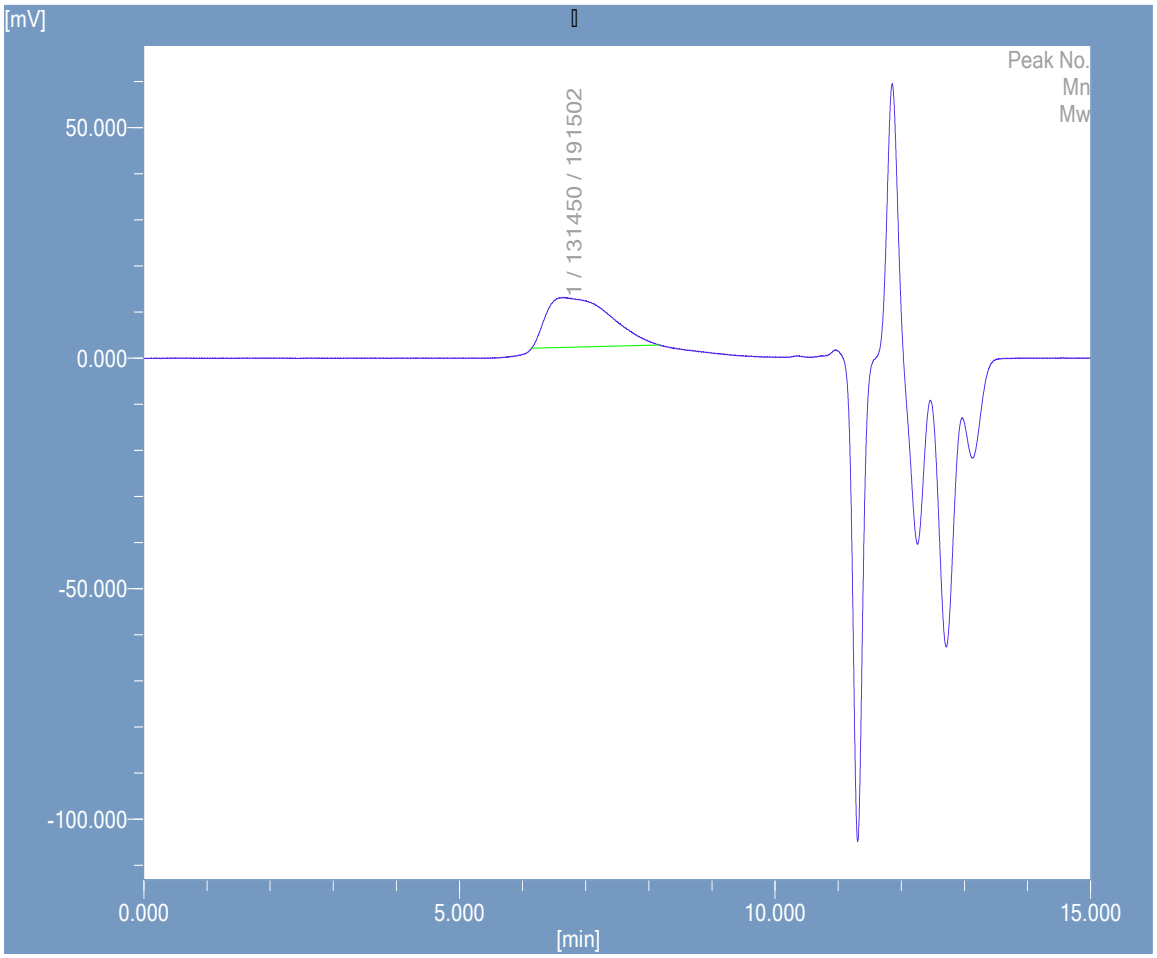


2019-11-01
: RSLT0034
: ZYH-3

: ChromatogramRI (-98.494 - 18.974 [mV])

-RI- MN: 240633 Mw: 304987 Mz: 364864 Mw/Mn: 1.267

Figure S27. GPC curve of poly(*p*-fluorostyrene-butadiene) obtained by complex **2b** (Table 1, entry 8).



2019-10-25
: RSLT0006
: ZYH-7

: ChromatogramRI (-113.052 - 67.763 [mV])

-RI- MN: 131450 Mw: 191502 Mz: 255588 Mw/Mn: 1.457

Figure S28. GPC curve of poly(*p*-fluorostyrene-butadiene) obtained by complex **2b** (Table 1, entry 9).

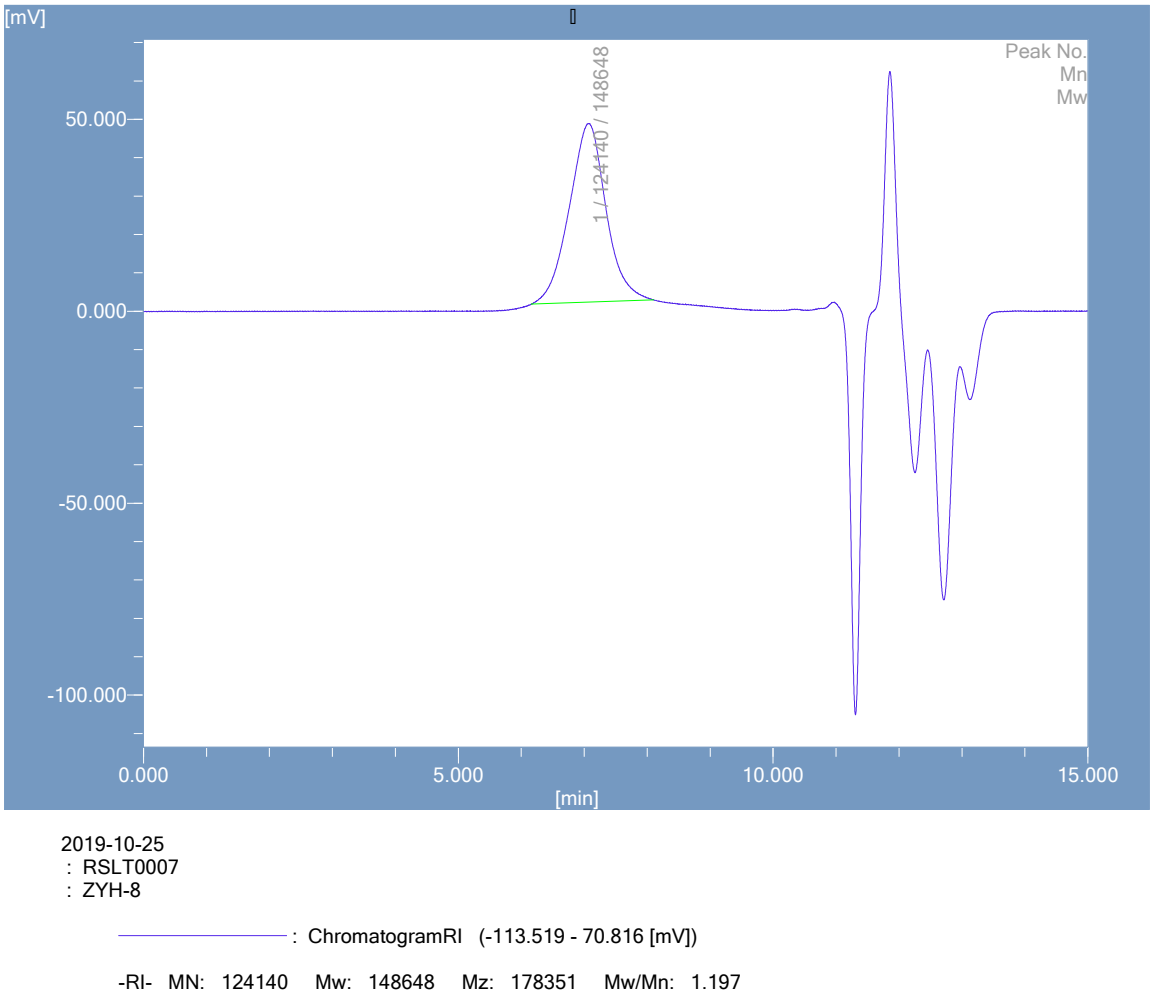


Figure S29. GPC curve of poly(*p*-fluorostyrene-butadiene) obtained by complex **2b** (Table 1, entry 10).

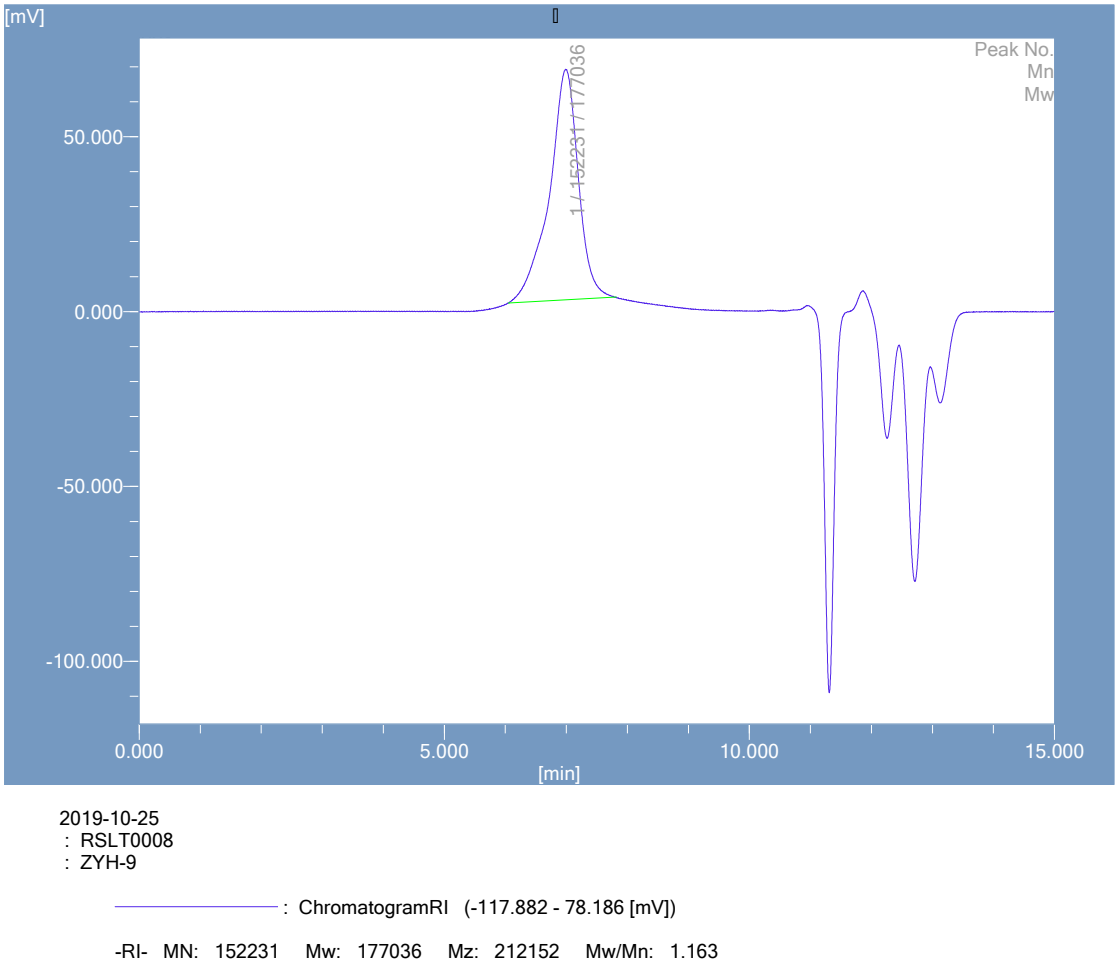


Figure S30. GPC curve of poly(*p*-fluorostyrene-butadiene) obtained by complex **2b** (Table 1, entry 11).

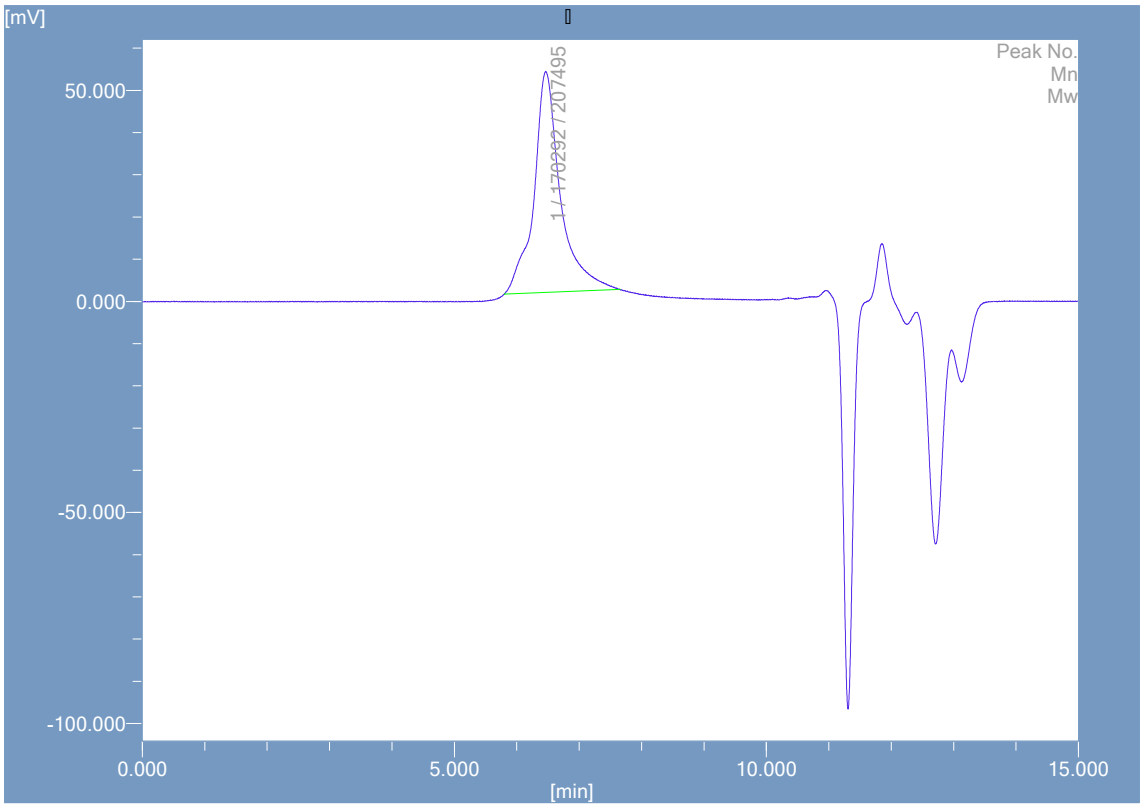


Figure S31. GPC curve of poly(*p*-fluorostyrene-butadiene) obtained by complex **2b** (Table 1, entry 12).

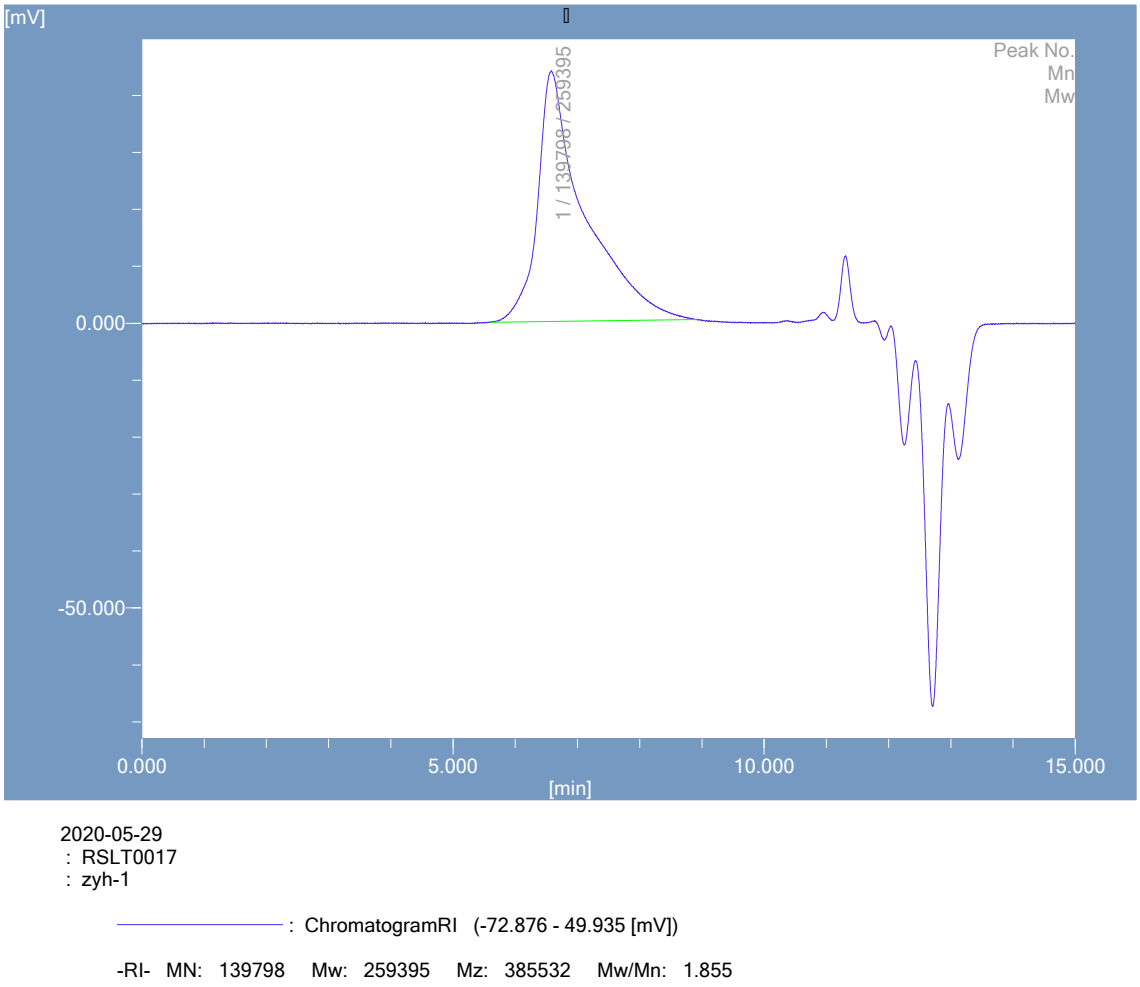


Figure S32. GPC curve of multi-block poly(*p*-fluorostyrene-butadiene) obtained by complex **2a**.

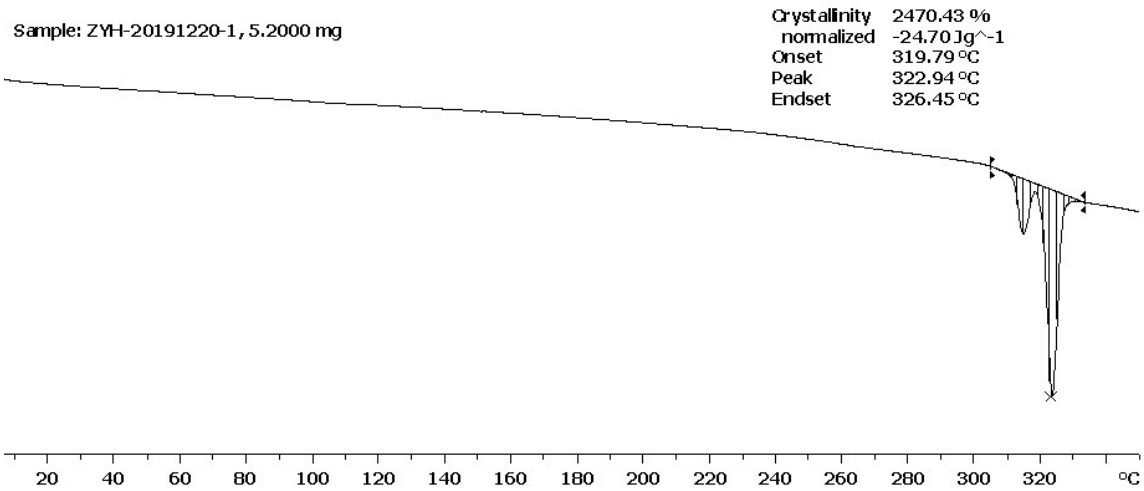


Figure S33. DSC curve of poly(*p*-fluorostyrene) obtained by complex **2a** at 20℃ (Table 2, entry 1).

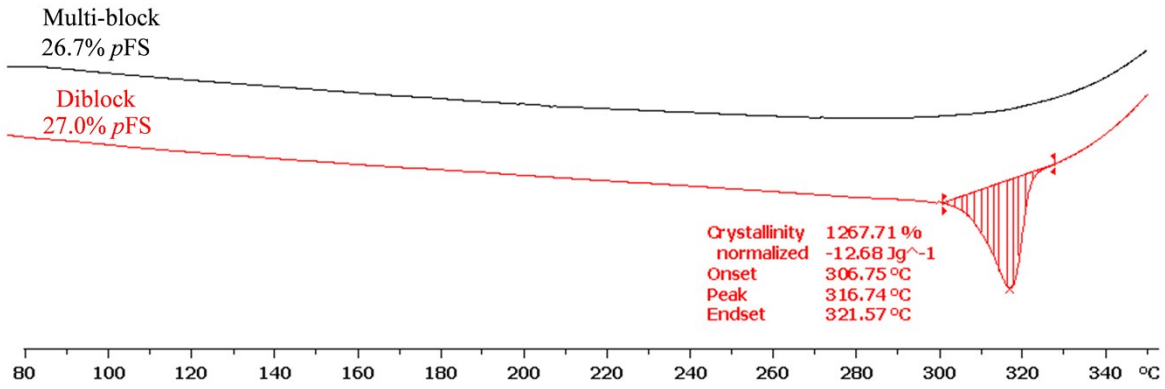


Figure S34. DSC curves of multi-block poly(*p*FS-BD)(up) and diblock poly(*p*FS-BD)(down) obtained by complex **2a**.