Supporting Information

Convenient Synthesis of Versatile Syndiotactic Polystyrene Material Containing Pendant Vinyl Groups with Scandium Catalyst System

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Experimental section

Materials

All reactions were carried out under an argon atmosphere in an MBraun glovebox. Solvents were purified by SPS-800 solvent purification system (Mbraun) and stored over fresh Na chips in the glove box (MBraun Labmaster). Styrene (St) was dried over CaH_2 overnight, distilled, and degassed by three freeze-pump-thaw cycles. Functionalized styrene compounds, including divinylbenzene (FSt1), 4-isopropenylstyrene (FSt2), 4-(1-isopropylvinyl)styrene (FSt3), 4-(2-propenyl)styrene (FSt4) and 4-(2-methyl-2-propenyl)styrene (FSt5) were synthesized according to the literatures and purified just before use. (Fig. S29 - S38, ESI)[28,29] $[C_5Me_4SiMe_3Sc(CH_2C_6H_4NMe_2\text{-}o)_2]$ complex was synthesized as reported in the literature. [26]

Measurements

NMR (in $CDCl_3$) spectra were recorded on Bruker AvanceII 400M NMR spectrometer with tetramethylsilane as the internal standard. Gel Permeation Chromatography (GPC) analyses were performed on Waters HPLC component system (2414 refractive index detector) at a flow rate of 1.0 ml/min in THF at 30 ^oC with polystyrene calibration. Glass transition temperature (T_g) and melting point (T_m) were measured under nitrogen atmosphere on TA Instrument differential scanning calorimeter (DSC Q2000), with the heating rate of 10 $^oC\ min^{-1}$ in range of 0 to 300 ^oC.

Polymerizations of functional styrenic monomers and copolymerization with styrene by $[C_5Me_4SiMe_3Sc(CH_2C_6H_4NMe_2\text{-}o)_2]/[Ph_3C][B(C_6F_5)_4]$

All the polymerization reactions were carried out using a 100ml glass flask in an argon atmosphere glove box. A typical polymerization process was illustrated. In the glove box, 0.2 g functional styrenic monomer (the mixture of styrene with functional styrenic monomer) was added into a toluene solution (4 ml) in a glass flask. Then, $C_5Me_4SiMe_3Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (5.1 mg, 1×10^{-5} mol) and 1 equiv $[Ph_3C][B(C_6F_5)_4]$ (9.5 mg, 1×10^{-5} mol) were dissolved in 2 ml of toluene and added into the glass flask. After the mixture was stirred for 5 min, the reaction was terminated by injecting 10ml cold methanol. The obtained white polymer was filtered and then dried under vacuum at 45 ^oC to a constant weight.

Thiol−ene click reactions of functional sPS

All the thiol-ene click reactions were carried out in a 100 ml glass flask. A typical reaction process was illustrated. 0.1 g functional copolymer (C=C content = 10 mol%) was added into 30 ml tetrahydrofuran (THF) in the glass flask. Then, a small amount of 2,2-dimethoxy-2-phenylacetophenone and 120 umol methyl 3-mercaptopropionate (in 5 ml THF) were added into the glass flask. After the mixture was stirred for 30 min under UV light (365 nm, 12 w), the reaction was terminated by pouring into 50 ml methanol and the white solid was filtered. Then the product was dried under vacuum at 45 °C to a constant weight.

Epoxidation reactions of functional sPS

All epoxidation reactions were carried out in a 100 ml glass flask. A typical reaction process was illustrated. 0.1 g functional copolymer (C=C content = 10 mol%) was added into 30 ml chloroform in the glass flask. Then, 0.02g m-chloroperoxybenzoic acid (in 5 ml chloroform) was added into the glass flask. After the mixture was stirred for 10 h, the reaction was terminated by pouring into 50 ml methanol and the white solid was filtered. Then the product was dried under vacuum at 45 °C to a constant weight.

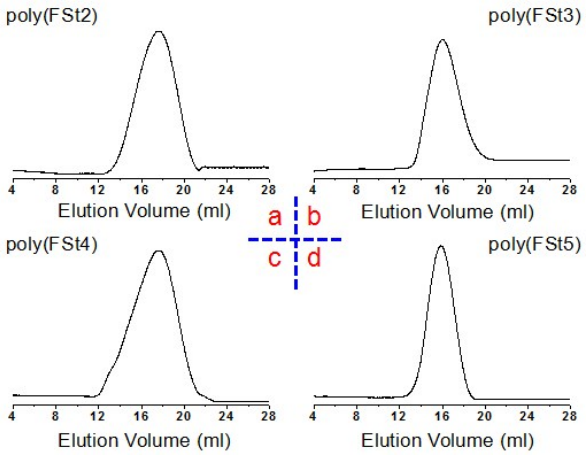

Fig. S1 GPC curves of functional homopolymers

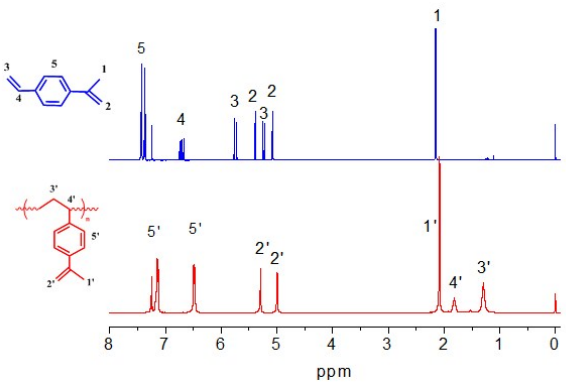

Fig. S2 ^{1}H NMR spectra of FSt2 and poly(FSt2)

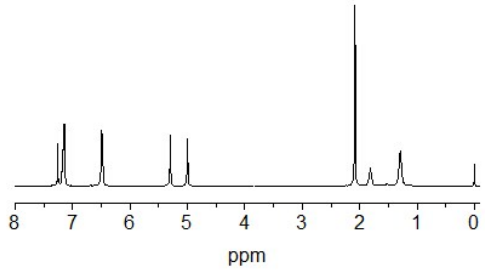

Fig. S3 ^{1}H NMR spectrum of poly(FSt2)

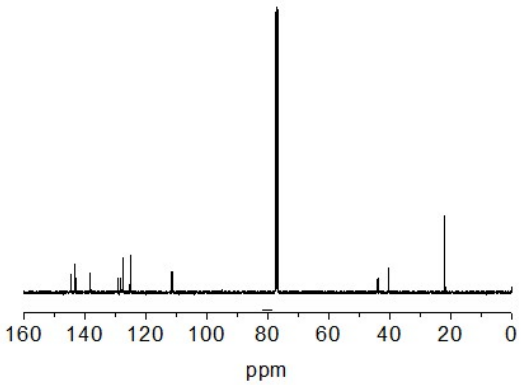

Fig. S4 ^{13}C NMR spectrum of poly(FSt2)

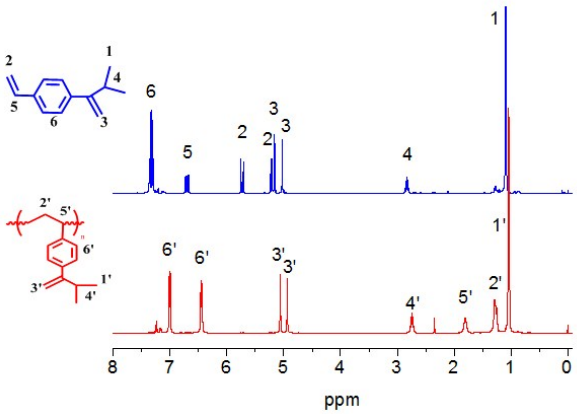

Fig. S5 ^{1}H NMR spectra of FSt3 and poly(FSt3)

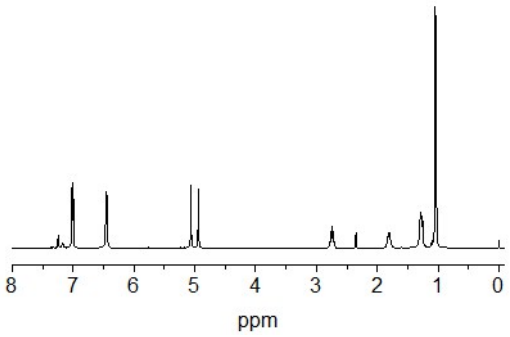

Fig. S6 ^{1}H NMR spectrum of poly(FSt3)

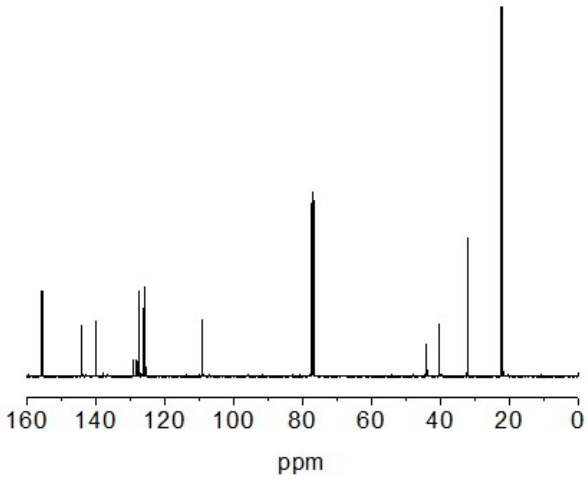

Fig. S7 ^{13}C NMR spectrum of poly(FSt3)

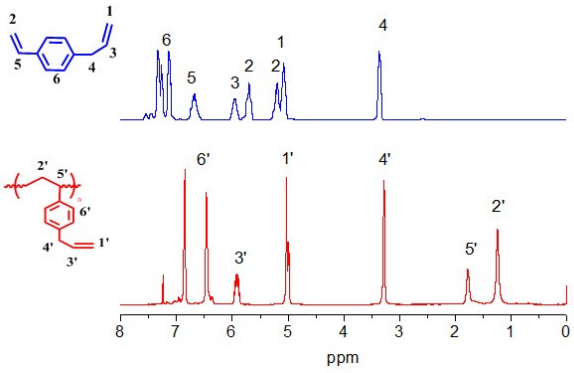

Fig. S8 ^{1}H NMR spectra of FSt4 and poly(FSt4)

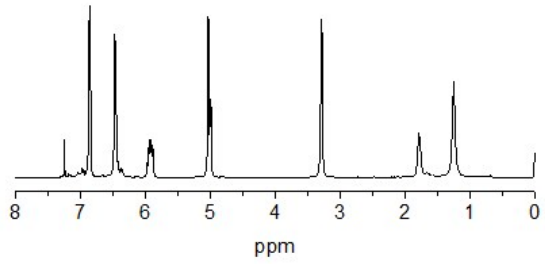

Fig. S9 ^{1}H NMR spectrum of poly(FSt4)

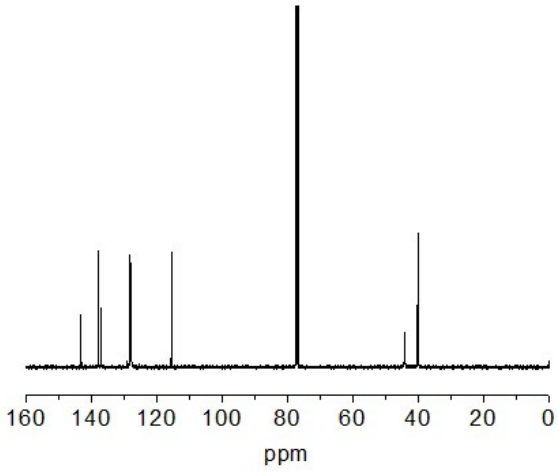

Fig. S10 ^{13}C NMR spectrum of poly(FSt4)

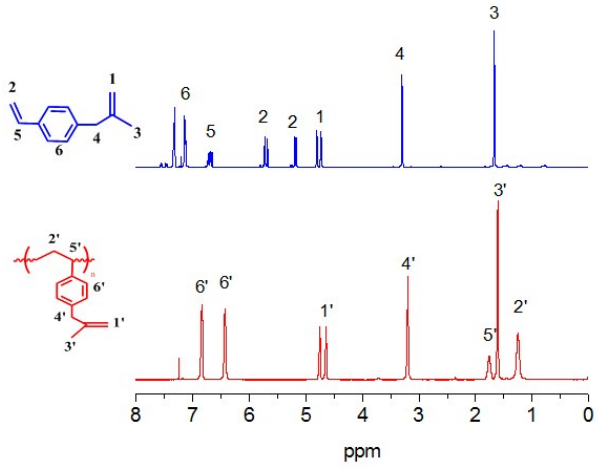

Fig. S11 ^{1}H NMR spectra of FSt5 and poly(FSt5)

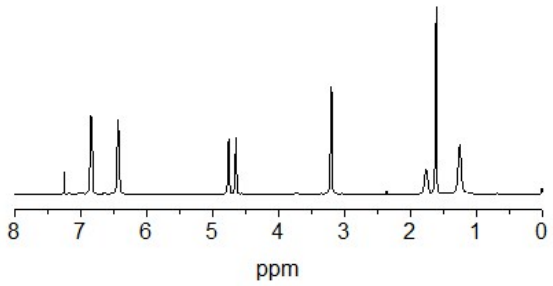

Fig. S12 ^{1}H NMR spectrum of poly(FSt5)

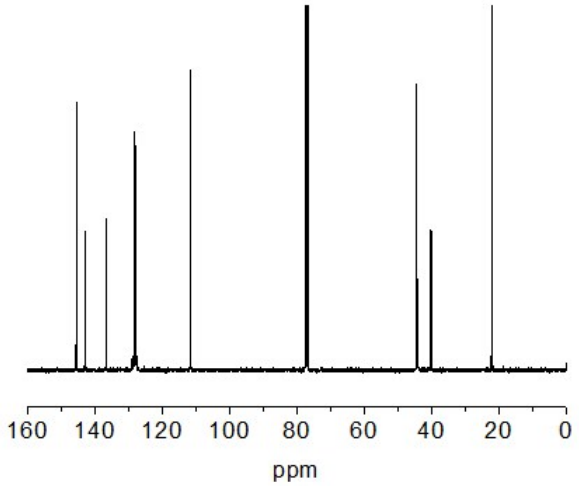

Fig. S13 ^{13}C NMR spectrum of poly(FSt5)

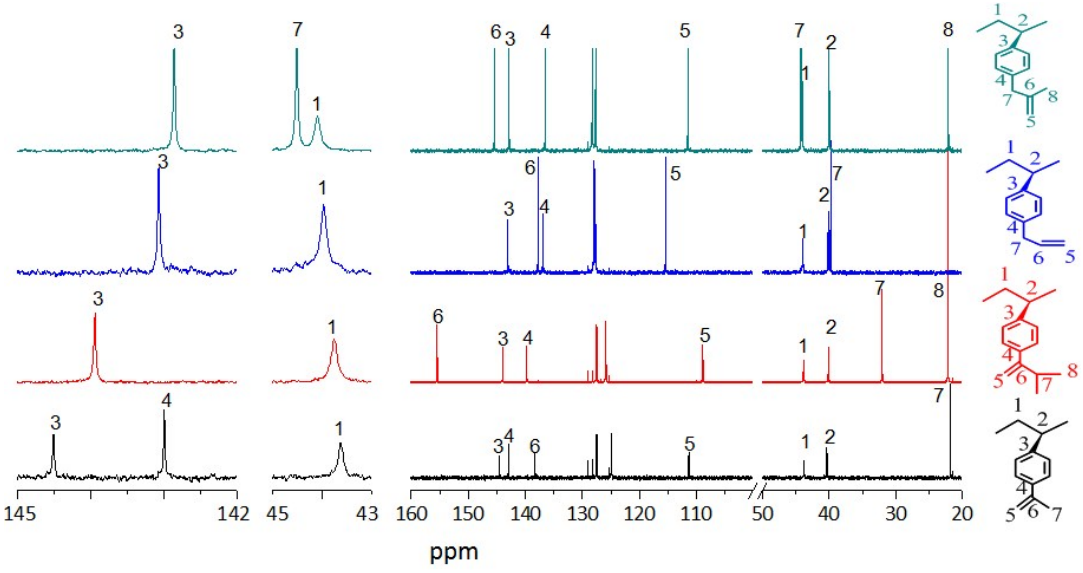

Fig. S14 ^{13}C NMR spectra of syndiotactic functional homopolymers

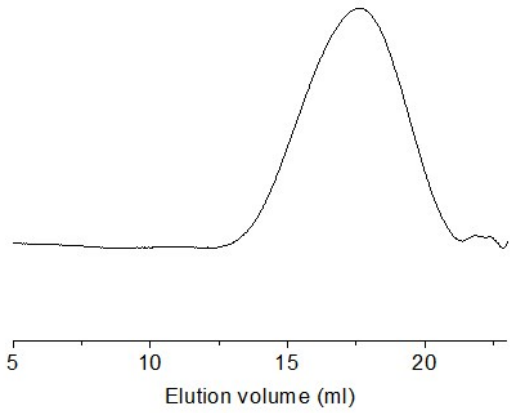

Fig. S15 GPC of poly(St-*co*-FSt2) (FSt2=20 mol%)

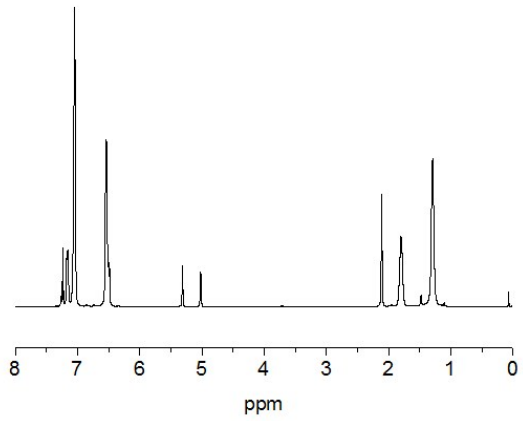

Fig. S16 ^{1}H NMR spectrum of poly(St-*co*-FSt2) (FSt2=20 mol%)

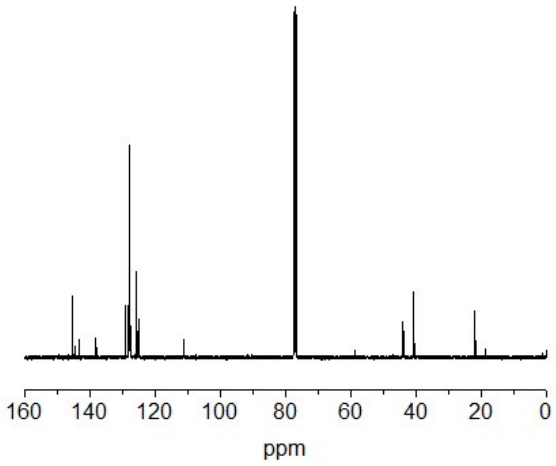

Fig. S17 ^{13}C NMR spectrum of poly(St-*co*-FSt2) (FSt2=20 mol%)

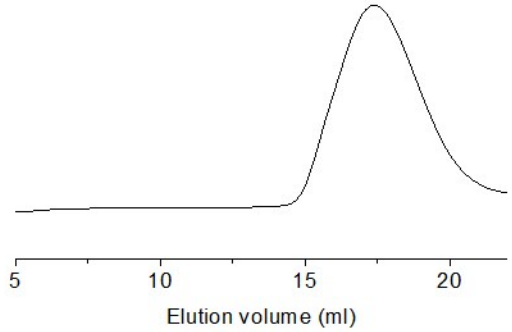

Fig. S18 GPC of poly(St-*co*-FSt3) (FSt3=20 mol%)

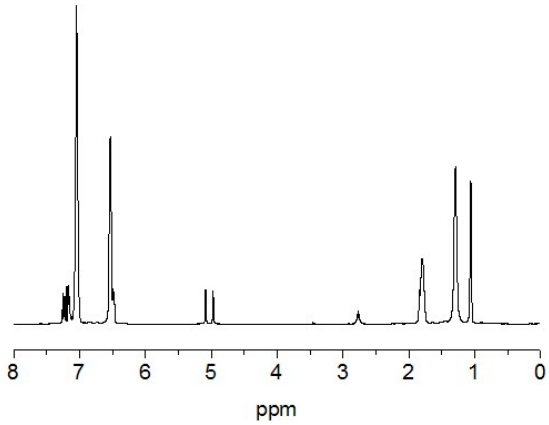

Fig. S19 ^{1}H NMR spectrum of poly(St-*co*-FSt3) (FSt3=20 mol%)

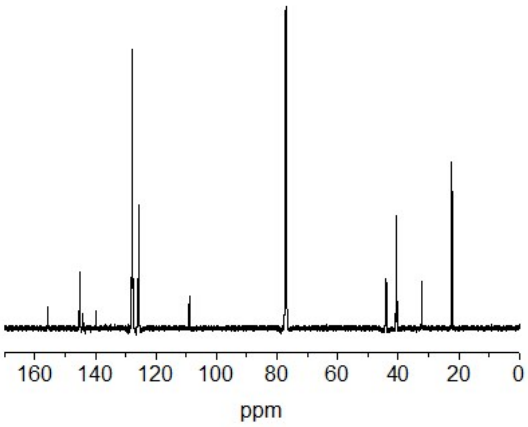

Fig. S20 ^{13}C NMR spectrum of poly(St-*co*-FSt3) (FSt3=20 mol%)

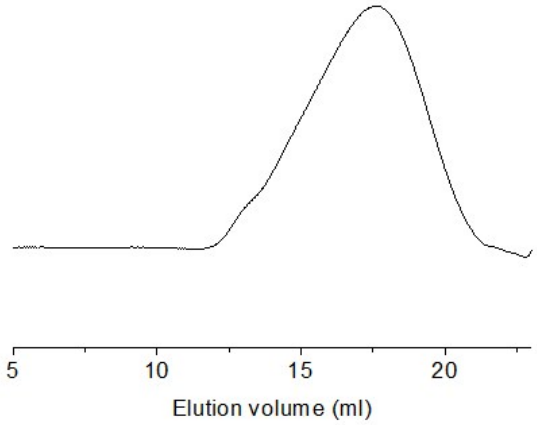

Fig. S21 GPC of poly(St-*co*-FSt4) (FSt4=20 mol%)

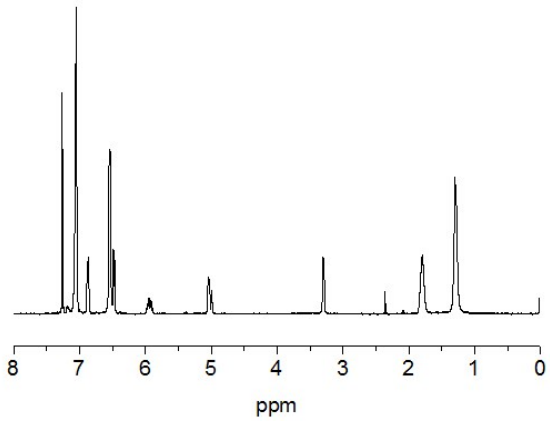

Fig. S22 ^{1}H NMR spectrum of poly(St-*co*-FSt4) (FSt4=20 mol%)

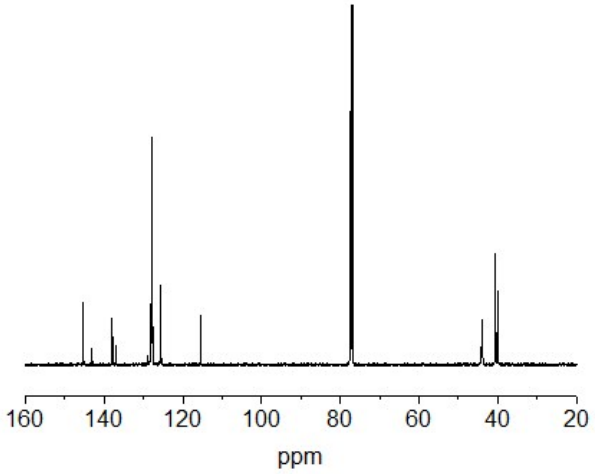

Fig. S23 ^{13}C NMR spectrum of poly(St-*co*-FSt4) (FSt4=20 mol%)

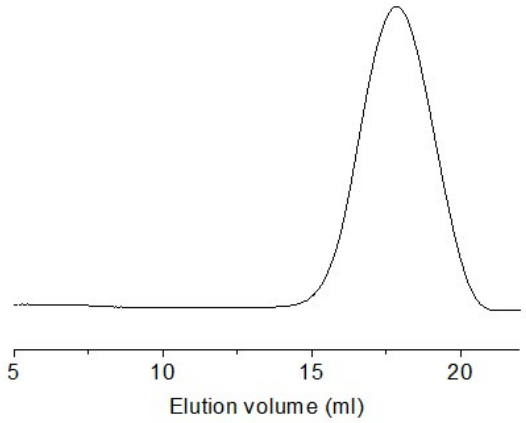

Fig. S24 GPC of poly(St-*co*-FSt5) (FSt5=20 mol%)

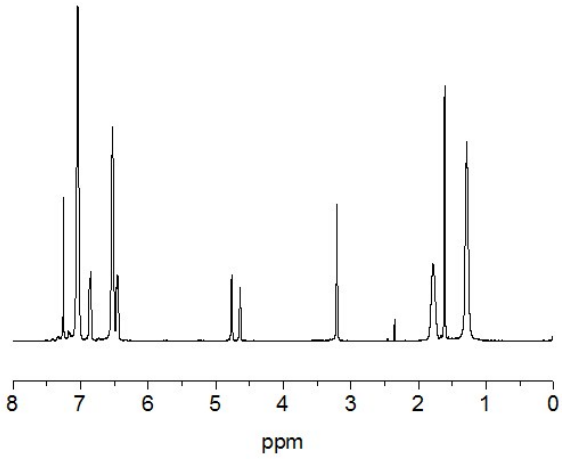

Fig. S25 ^{1}H NMR spectrum of poly(St-*co*-FSt5) (FS t5=20 mol%)

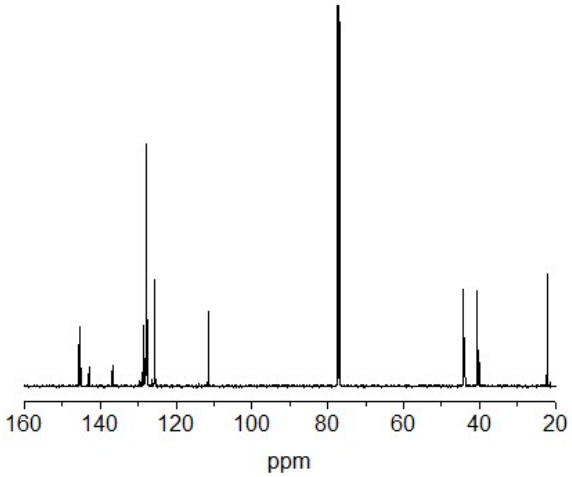

Fig. S26 ^{13}C NMR spectrum of poly(St-*co*-FSt5) (FS t5=20 mol%)

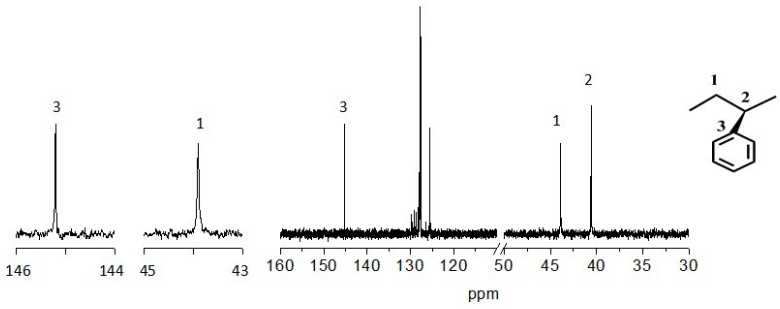

Fig. S27 ^{13}C NMR spectrum of syndiotactic polystyrene

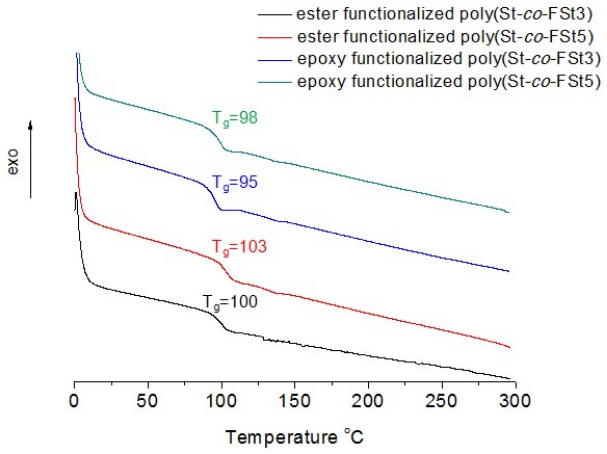

Fig. S28 DSC curves of polar-group functionalized copolymers

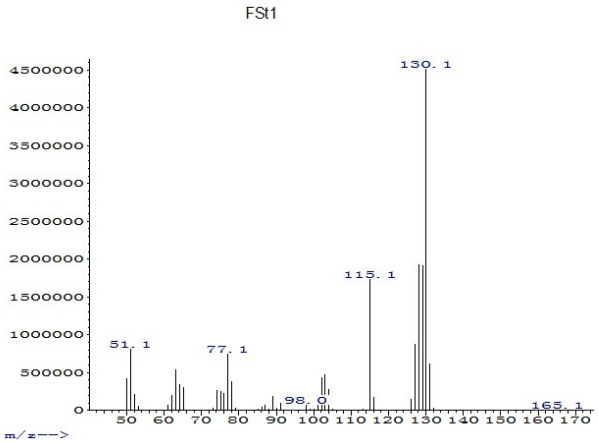

Fig. S29 GC-MS of FSt1

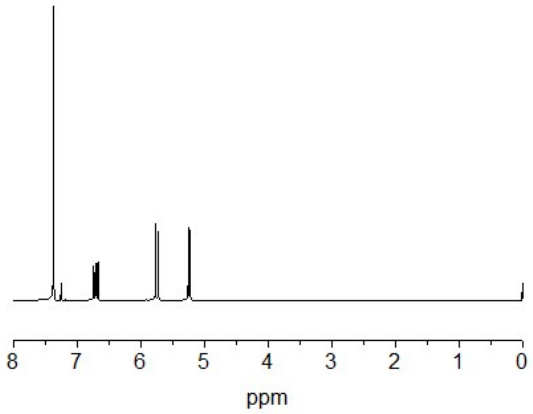

Fig. S30 ^{1}H NMR spectrum of FSt1

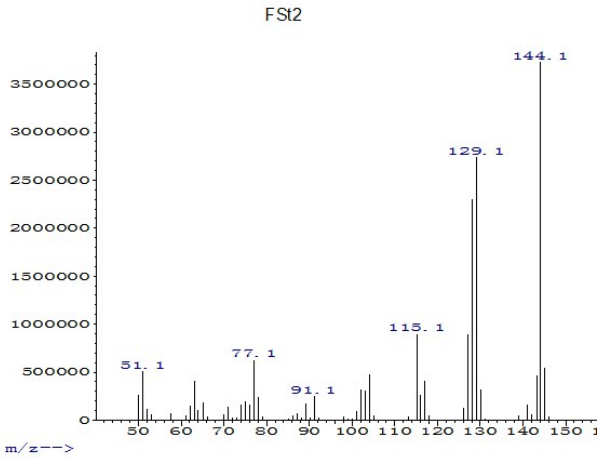

Fig. S31 GC-MS of FSt2

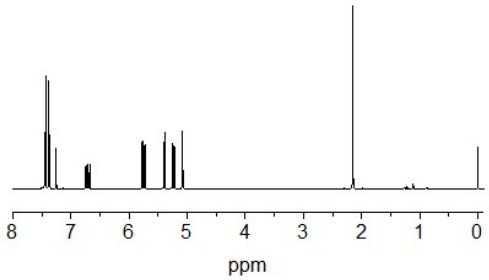

Fig. S32 ^{1}H NMR spectrum of FSt2

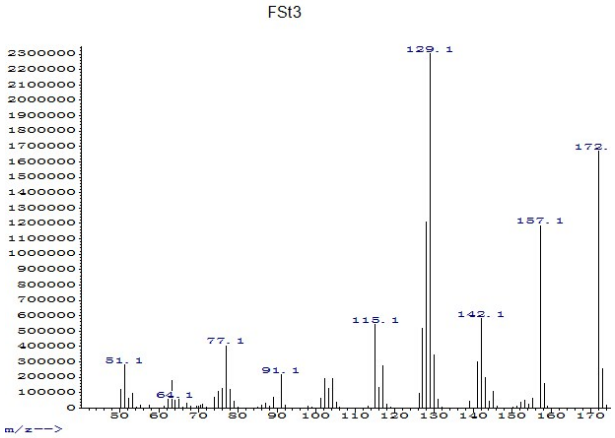

Fig. S33 GC-MS of FSt3

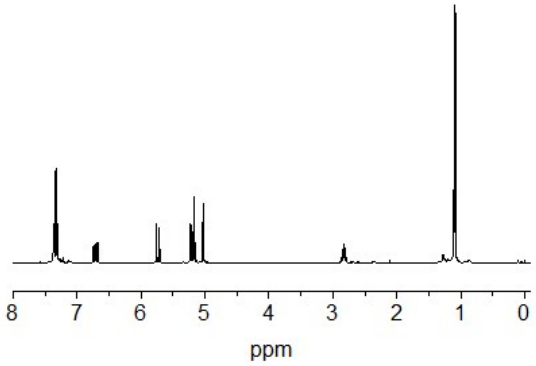

Fig. S34 [1]H NMR spectrum of FSt3

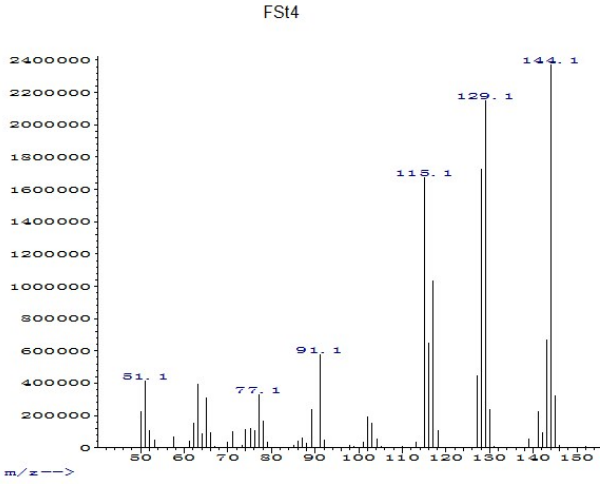

Fig. S35 GC-MS of FSt4

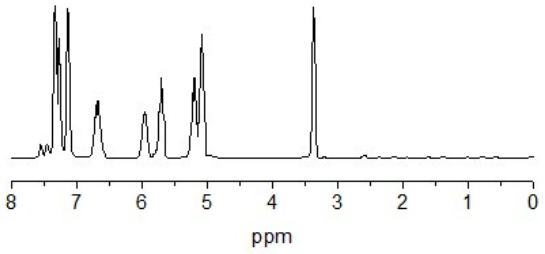

Fig. S36 [1]H NMR spectrum of FSt4

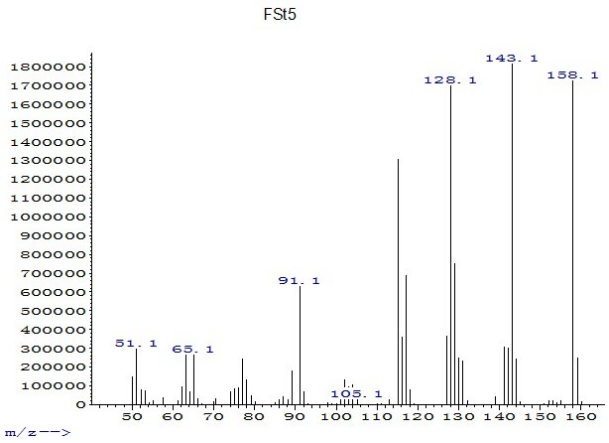

Fig. S37 GC-MS of FSt5

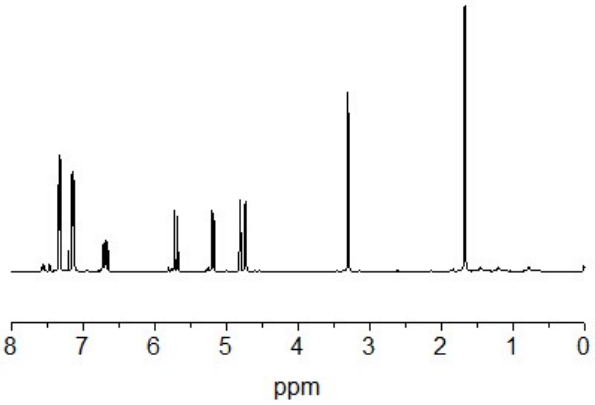

Fig. S38 ^{1}H NMR spectrum of FSt5