

Isospecific Polymerization of Halide- and Amino-Substituted Styrenes Using a Bis(phenolate) Titanium Catalyst

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Experimental Procedures

General Methods. All manipulations were performed under a dry and oxygen-free nitrogen atmosphere using standard high-vacuum Schlenk techniques or in a glovebox. All solvents were purified with a SPS system. *Para*-fluorostyrene (*p*FS), *para*-chlorostyrene (*p*ClS), *para*-bromostyrene (*p*BrS), *para*-(*N,N*-diethylamino)styrene (DMAS), $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ and dry methylaluminoxane (DMAO) were purchased from Energy Chemical. The monomers were dried by stirring with CaH_2 for 24 h and distilled before use. Complex 1 were prepared according to the literature [49].

^1H and ^{13}C NMR spectra were recorded on a Bruker AV400 (400 MHz for ^1H NMR; 100 MHz for ^{13}C NMR) spectrometer. The molecular weight and molecular weight distribution of the polymers were measured by means of gel permeation chromatography (GPC) on a PL-GPC 220 type high temperature chromatography equipped with three PL-gel 10 μm Mixed-BLS type columns at 150 $^\circ\text{C}$. And the molecular weight and molecular weight distribution of the poly(DMAS) were measured by TOSOH HLC-8420 GPC at 40 $^\circ\text{C}$ using THF as the eluent (the flowing rate is 0.35 mL/min) against polystyrene standards. The glass transition temperature (T_g) of the polymer was measured through differential scanning calorimetry (DSC) analysis, which was carried out on a METTLER TOPEM DSC instrument under nitrogen atmosphere. Any thermal history difference in the polymers was eliminated by first heating the specimen to 300 $^\circ\text{C}$, cooling at 10 $^\circ\text{C}/\text{min}$ to room temperature, and then recording the second DSC scan from 25 $^\circ\text{C}$ to 300/320/350 $^\circ\text{C}$ at 10 $^\circ\text{C}/\text{min}$.

***Para*-Fluorostyrene Polymerization.** (a) A typical polymerization procedure (Table 1, entry 2) was described as follow. In a glovebox, 30 equivalents of Al^iBu_3 (0.60 mL, 0.5 mol/L) and a toluene solution (0.5 mL) of complex 1 (5.1 mg, 10 μmol) was added into a 10 mL flask and stirred for 3 min. Then, a toluene solution (0.5 mL) of 1 equivalent of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (9.2 mg, 10 μmol) were added to the flask. The flask was placed in a bath at 40 $^\circ\text{C}$. Then, *p*FS (0.611 g, 5 mmol) was injected into the flask. After the mixture had been stirred for 30 min, methanol was injected to terminate the polymerization. The viscous mixture was poured into a large quantity of methanol to precipitate the polymeric product, which was then collected by filtration, washed with methanol, and dried under vacuum at 40 $^\circ\text{C}$ to a constant weight. The conversion was calculated by weight. (b) A typical polymerization procedure (Table 2, entry 2) was described as follow. In a glovebox, a toluene solution (0.1 mL) of 1 (0.5 mg, 1 μmol), 2000 equivalents of DMAO (0.116 g, 2000 μmol) and 1.5 mL toluene were added to a flask. Then, the mixture was stirred at 40 $^\circ\text{C}$. 1.221 g (10 mmol) *p*FS was injected into the flask. After 2 h, acidified methanol was injected to terminate the polymerization. The viscous mixture was poured into a large quantity of methanol to precipitate the polymeric product, which was then collected by filtration, washed with methanol, and dried under vacuum at 40 $^\circ\text{C}$ to a constant weight. The conversion was calculated by weight.

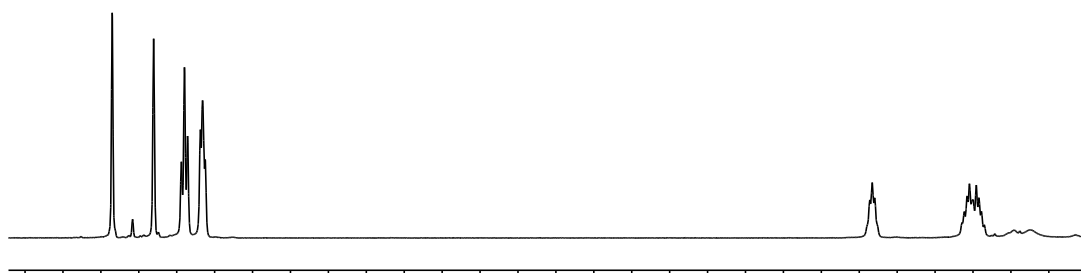


Figure S1. ^1H NMR spectrum of poly(*p*FS) (400MHz, $\text{C}_6\text{Cl}_2\text{D}_4$, 110 $^\circ\text{C}$) (Table 1, entry 1).

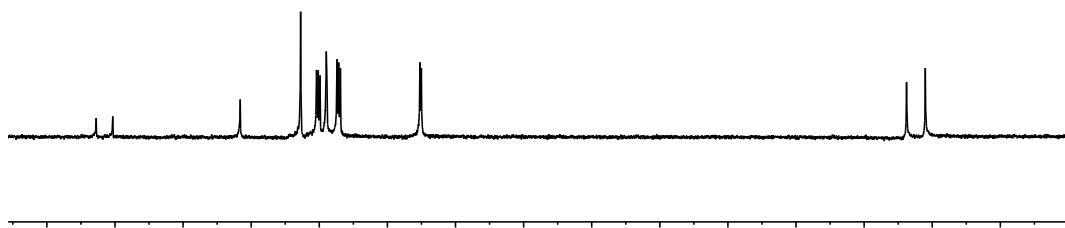


Figure S2. ^{13}C NMR spectrum of poly(*p*FS) (100MHz, $\text{C}_6\text{Cl}_2\text{D}_4$, 110 °C) (Table 1, entry 1).

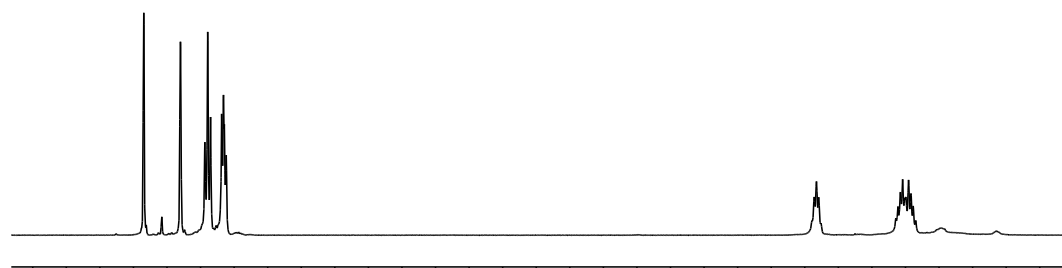


Figure S3. ^1H NMR spectrum of poly(*p*FS) (400MHz, $\text{C}_6\text{Cl}_2\text{D}_4$, 110 °C) (Table 1, entry 3).

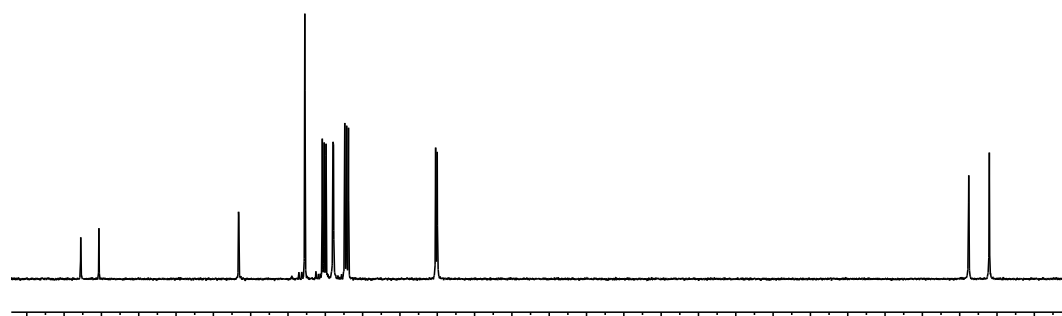


Figure S4. ^{13}C NMR spectrum of poly(*p*FS) (100MHz, $\text{C}_6\text{Cl}_2\text{D}_4$, 110 °C) (Table 1, entry 3).

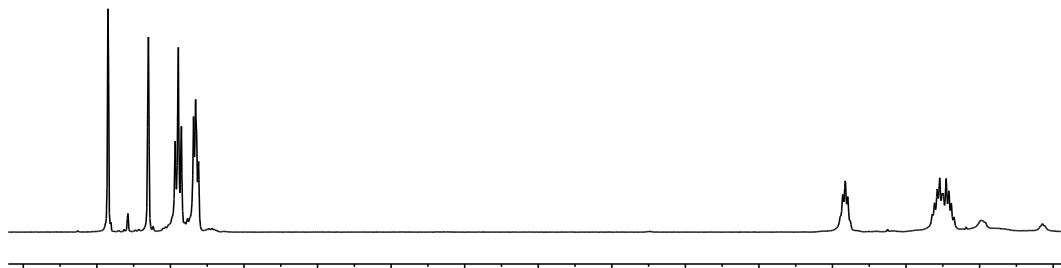


Figure S5. ¹H NMR spectrum of poly(*p*FS) (400MHz, C₆Cl₂D₄, 110 °C) (Table 1, entry 4).

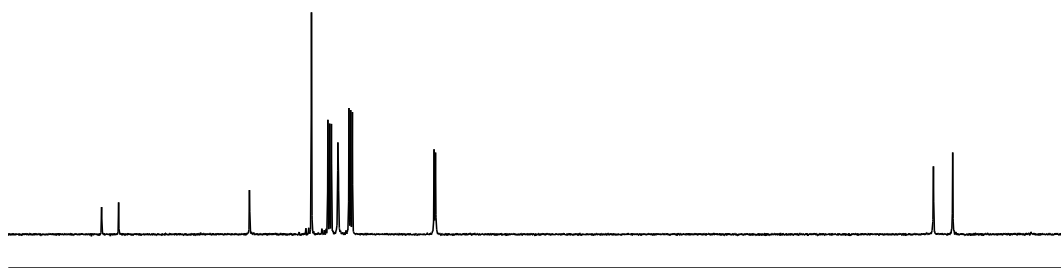


Figure S6. ¹³C NMR spectrum of poly(*p*FS) (100MHz, C₆Cl₂D₄, 110 °C) (Table 1, entry 4).

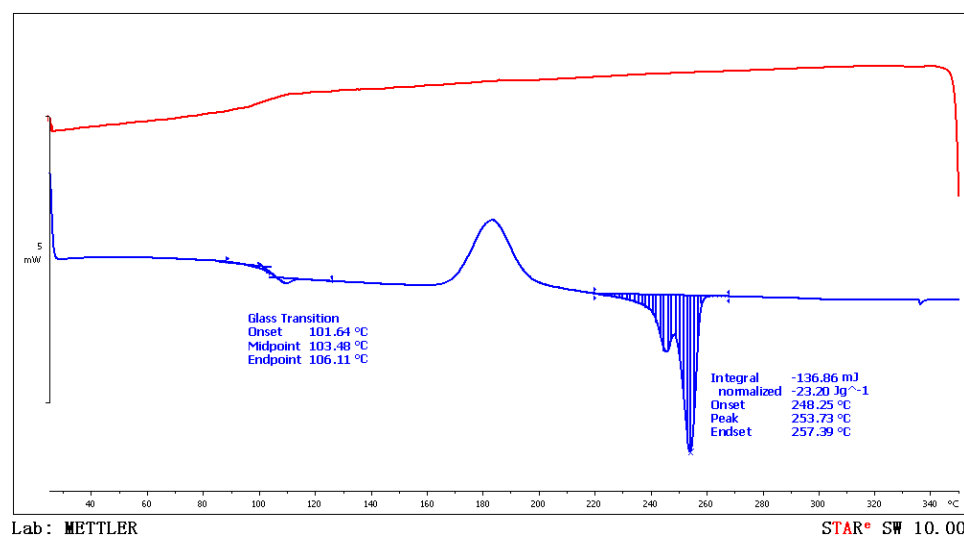


Figure S7. The DSC curve of poly(*p*FS) (Table 1, entry 1).

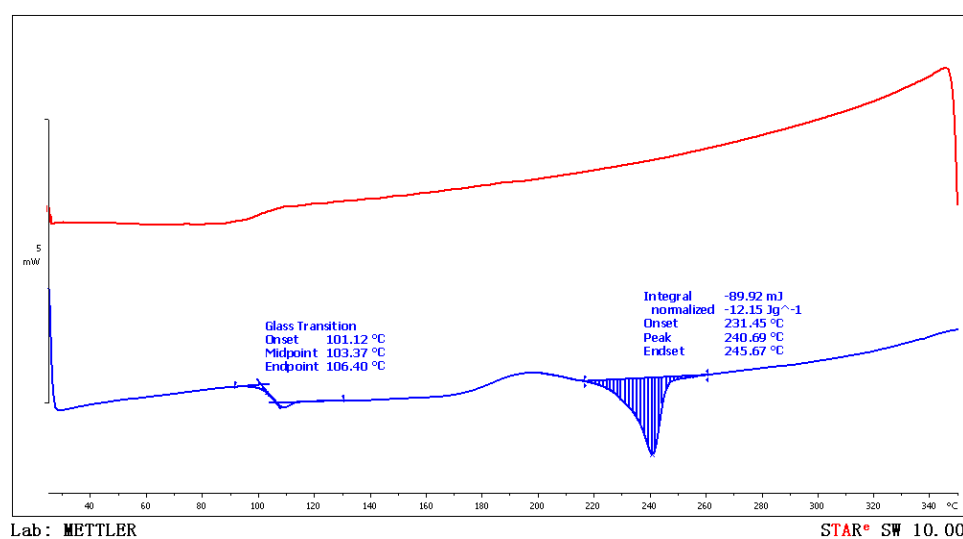


Figure S8. The DSC curve of poly(*p*FS) (Table 1, entry 2).

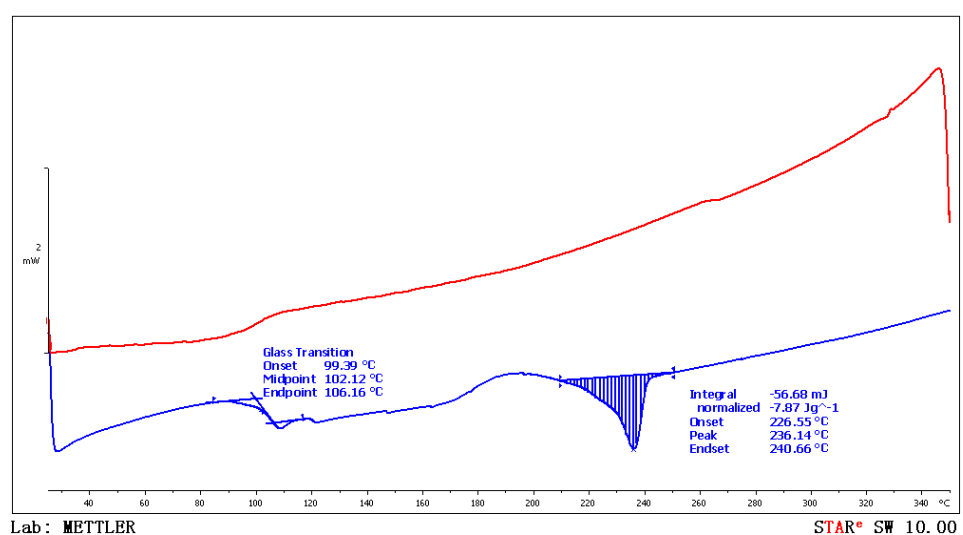


Figure S9. The DSC curve of poly(*p*FS) (Table 1, entry 3).

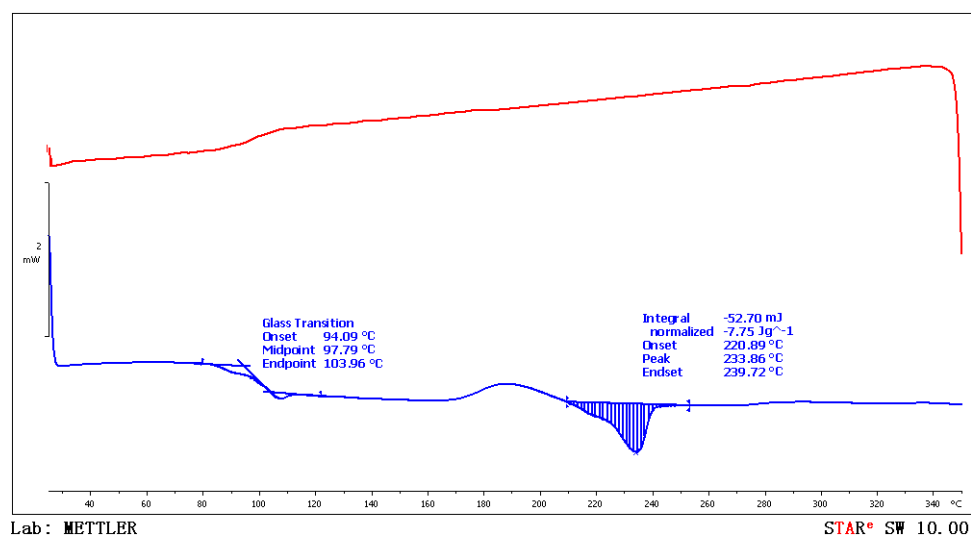


Figure S10. The DSC curve of poly(*p*FS) (Table 1, entry 4).

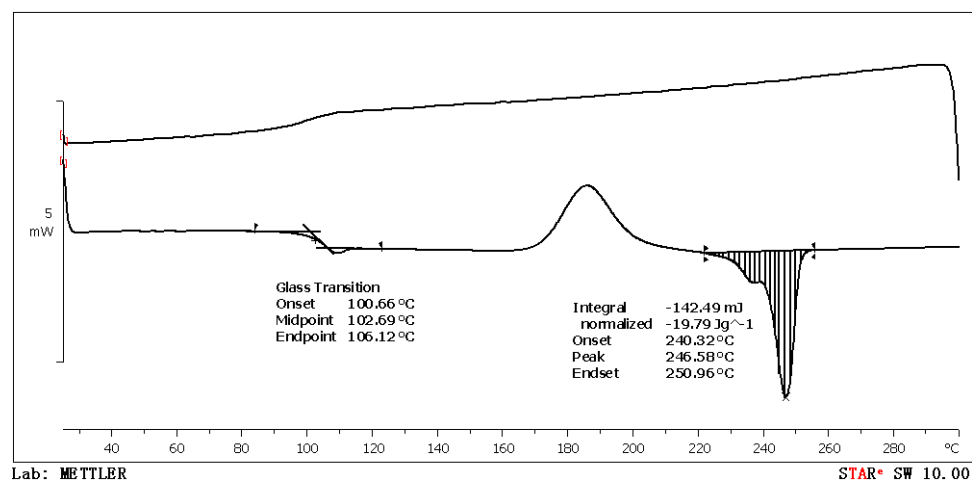


Figure S11. The DSC curve of poly(*p*FS) (Table 1, entry 5).

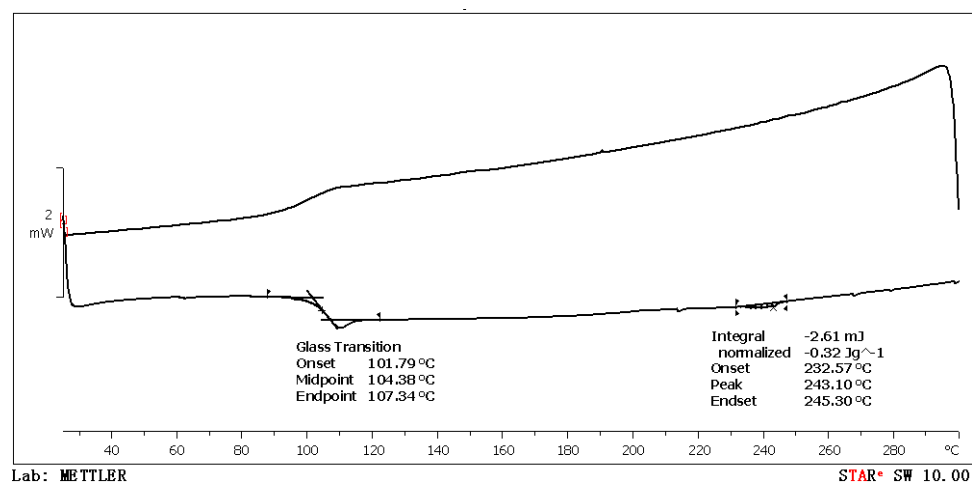


Figure S12. The DSC curve of poly(*p*FS) (Table 1, entry 6).

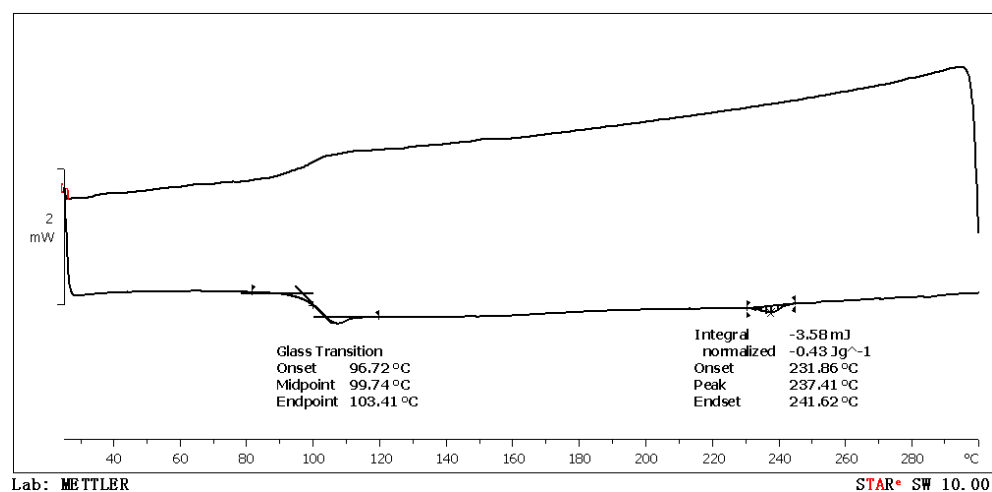


Figure S13. The DSC curve of poly(*p*FS) (Table 1, entry 7).

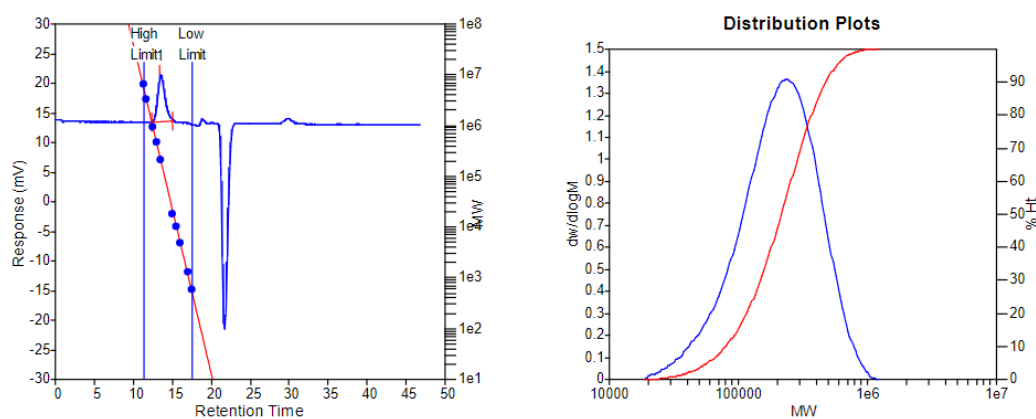


Figure S14. The GPC curve of poly(pFS) (Table 1, entry 1).

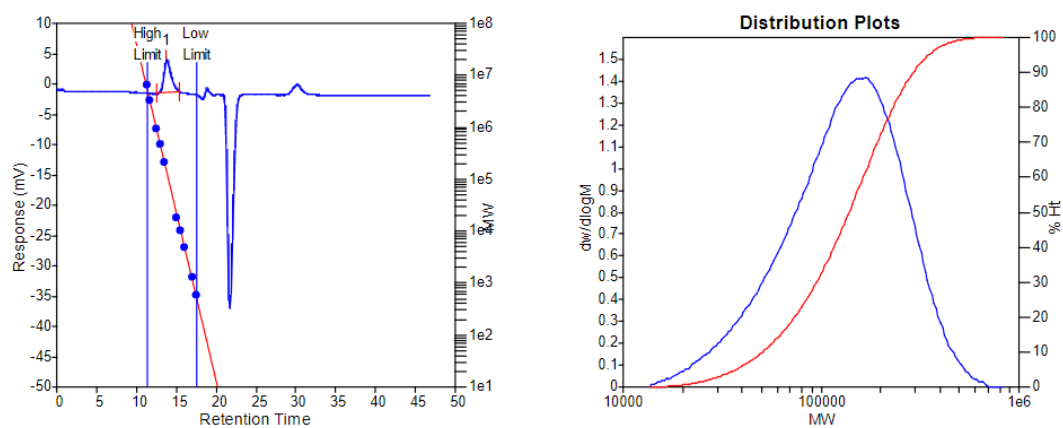


Figure S15. The GPC curve of poly(pFS) (Table 1, entry 2).

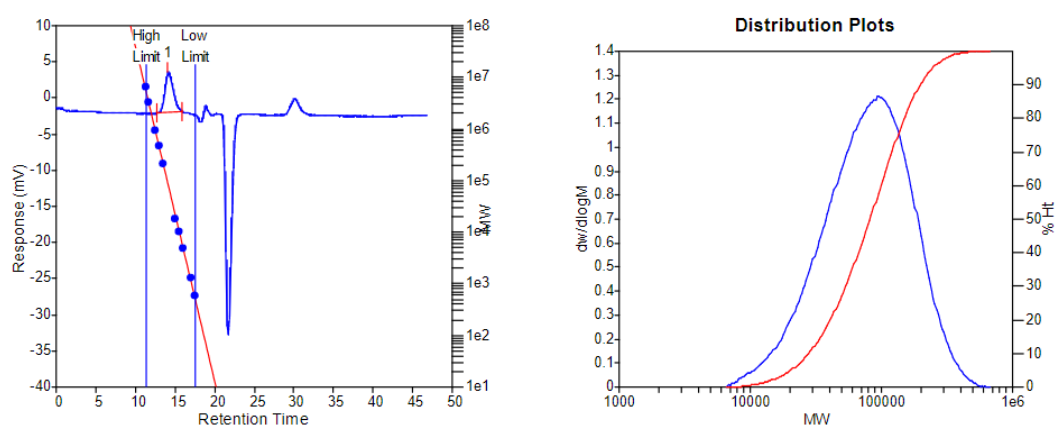


Figure S16. The GPC curve of poly(pFS) (Table 1, entry 3).

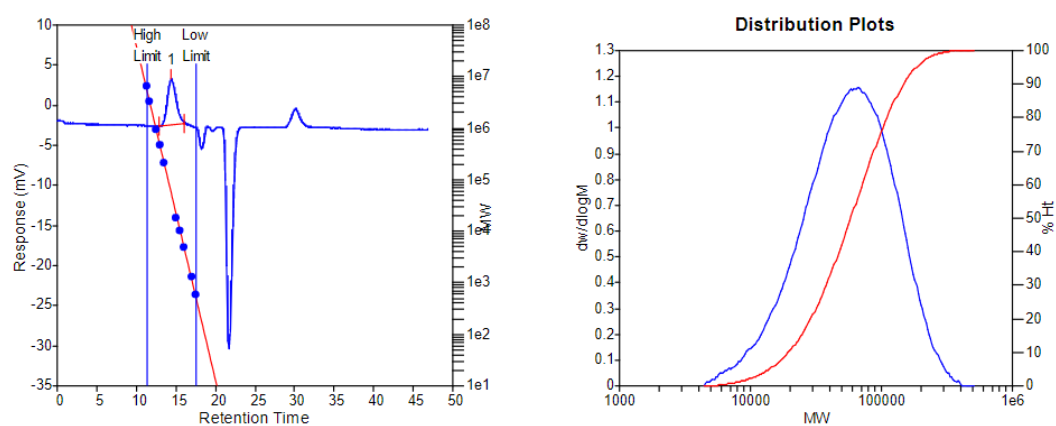


Figure S17. The GPC curve of poly(*p*FS) (Table 1, entry 4).

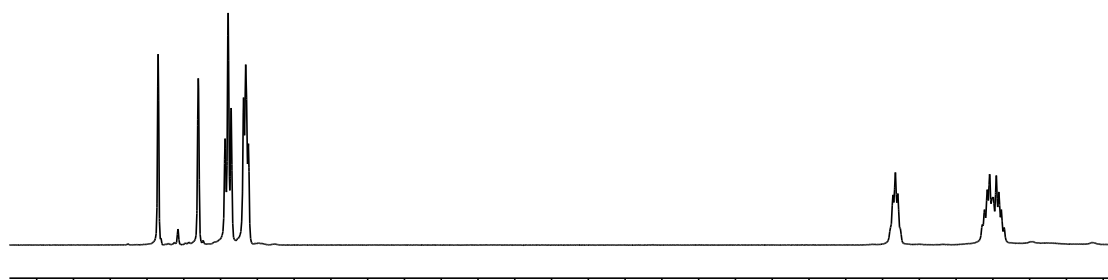


Figure S18. ¹H NMR spectrum of poly(*p*FS) (400MHz, C₆Cl₂D₄, 110 °C) (Table 2, entry 2).

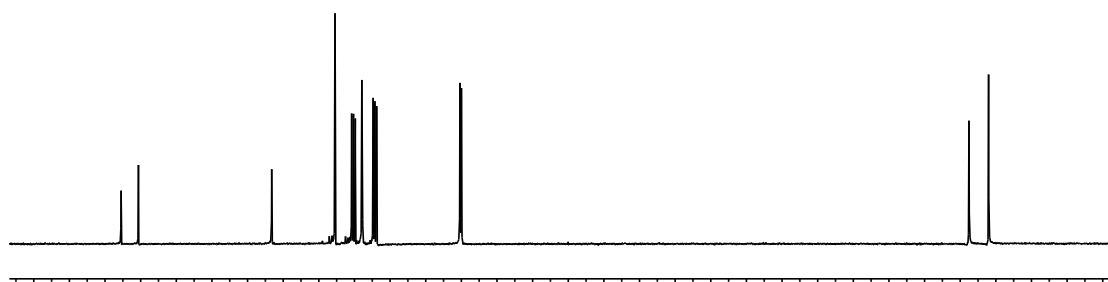


Figure S19. ¹³C NMR spectrum of poly(*p*FS) (100MHz, C₆Cl₂D₄, 110 °C) (Table 2, entry 2).

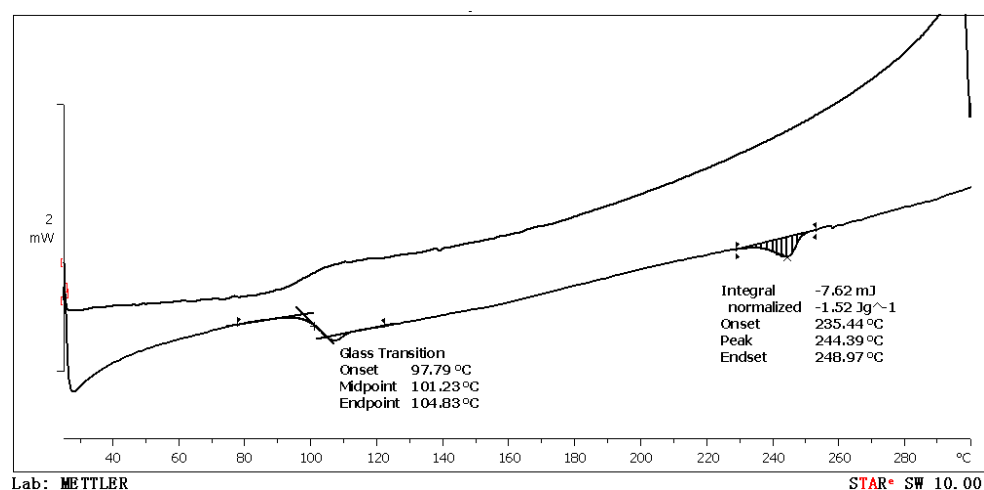


Figure S20. The DSC curve of poly(*p*FS) (Table 2, entry 1).

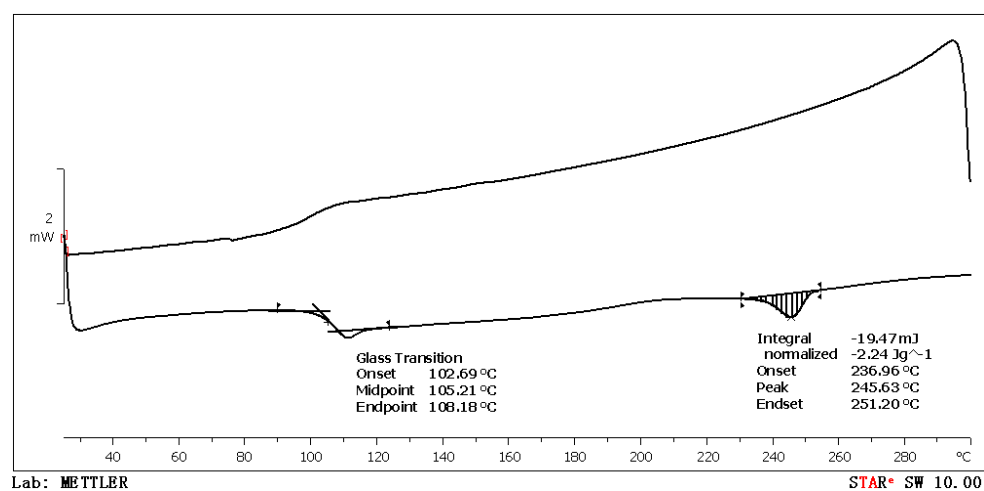


Figure S21. The DSC curve of poly(*p*FS) (Table 2, entry 2).

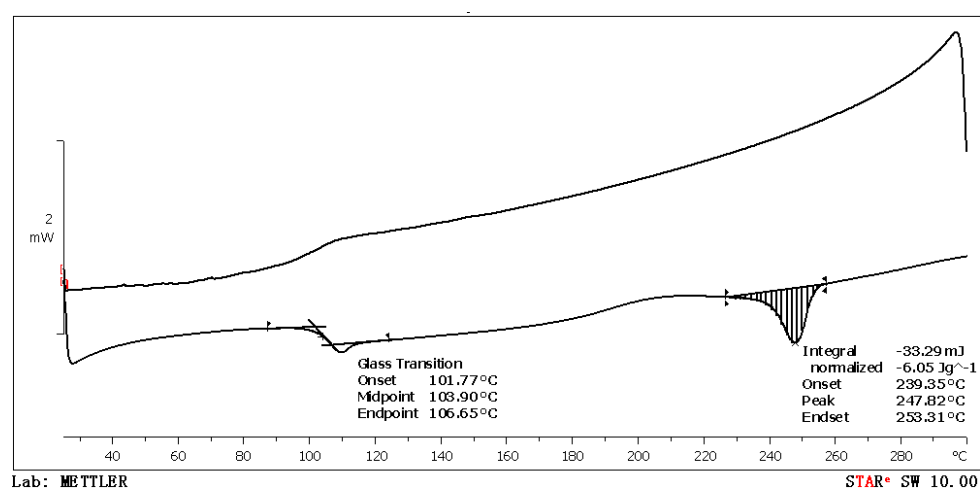


Figure S22. The DSC curve of poly(*p*FS) (Table 2, entry 3).

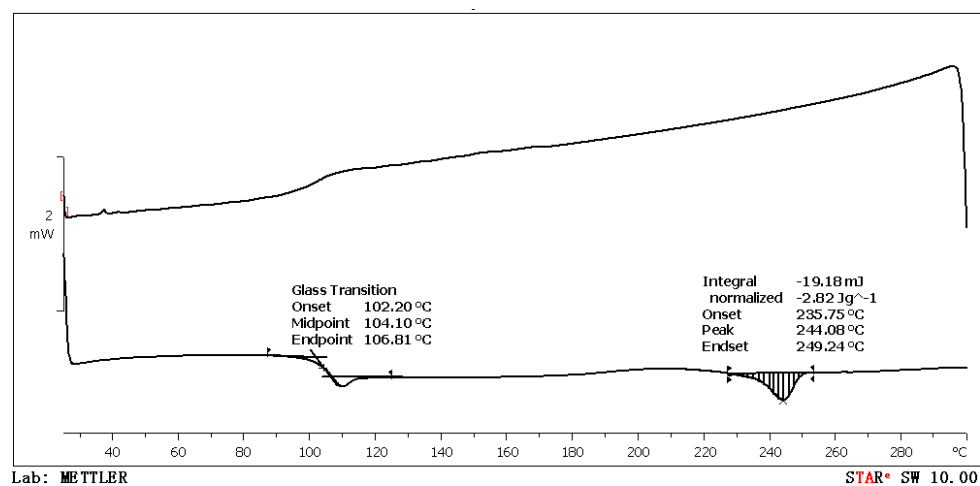


Figure S23. The DSC curve of poly(*p*FS) (Table 2, entry 4).

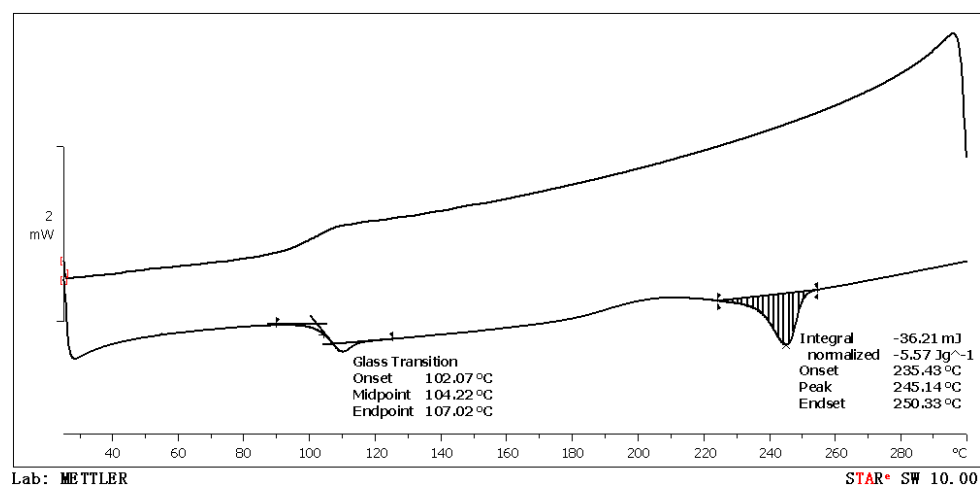


Figure S24. The DSC curve of poly(*p*FS) (Table 2, entry 5).

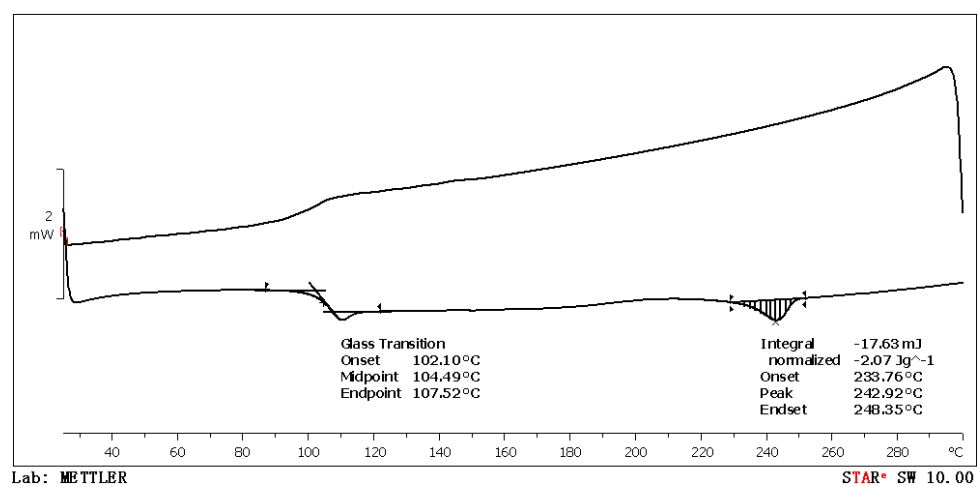


Figure S25. The DSC curve of poly(*p*FS) (Table 2, entry 6).

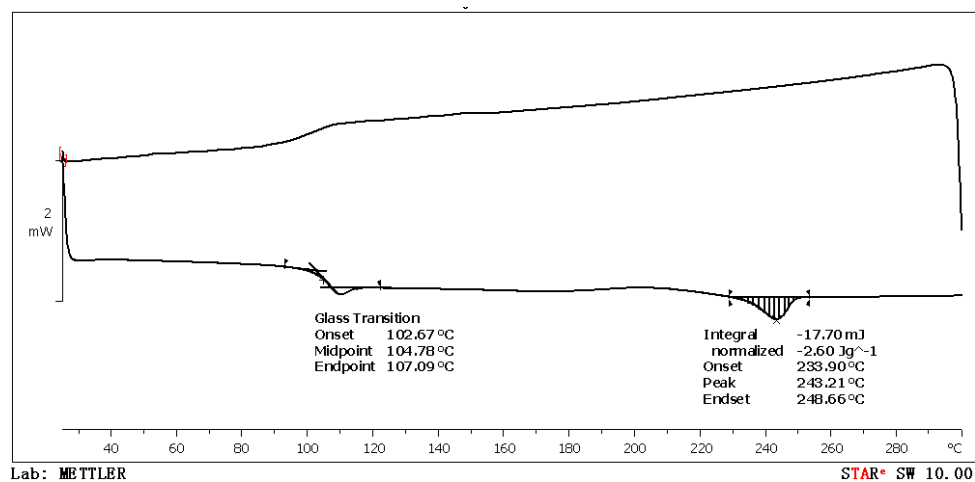


Figure S26. The DSC curve of poly(pFS) (Table 2, entry 7).

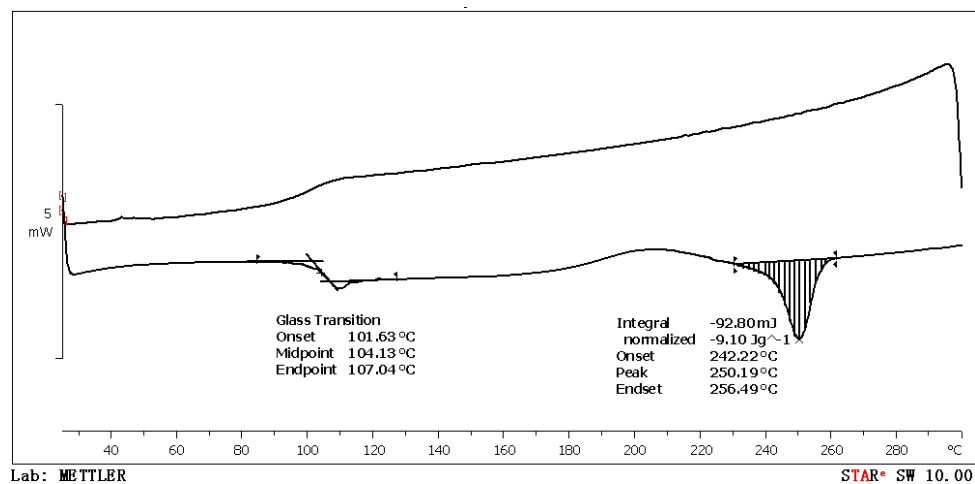


Figure S27. The DSC curve of poly(pFS) (Table 2, entry 8).

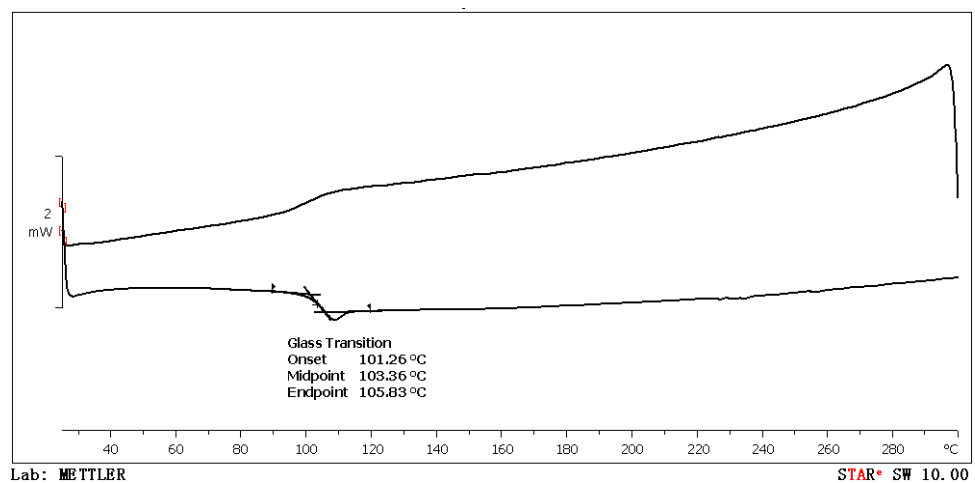


Figure S28. The DSC curve of poly(pFS) (Table 2, entry 9).

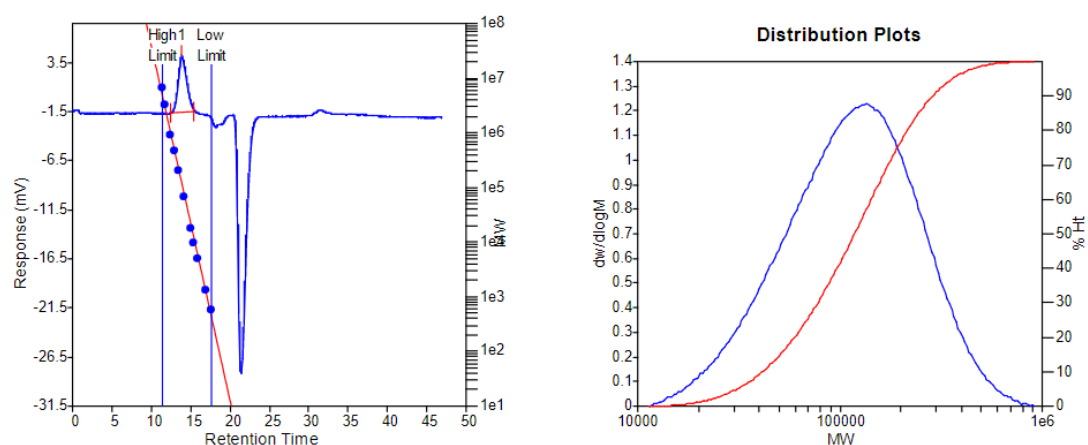


Figure S29. The GPC curve of poly(pFS) (Table 2, entry 1).

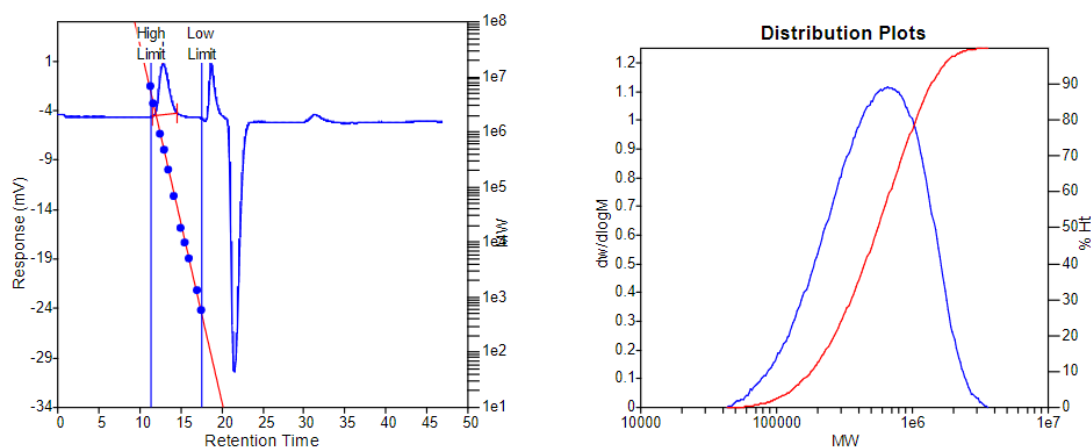


Figure S30. The GPC curve of poly(pFS) (Table 2, entry 2).

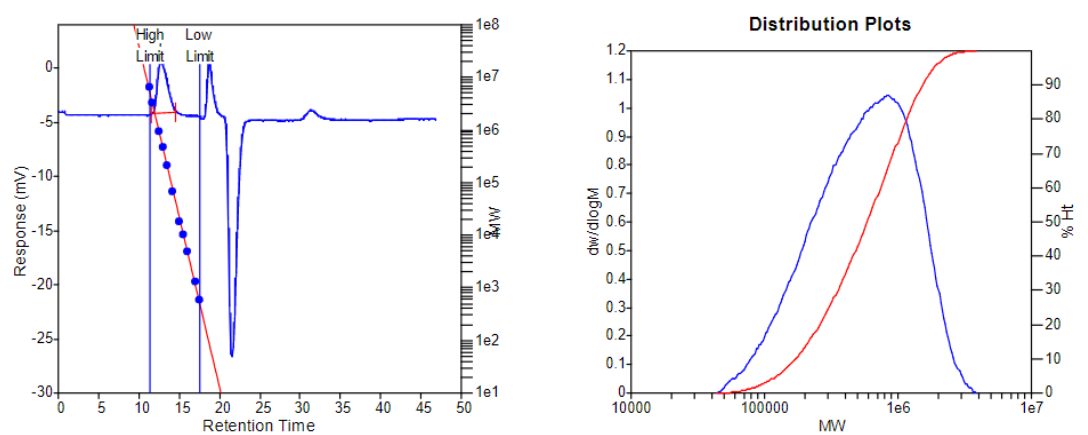


Figure S31. The GPC curve of poly(pFS) (Table 2, entry 3).

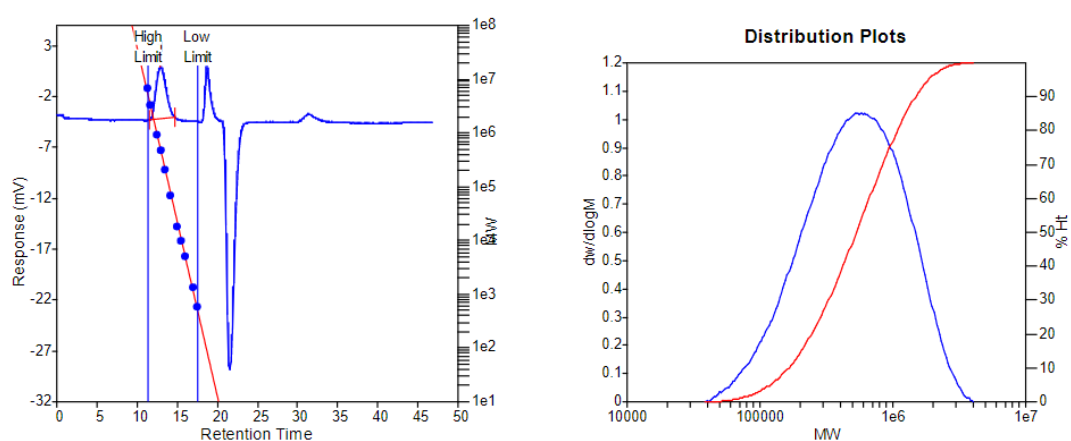


Figure S32. The GPC curve of poly(pFS) (Table 2, entry 4).

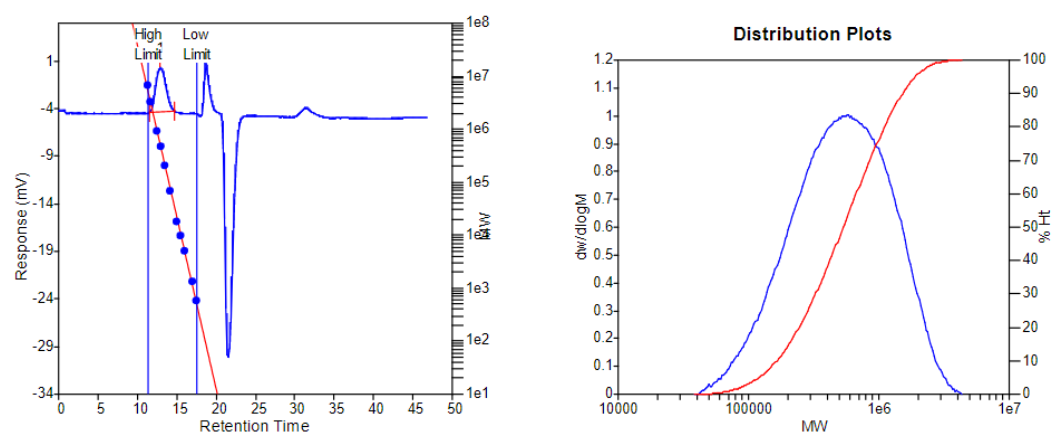


Figure S33. The GPC curve of poly(pFS) (Table 2, entry 5).

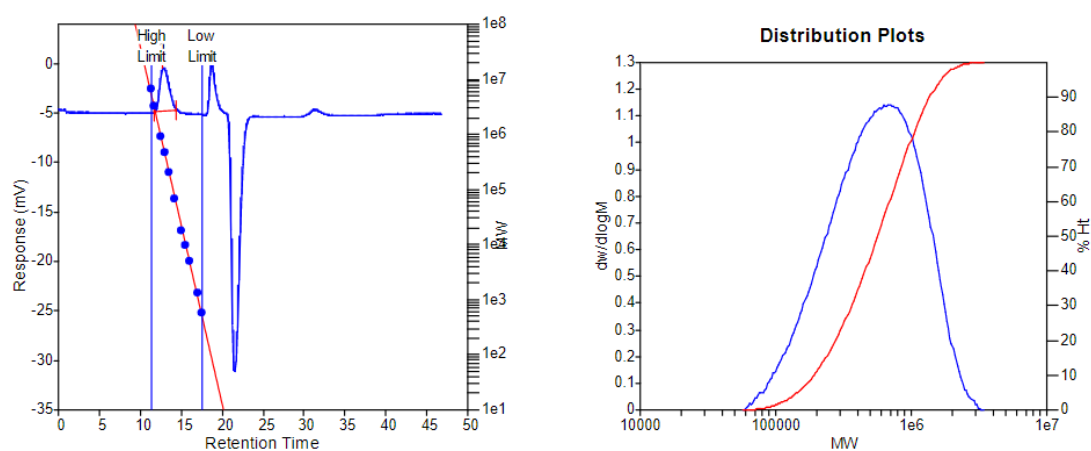


Figure S34. The GPC curve of poly(pFS) (Table 2, entry 6).

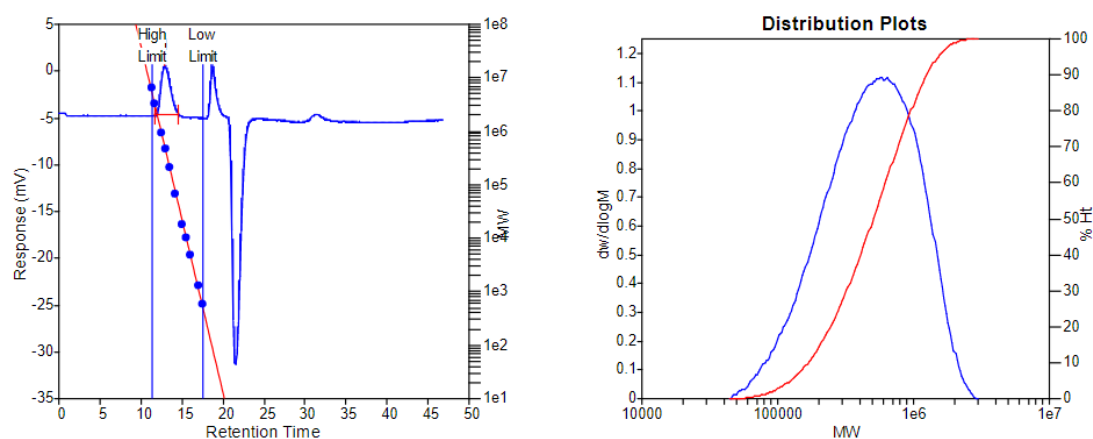


Figure S35. The GPC curve of poly(pFS) (Table 2, entry 7).

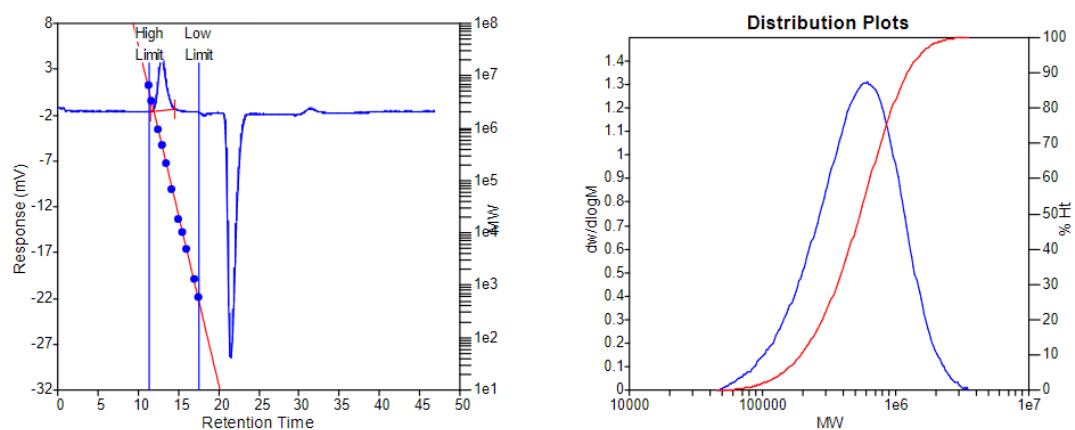


Figure S36. The GPC curve of poly(pFS) (Table 2, entry 8).

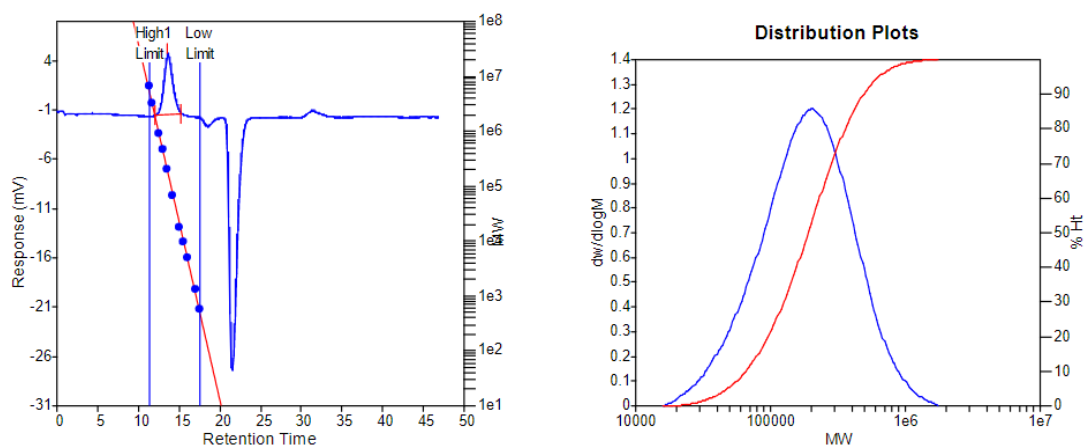
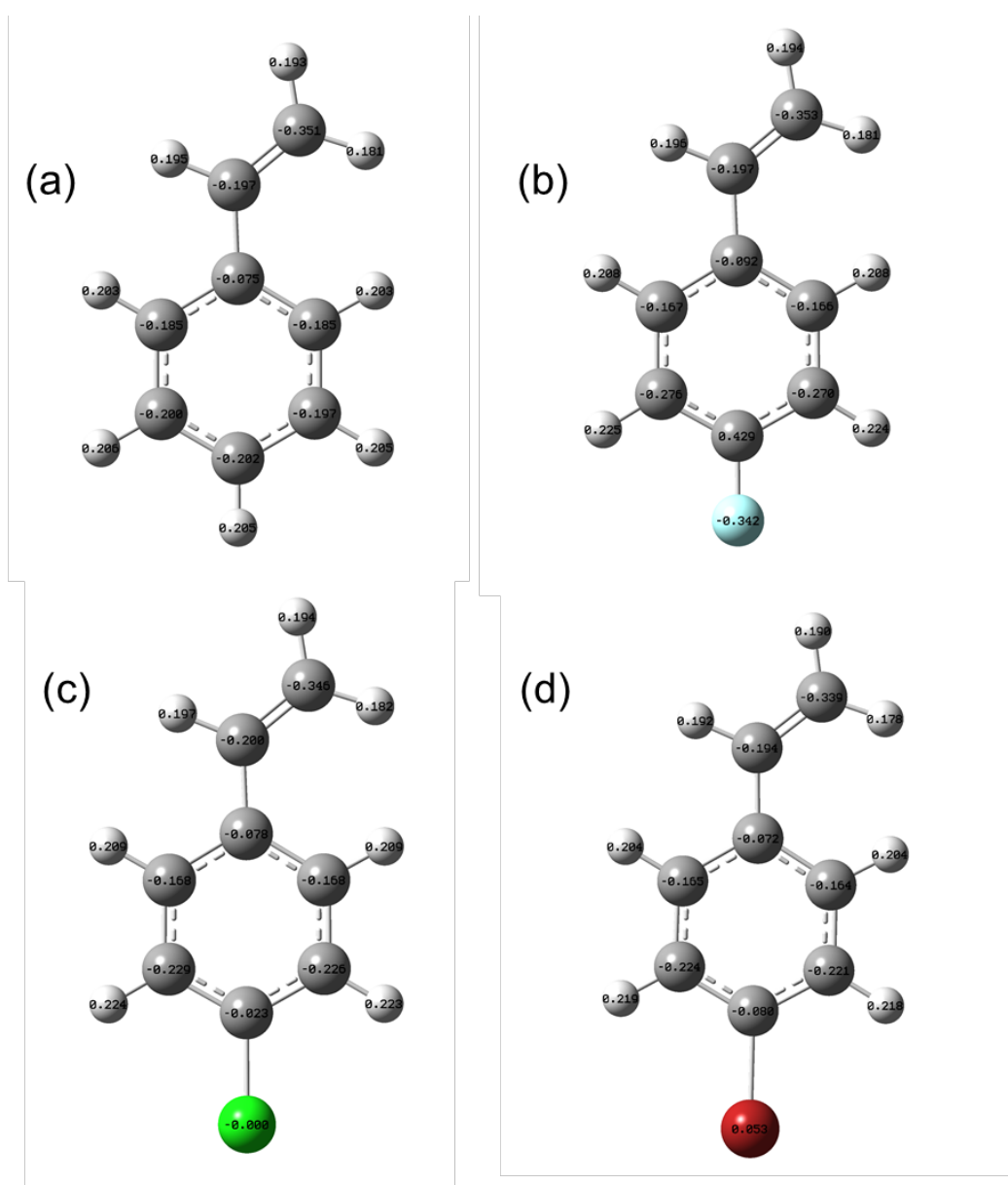


Figure S37. The GPC curve of poly(pFS) (Table 2, entry 9).



	St	<i>p</i> FS	<i>p</i> ClS	<i>p</i> BrS
CH(vinyl group)	-0.197	-0.197	-0.200	-0.194
CH ₂ (vinyl group)	-0.351	-0.353	-0.346	-0.339

Figure S38. NBO charge of the monomers. (a) St; (b) *p*FS; (c) *p*ClS; (d) *p*BrS.

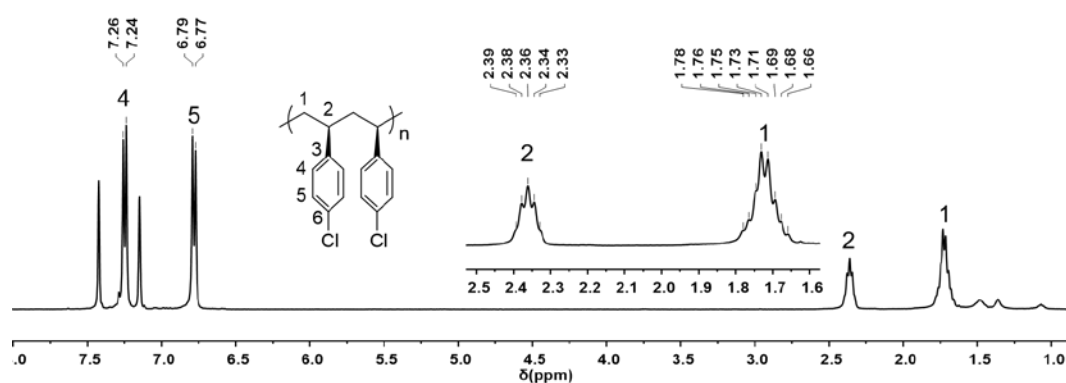


Figure S39. ^1H NMR spectrum of poly(*p*ClS) (400MHz, $\text{C}_6\text{Cl}_2\text{D}_4$, 110 °C) (Table 3, entry 1).

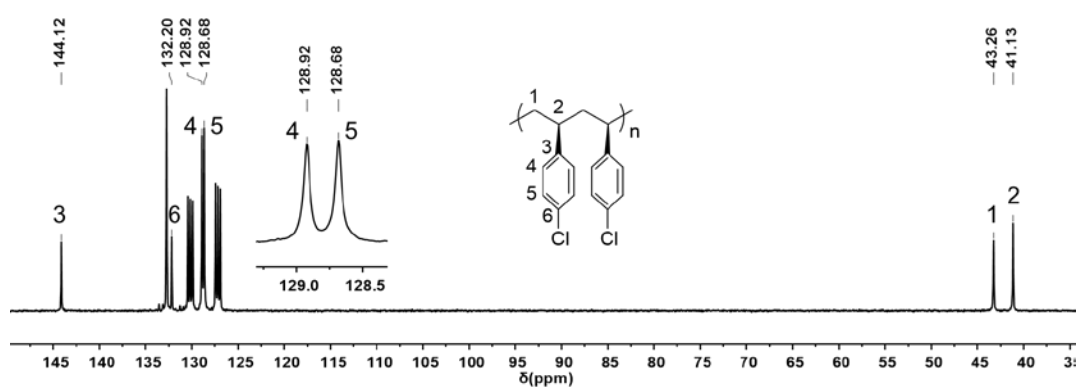


Figure S40. ^{13}C NMR spectrum of poly(*p*ClS) (100MHz, $\text{C}_6\text{Cl}_2\text{D}_4$, 110 °C) (Table 3, entry 1).

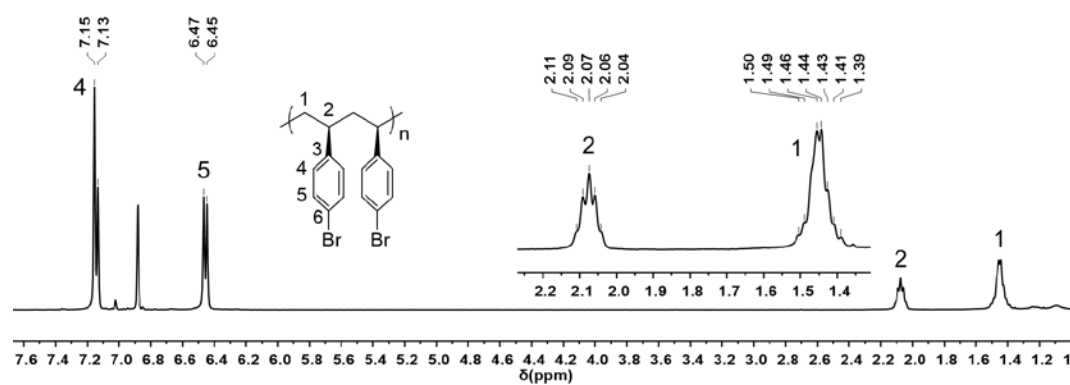


Figure S41. ^1H NMR spectrum of poly(*p*BrS) (400MHz, $\text{C}_6\text{Cl}_2\text{D}_4$, 110 °C) (Table 3, entry 2).

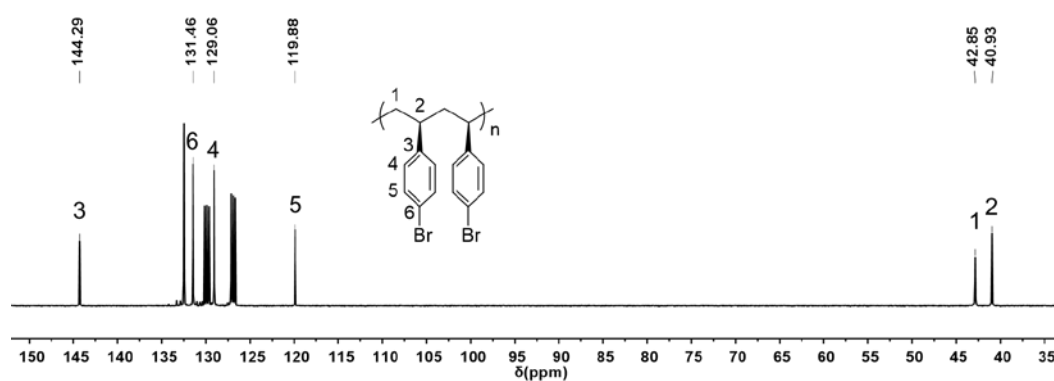


Figure S42. ¹³C NMR spectrum of poly(*p*BrS) (100MHz, C₆Cl₂D₄, 110 °C) (Table 3, entry 2).

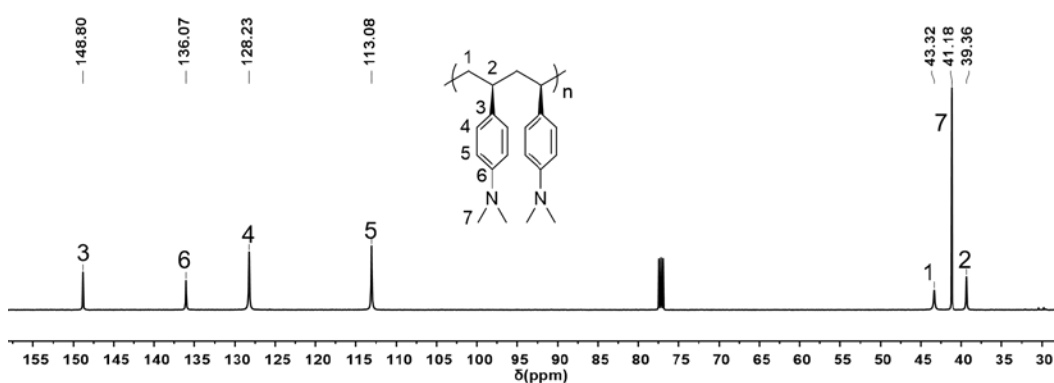


Figure S43. ¹³C NMR spectrum of poly(DMAS) (100MHz, CDCl₃, 25 °C) (Table 3, entry 4).

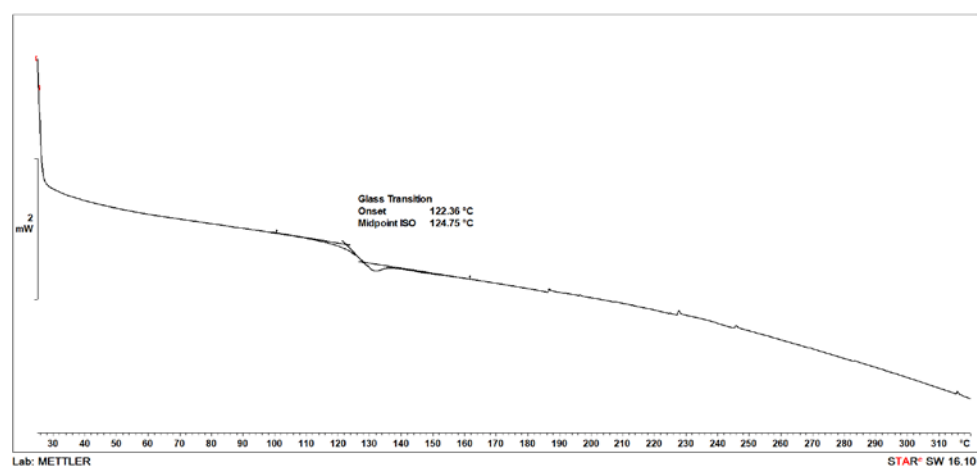


Figure S44. The DSC curve of poly(*p*ClS) (Table 3, entry 1).

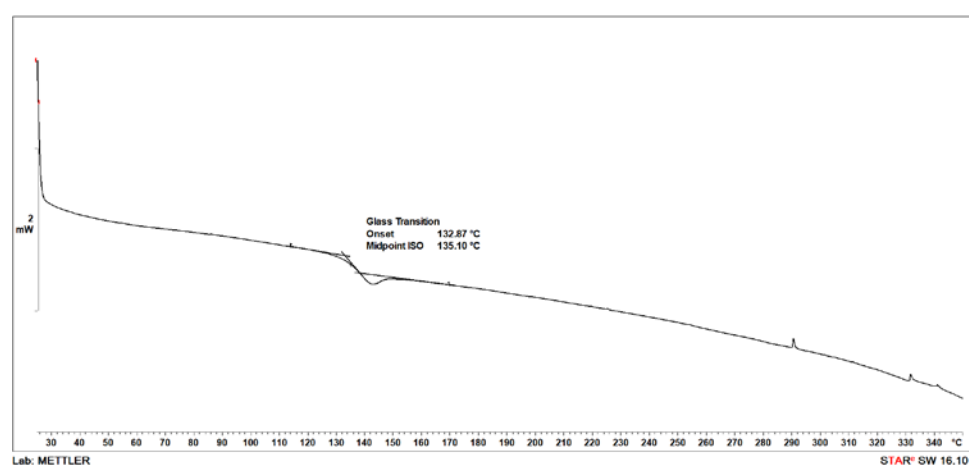


Figure S45. The DSC curve of poly(pBrS) (Table 3, entry 2).

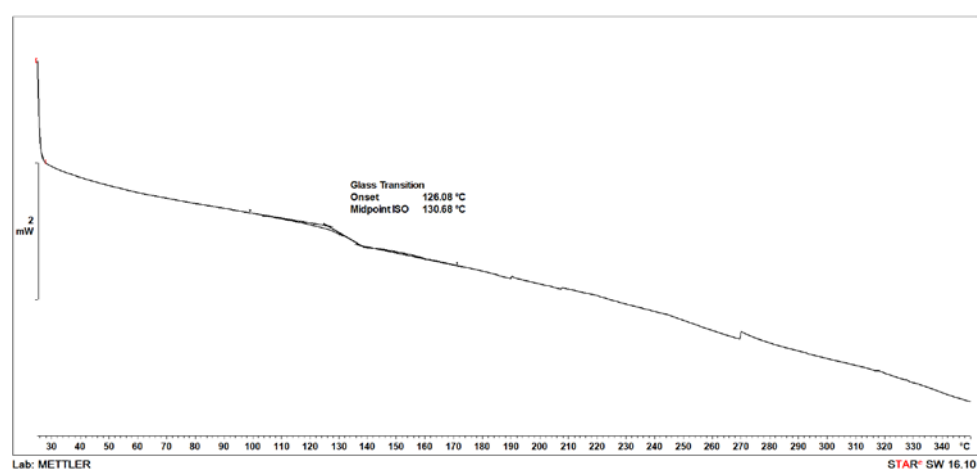


Figure S46. The DSC curve of poly(DMAS) (Table 3, entry 4).

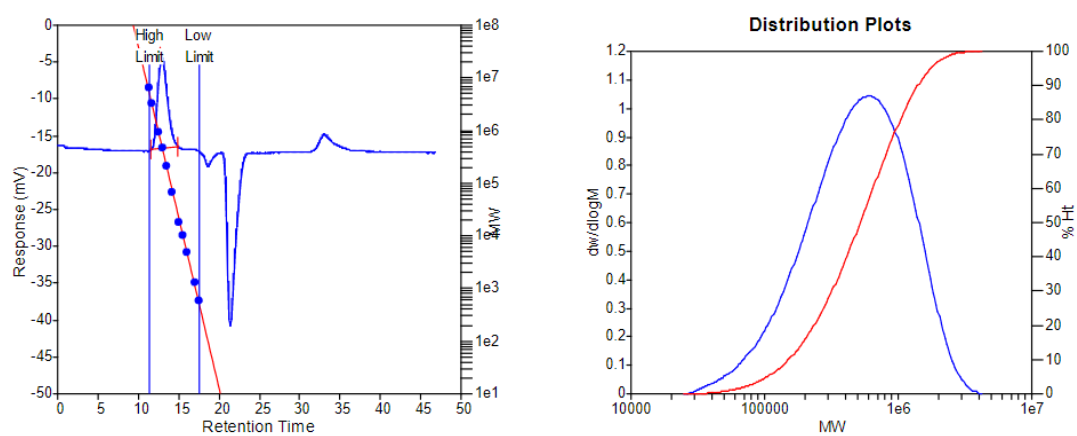


Figure S47. The GPC curve of poly(pClIS) (Table 3, entry 1).

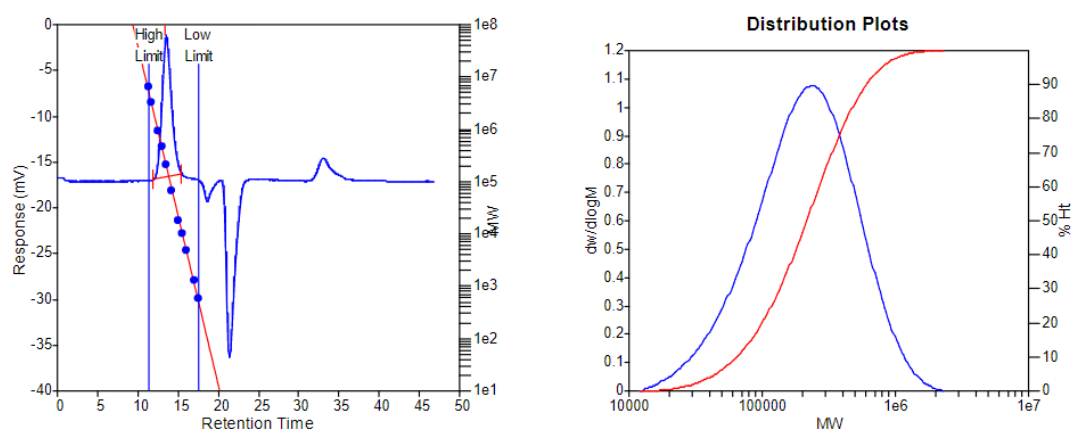


Figure S48. The GPC curve of poly(pBrS) (Table 3, entry 2).

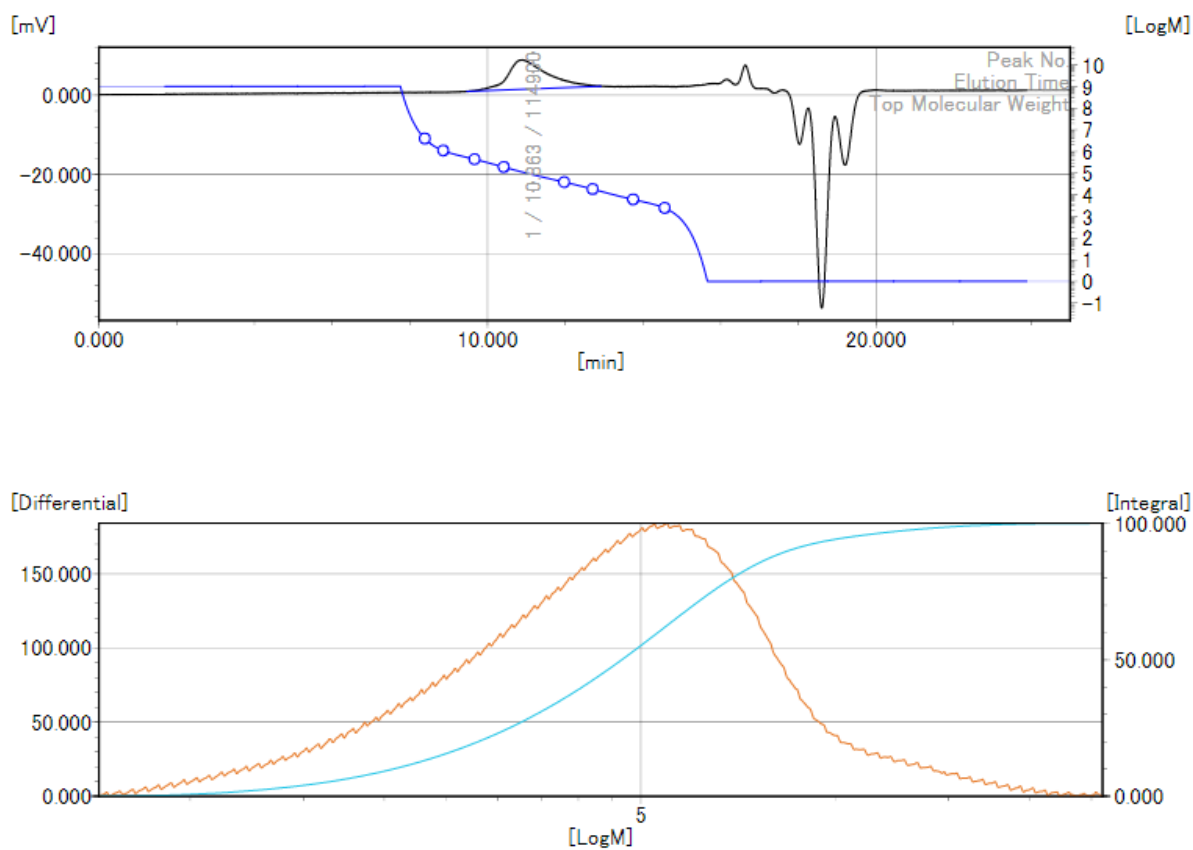


Figure S49. The GPC curve of poly(DMAS) (Table 3, entry 4).