

Electronic Supplementary Information

Copolymerization of Propylene with Styrene and Ethylene by a THF-Containing Half-Sandwich Scandium Catalyst: Efficient Synthesis of Polyolefins with Controllable Styrene Content

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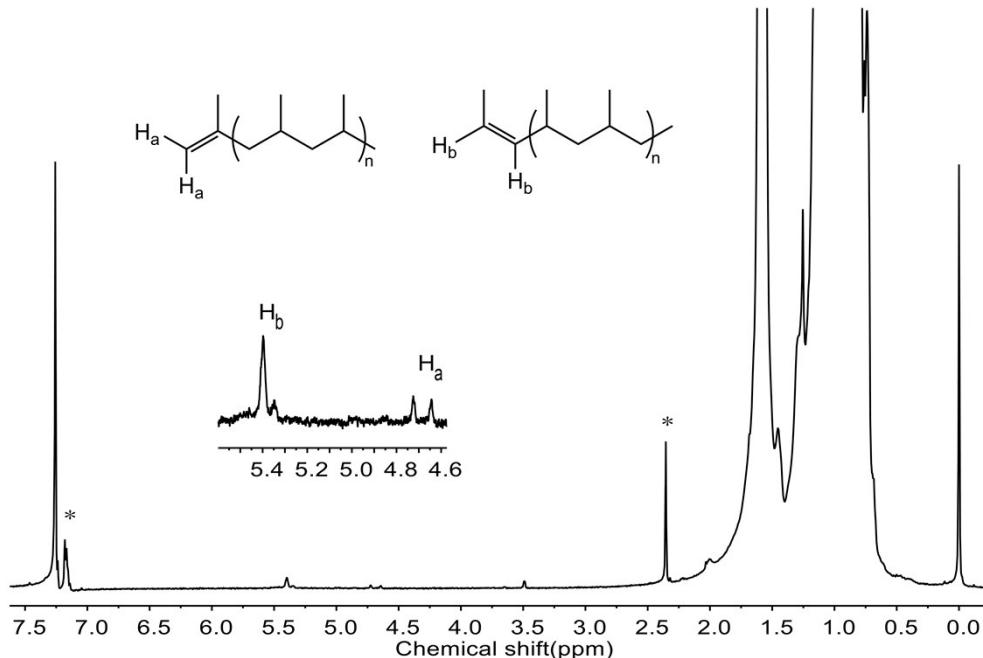


Fig. S1 ¹H-NMR spectrum of atactic polypropylene prepared by **4**/[Ph₃C][B(C₆F₅)₄]. *, toluene (Table 1, runs 11).

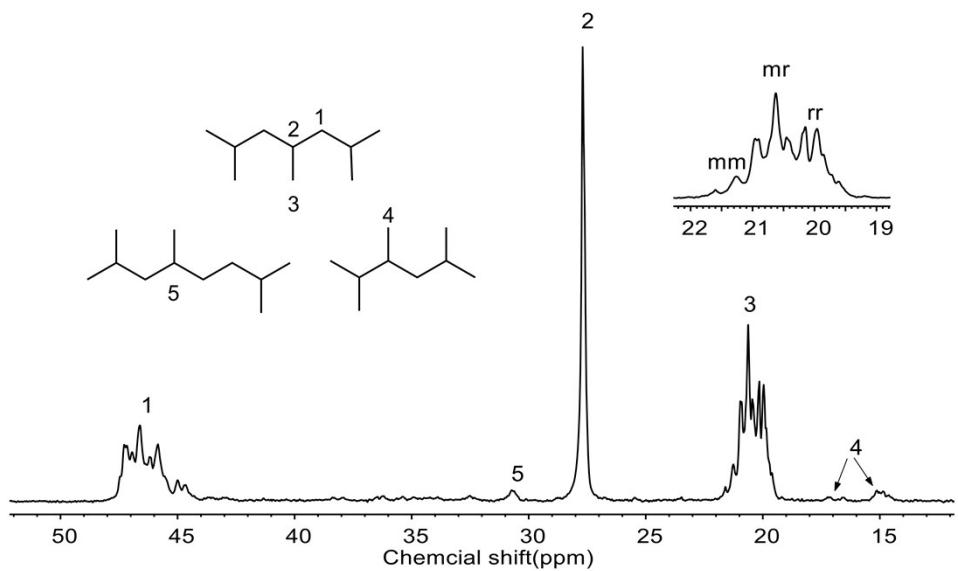


Fig. S2 ^{13}C -NMR spectrum of atactic polypropylene prepared by **4**/[Ph_3C][$\text{B}(\text{C}_6\text{F}_5)_4$] (Table 1, runs 11).

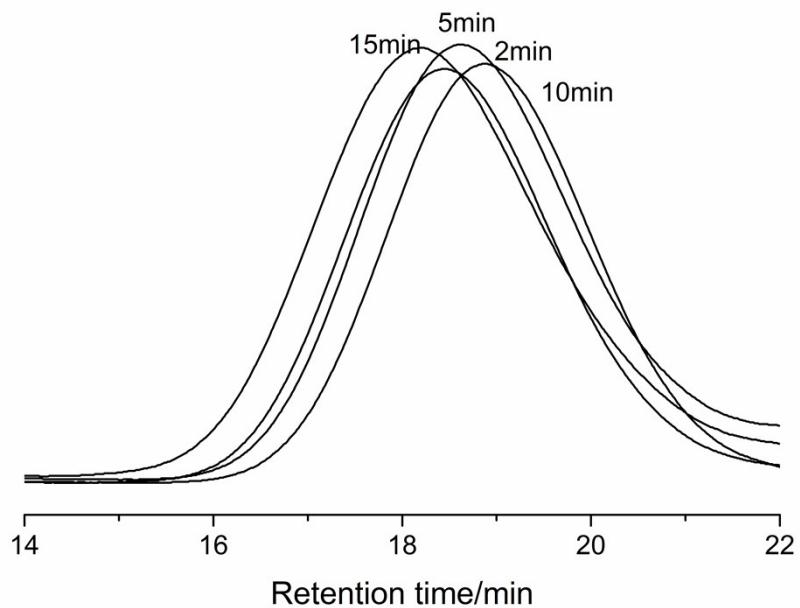


Fig. S3 GPC curves of atactic polypropylene prepared by **4**/[Ph_3C][$\text{B}(\text{C}_6\text{F}_5)_4$] (Table 1, runs 10-13).

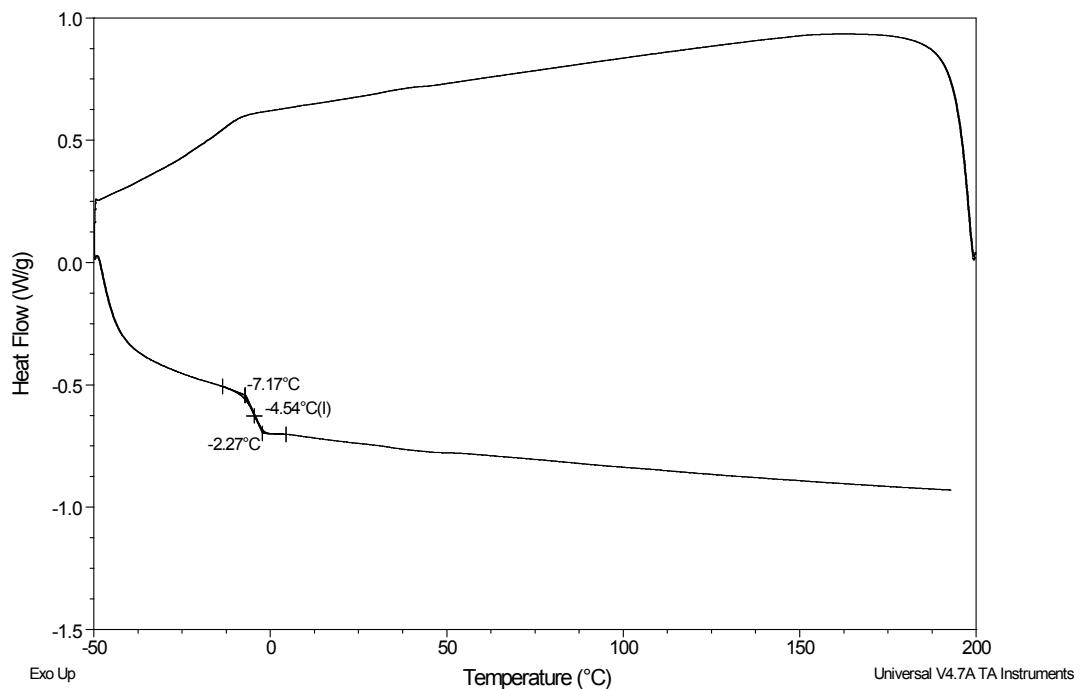


Fig. S4 DSC curve of a polypropylene prepared by **4**/[Ph₃C][B(C₆F₅)₄] (Table 1, run 11).

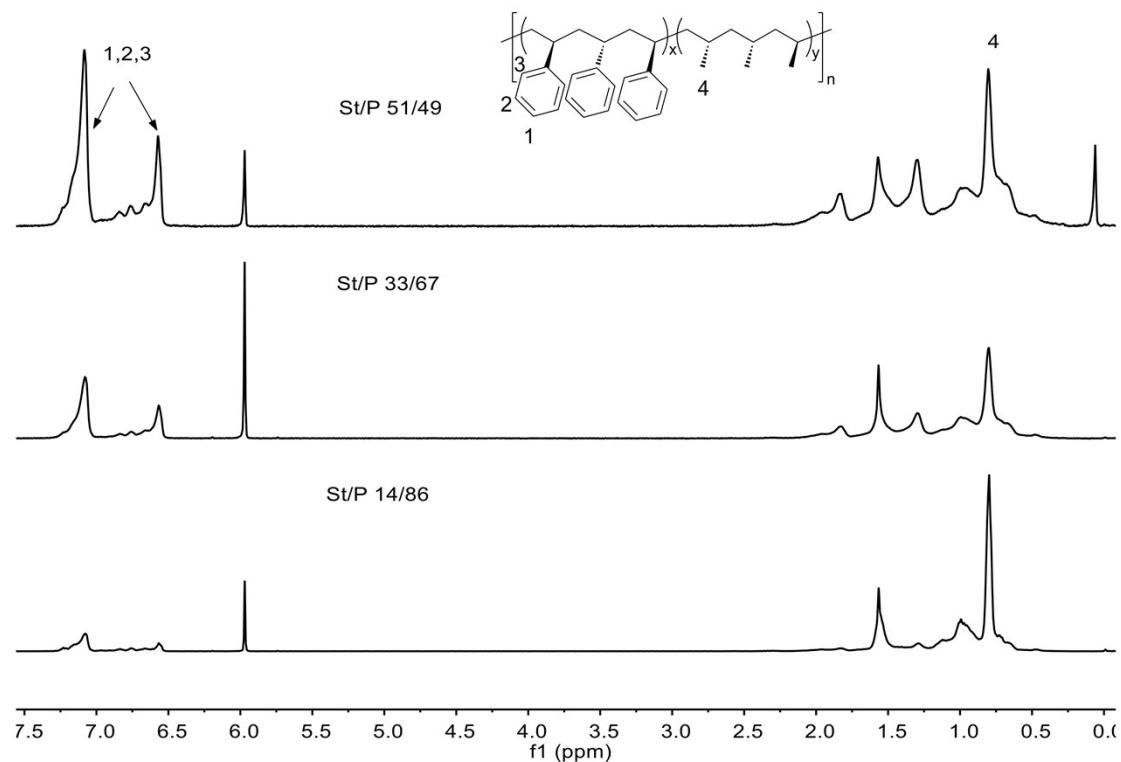


Fig. S5 ¹H-NMR spectra (400 MHz, C₂D₂Cl₄, 25 °C) of propylene-styrene copolymers prepared by **4**/[Ph₃C][B(C₆F₅)₄] (Table 2, runs 2, 5, 7).

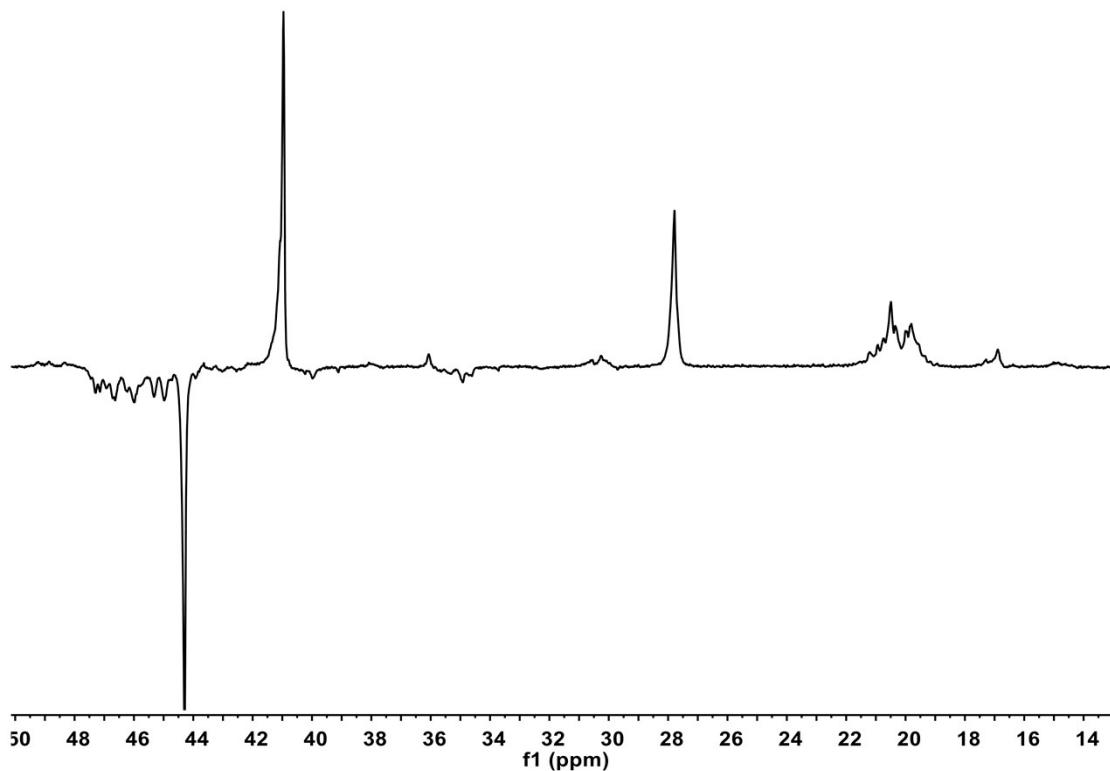


Fig. S6 DEPT 135 ^{13}C -NMR spectrum (125 MHz, CDCl_3 , 25 °C) of a propylene–styrene copolymer prepared by 4/[$\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (St content = 51%, Table 2, run 2)

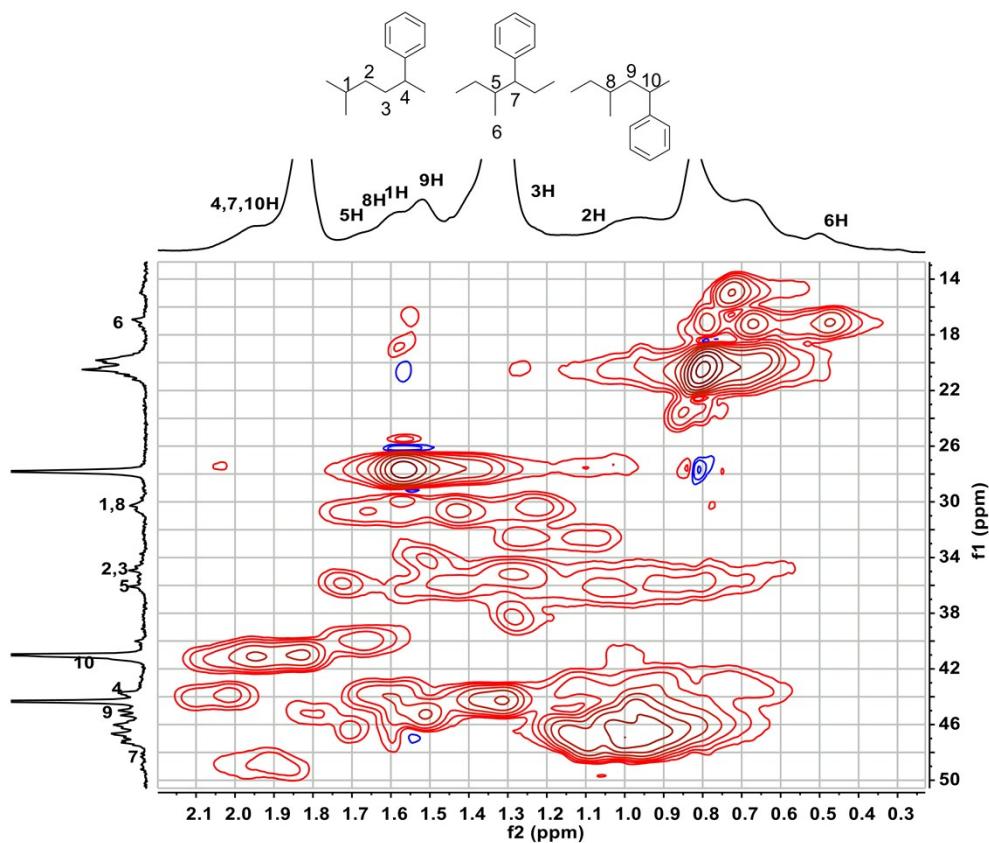


Fig. S7 Aliphatic part of the HSQC NMR spectrum (125 MHz, CDCl_3 , 25 °C) of a propylene–styrene copolymer prepared by 4/[$\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (St content = 51%, Table 2, run 2).

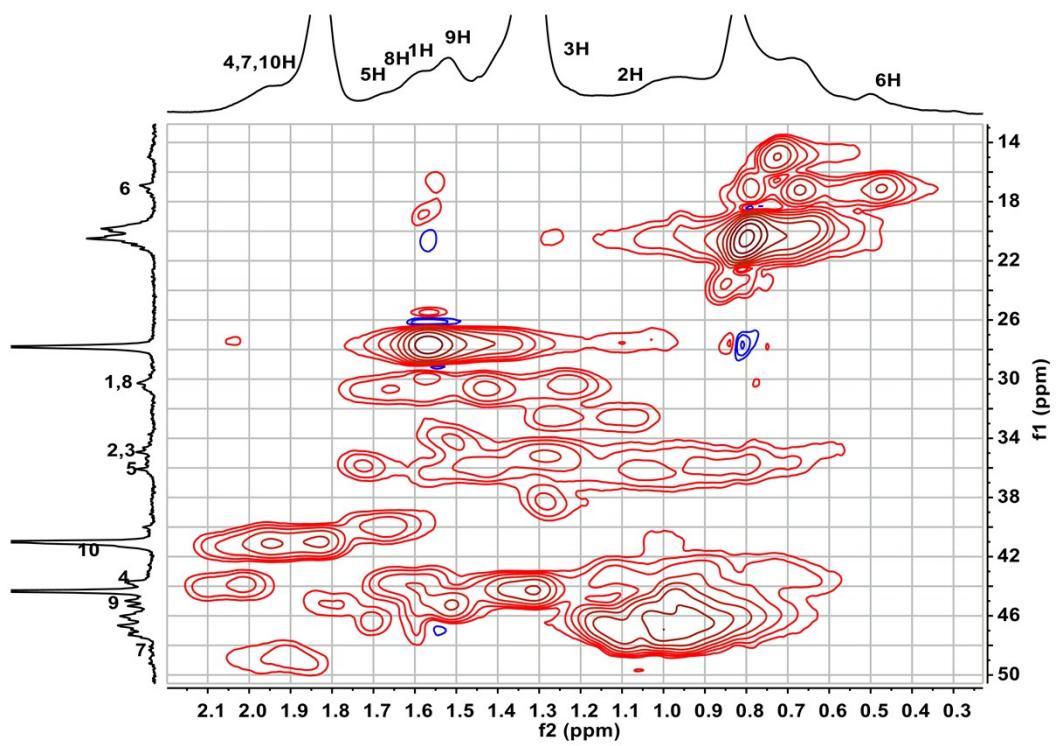


Fig. S8 Aliphatic part of the HMBC NMR spectrum (125 MHz, CDCl_3 , 25 °C) of a propylene–styrene copolymer prepared by **4**/[$\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (St content = 51%, Table 2, run 2).

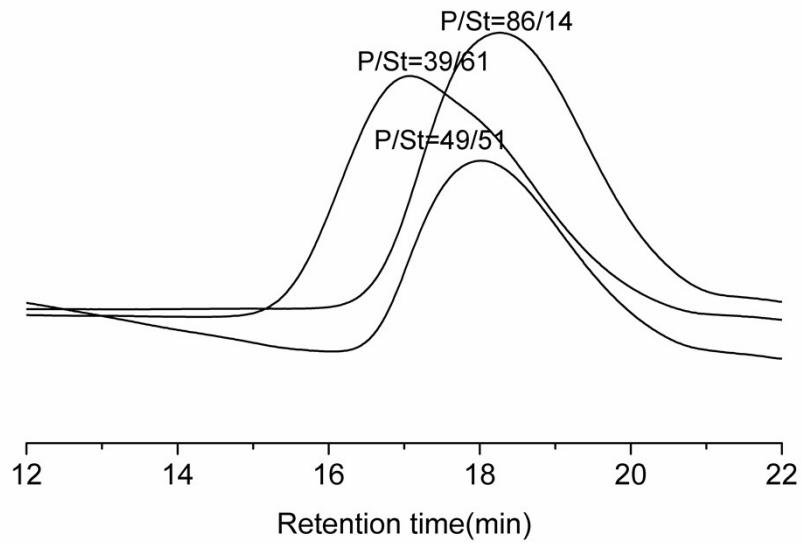


Fig. S9 GPC curves of propylene–styrene copolymers prepared by **4**/[$\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (Table 2, runs 2, 5, 8).

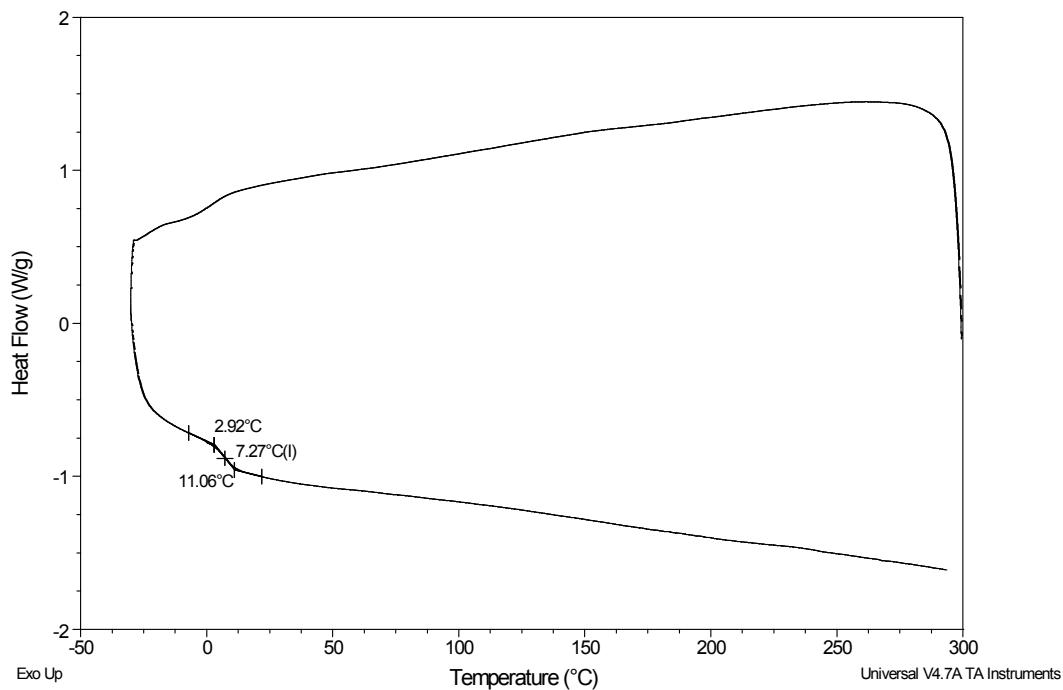


Fig. S10 DSC curve of a propylene–styrene copolymer prepared by **4**/[Ph₃C][B(C₆F₅)₄] (St content = 14%, Table 2, run 5).

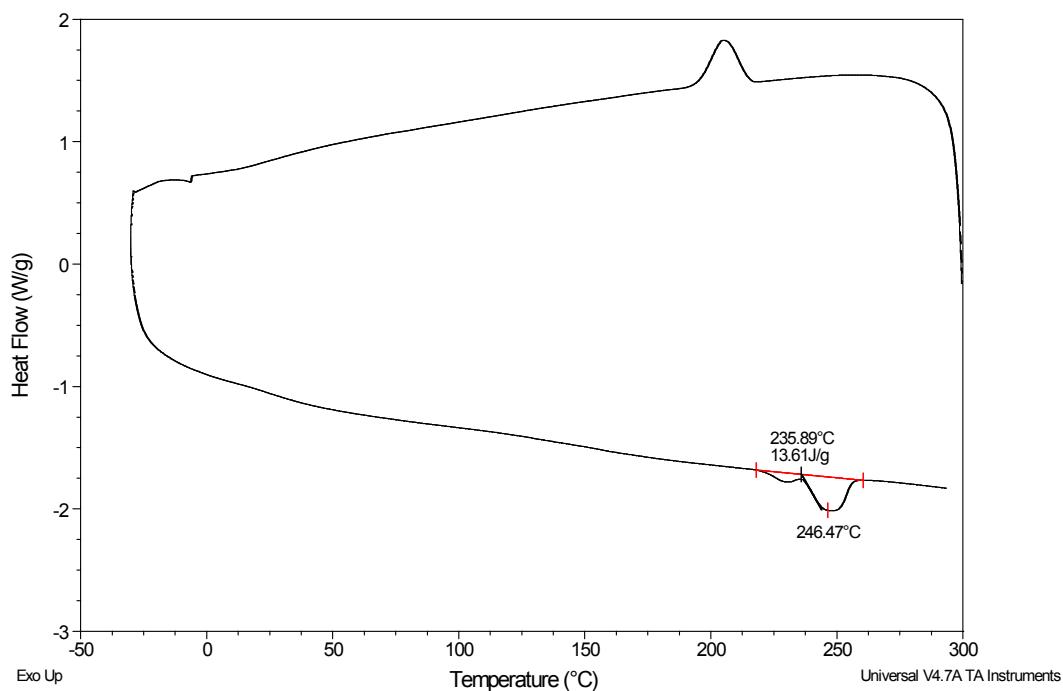
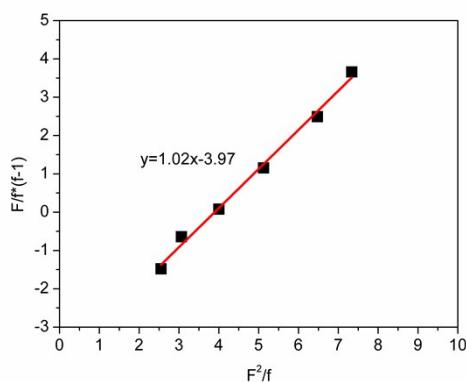


Fig. S11 DSC curve of a propylene–styrene copolymer prepared by **4**/[Ph₃C][B(C₆F₅)₄] (St content = 51%, Table 2, run 2).

Table S1 Calculation of the reactivity ratios.

[Propylene] (M)	[Styrene] (M)	P cont. mol%	St cont. mol%	F	f	X	Y
0.102	0.02	78	22	5.10	3.55	3.66	7.34
0.102	0.025	72	28	4.08	2.57	2.49	6.47
0.102	0.035	63	38	2.91	1.66	1.16	5.12
0.102	0.05	51	49	2.04	1.04	0.08	4.00
0.102	0.07	41	59	1.46	0.69	-0.64	3.06
0.102	0.1	29	71	1.02	0.41	-1.48	2.55



$$r_P = \frac{r_{P-P}}{r_{P-St}} = 1.02 \quad r_{St} = \frac{r_{St-St}}{r_{St-P}} = 3.97$$

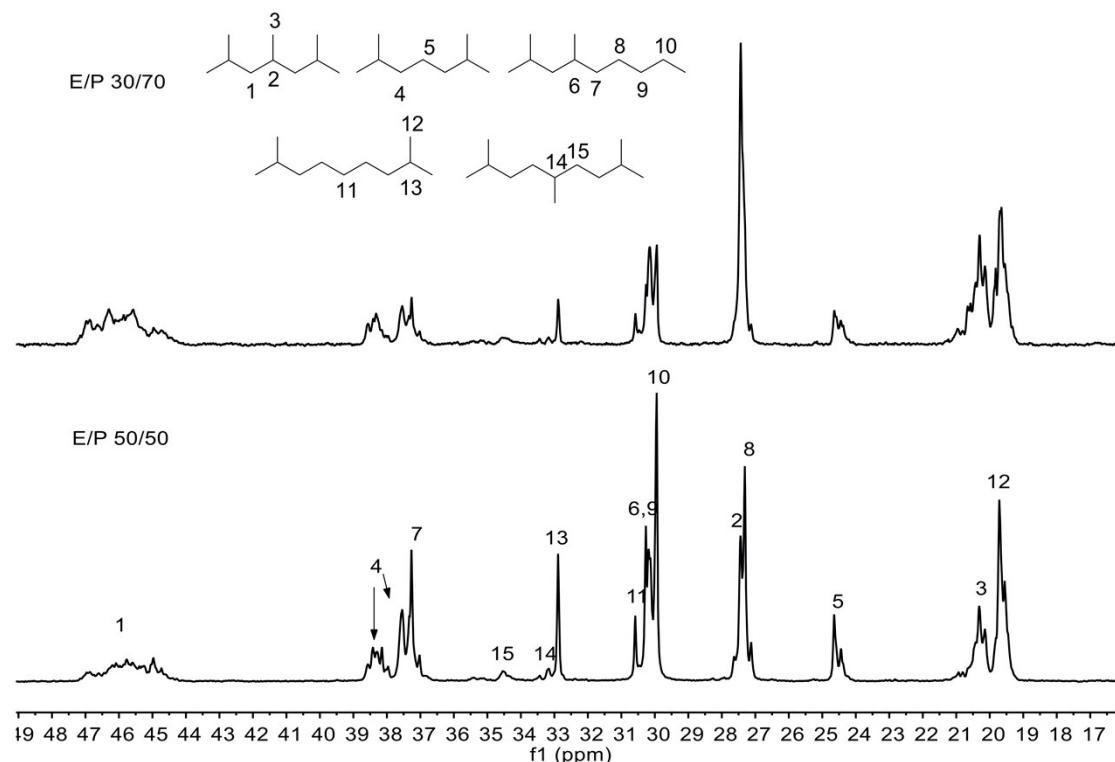


Fig. S12 ^{13}C -NMR spectra (125 MHz, CDCl_3 , 25 °C) of random ethylene-propylene copolymers prepared by **4**/[Ph_3C][$\text{B}(\text{C}_6\text{F}_5)_4$] (Table 3, runs 1, 2).

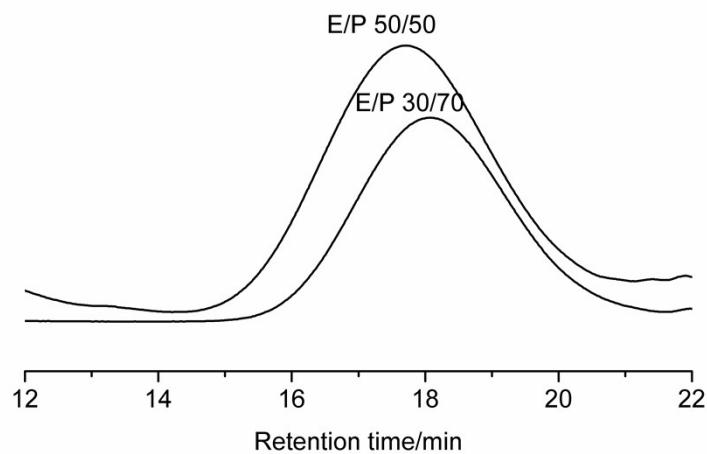


Fig. S13 GPC curves of random ethylene–propylene copolymers prepared by **4**/[Ph₃C][B(C₆F₅)₄] (Table 3, runs 1, 2).

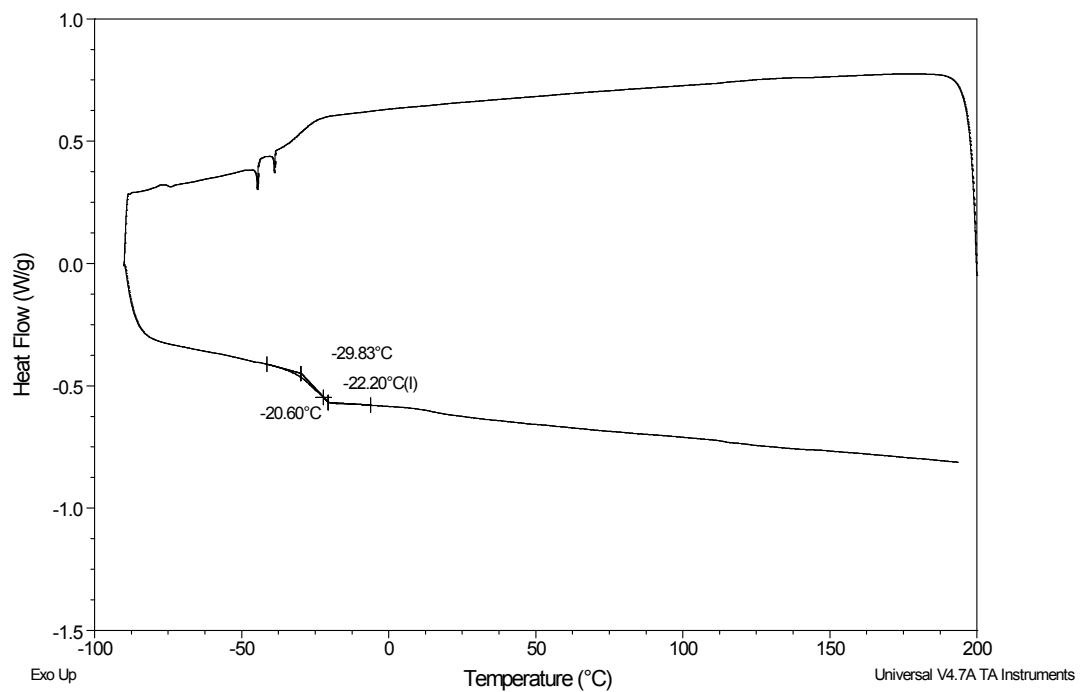


Fig. S14 DSC curve of a random propylene–ethylene copolymer prepared by **4**/[Ph₃C][B(C₆F₅)₄] (E content = 30%, P content = 70%, Table 3, run 2).

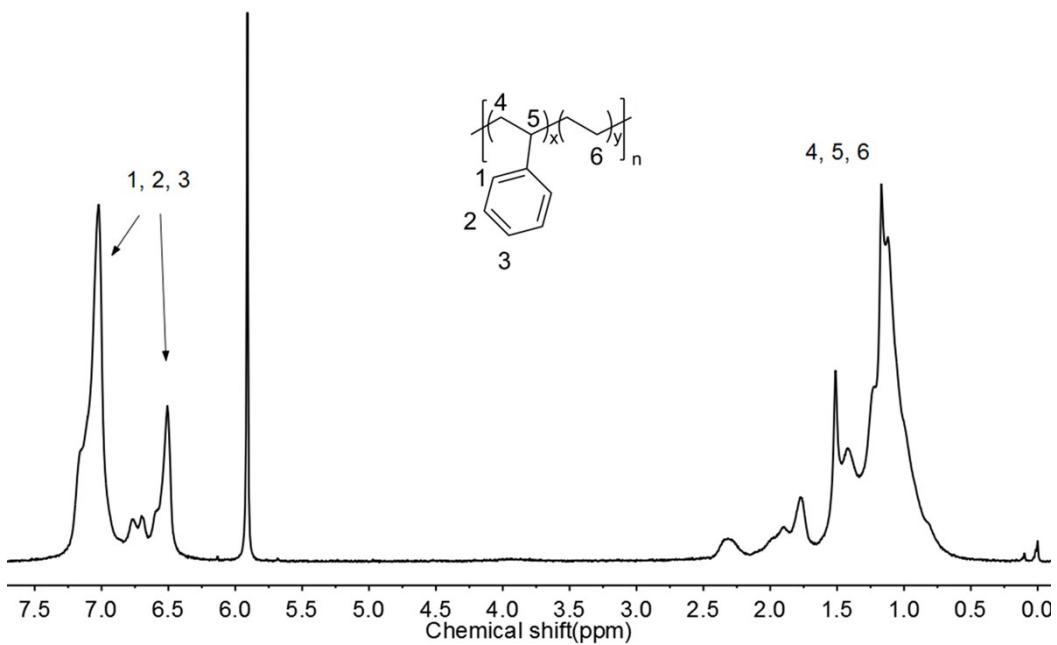


Fig. S15 ^1H -NMR spectra (400 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 25 °C) of ethylene–styrene copolymers prepared by **4**/[Ph_3C][$\text{B}(\text{C}_6\text{F}_5)_4$] (Table 3, run 3).

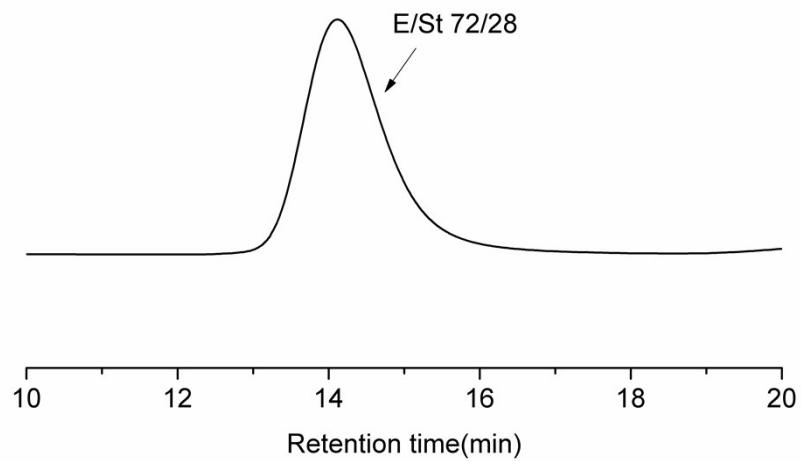


Fig. S16 GPC curves of ethylene–styrene copolymers prepared by **4**/[Ph_3C][$\text{B}(\text{C}_6\text{F}_5)_4$] (Table 3, runs 3).

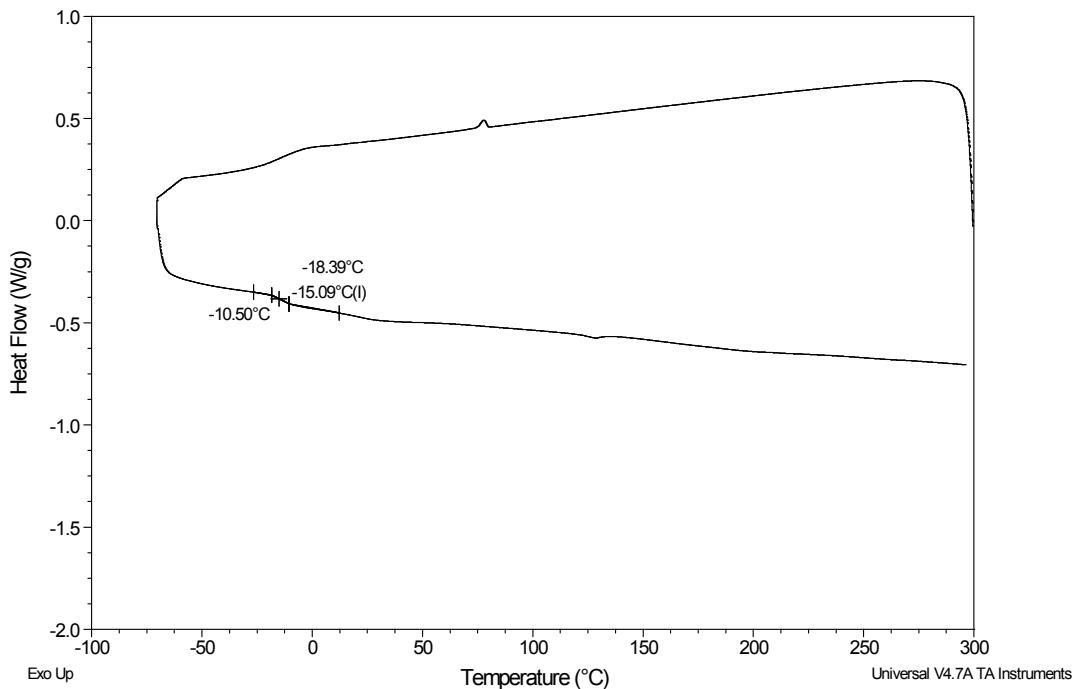


Fig. S17 DSC curve of an ethylene–styrene copolymer prepared by **4**/[Ph₃C][B(C₆F₅)₄] (St content = 28%, Table 3, run 3).

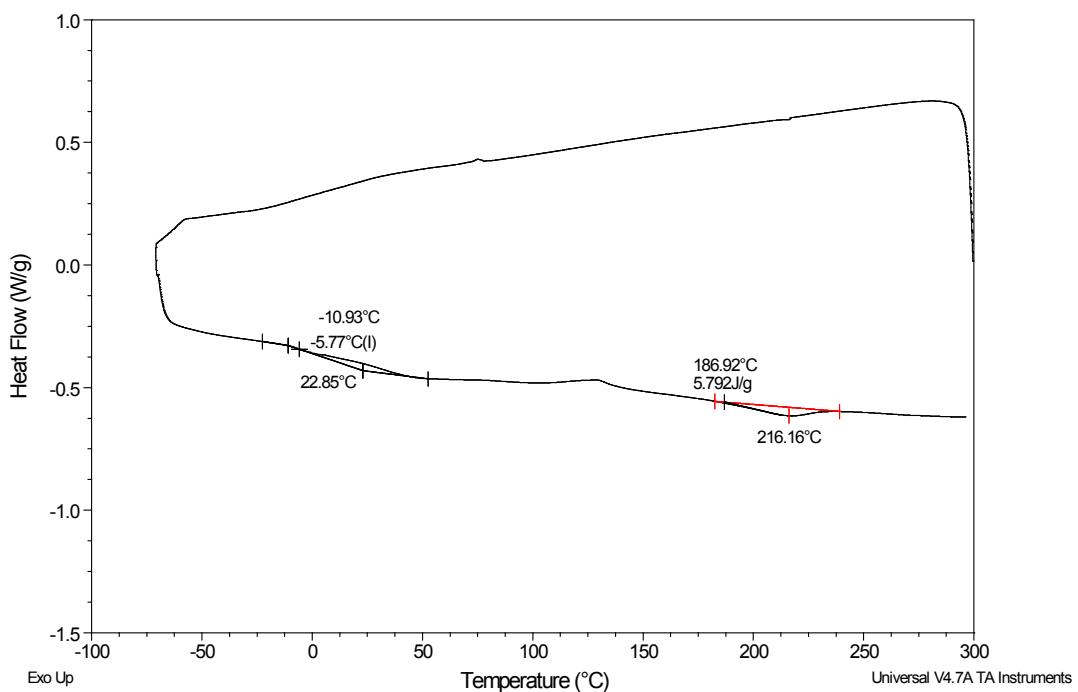


Fig. S18 DSC curve of an ethylene–styrene copolymer prepared by **4**/[Ph₃C][B(C₆F₅)₄] (St content = 38 %, Table 3, run 4).

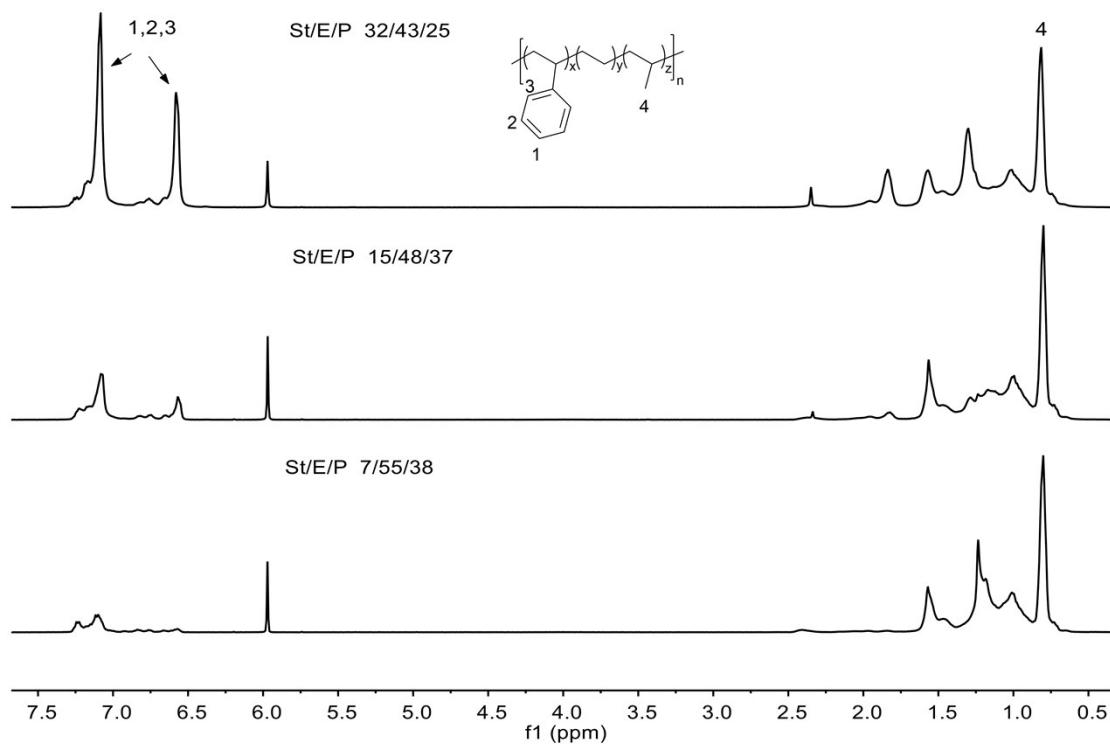


Fig. S19 ¹H-NMR spectra (400 MHz, C₂D₂Cl₄, 25 °C) of propylene-ethylene-styrene terpolymers prepared by **4**/[Ph₃C][B(C₆F₅)₄] (Table 3, runs 8–10).

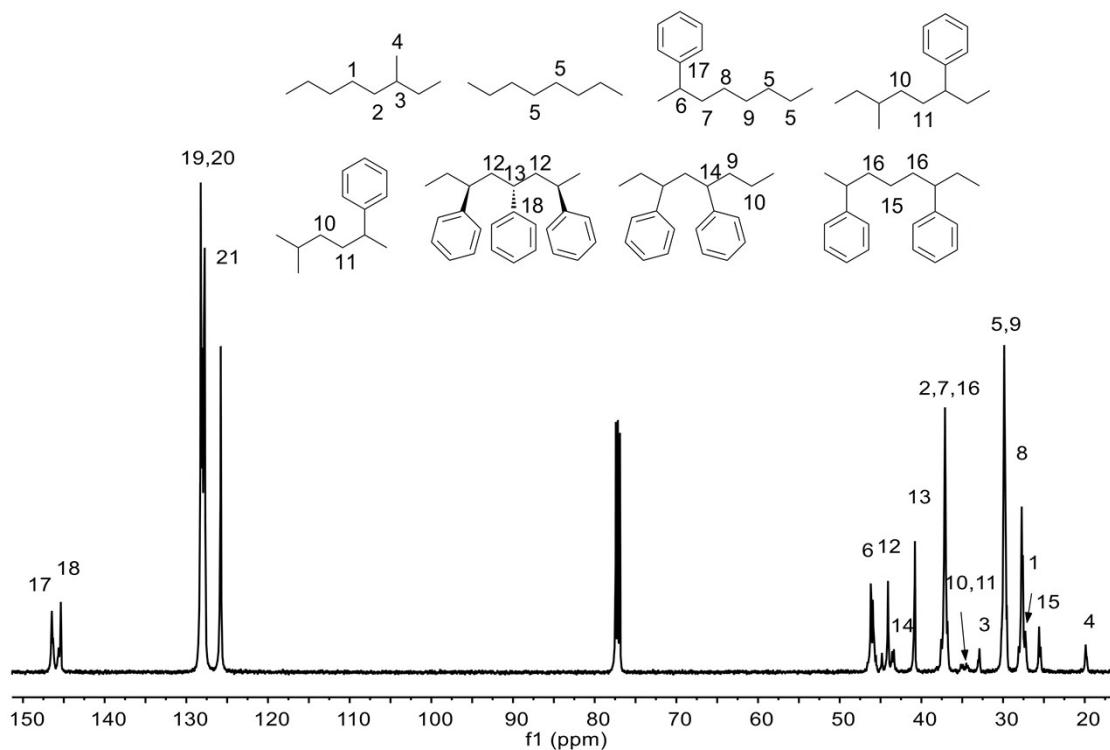


Fig. S20 ¹³C-NMR spectrum (125 MHz, CDCl₃, 25 °C) of a random propylene-ethylene-styrene terpolymer prepared by **4**/[Ph₃C][B(C₆F₅)₄] (St content = 23%, E content = 74%, Table 3, run 7).

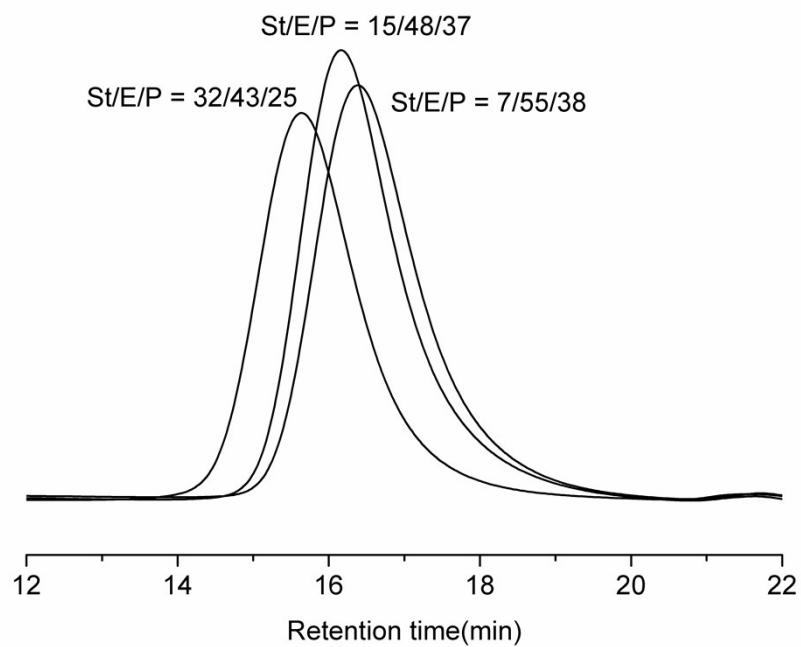


Fig. S21 GPC curves of random propylene–ethylene–styrene terpolymers prepared by **4**/[Ph_3C][$\text{B}(\text{C}_6\text{F}_5)_4$] (Table 3, runs 8–10).

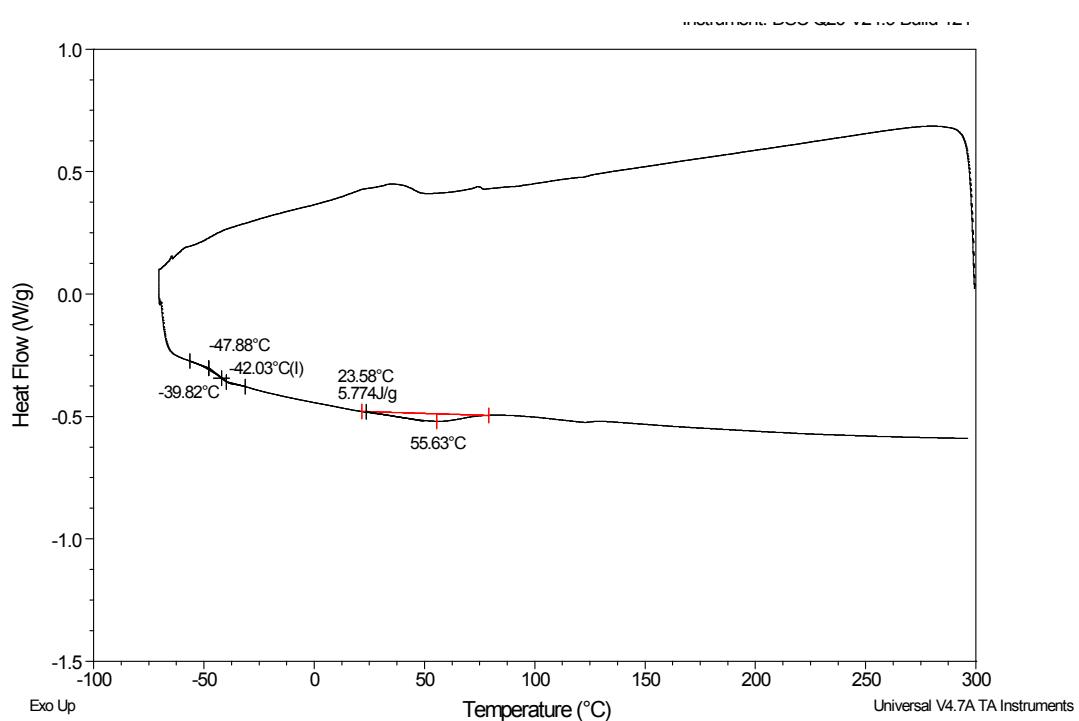


Fig. S22 DSC curve of a propylene–ethylene–styrene terpolymer prepared by **4**/[Ph_3C][$\text{B}(\text{C}_6\text{F}_5)_4$] (St content = 5%, E content = 65%, Table 3, run 5).

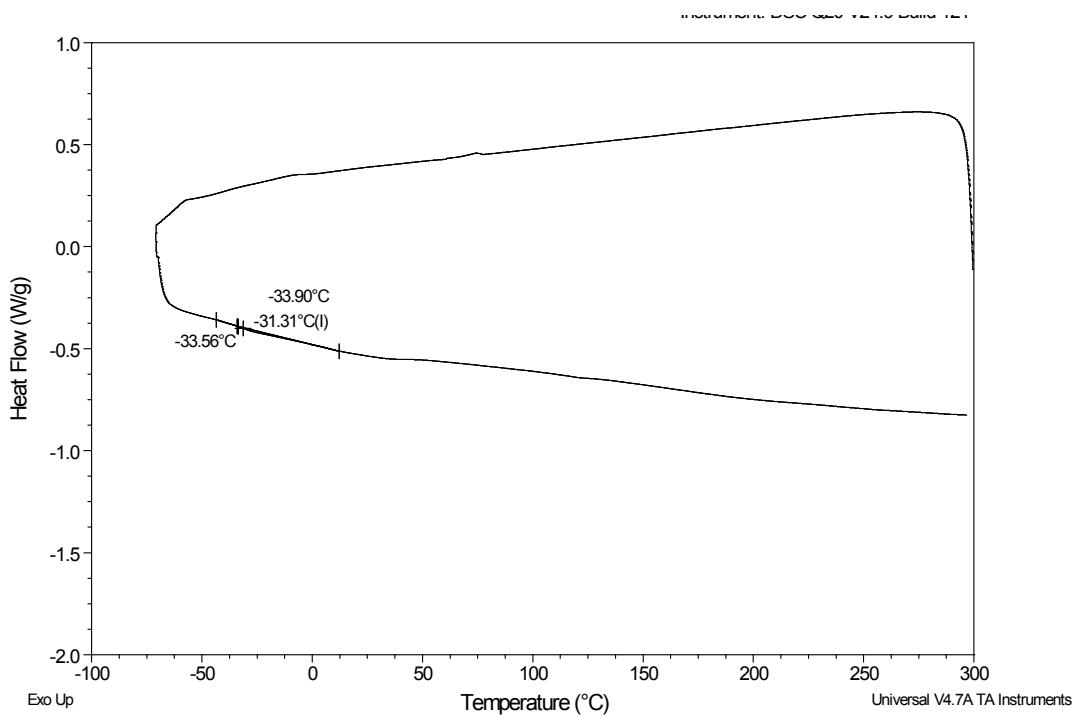


Fig. S23 DSC curve of a propylene–ethylene–styrene terpolymer prepared by **4**/[Ph₃C][B(C₆F₅)₄] (St content = 13%, E content = 65%, Table 3, run 6).

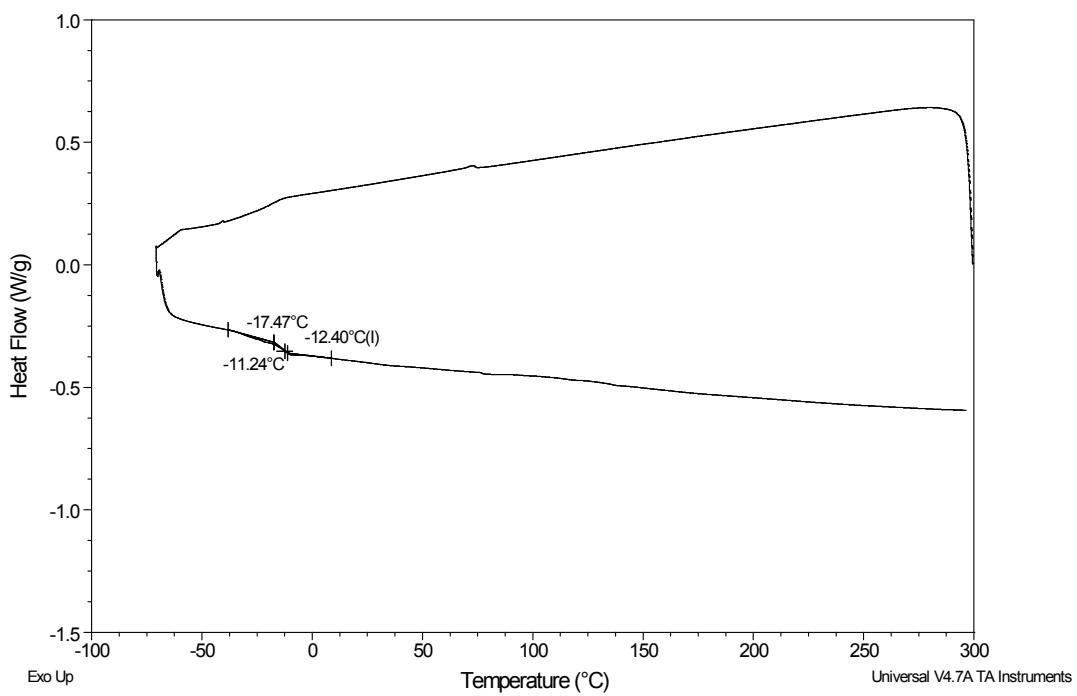


Fig. S24 DSC curve of a propylene–ethylene–styrene terpolymer prepared by **4**/[Ph₃C][B(C₆F₅)₄] (St content = 7%, E content = 55%, Table 3, run 8).

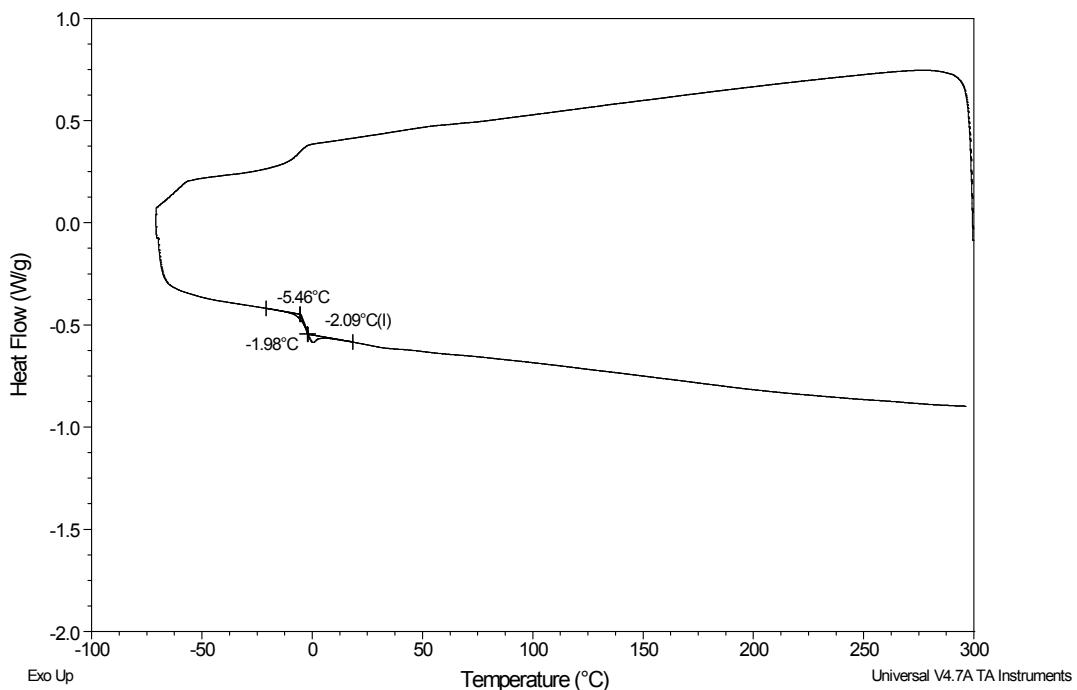


Fig. S25 DSC curve of a propylene–ethylene–styrene terpolymer prepared by **4**/[Ph₃C][B(C₆F₅)₄] (St content = 15%, E content = 48%, Table 3, run 9).

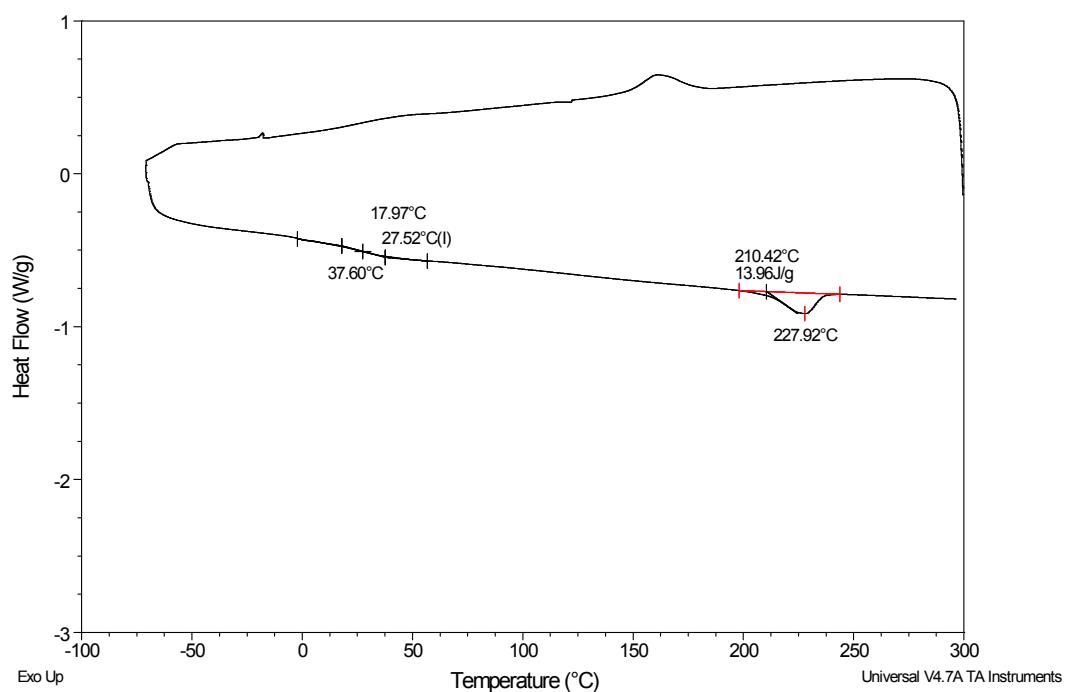


Fig. S26 DSC curve of a propylene–ethylene–styrene terpolymer prepared by **4**/[Ph₃C][B(C₆F₅)₄] (St content = 32%, E content = 43%, Table 3, run 10).

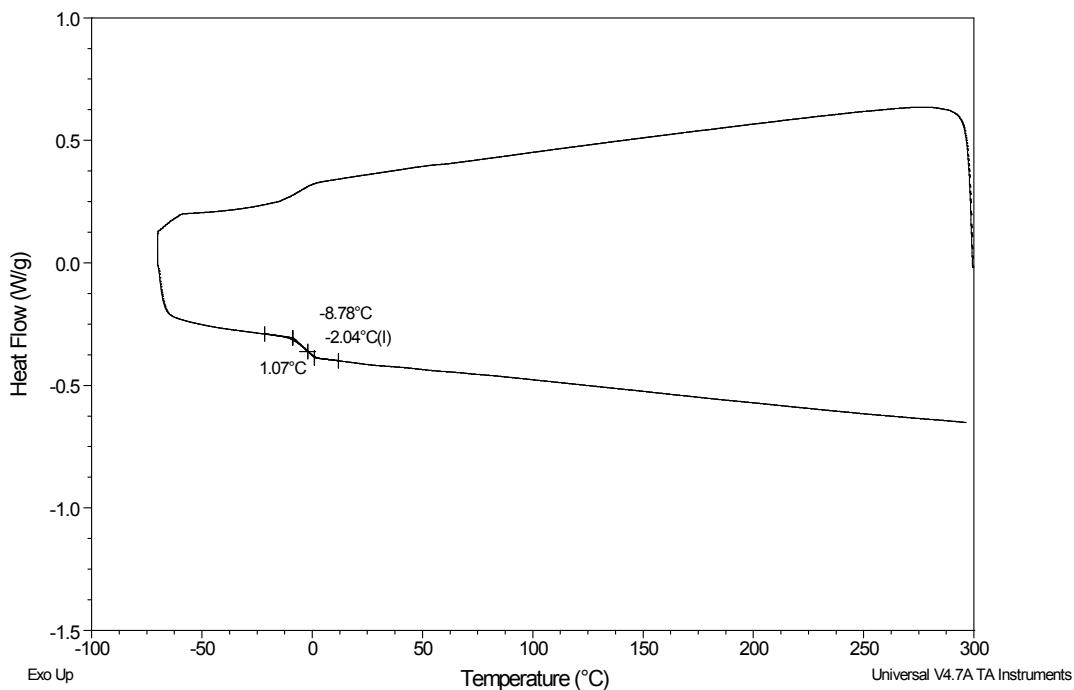


Fig. S27 DSC curve of a propylene–ethylene–styrene terpolymer prepared by **4**/[Ph_3C][$\text{B}(\text{C}_6\text{F}_5)_4$] (St content = 12%, E content = 45%, Table 3, run 11).

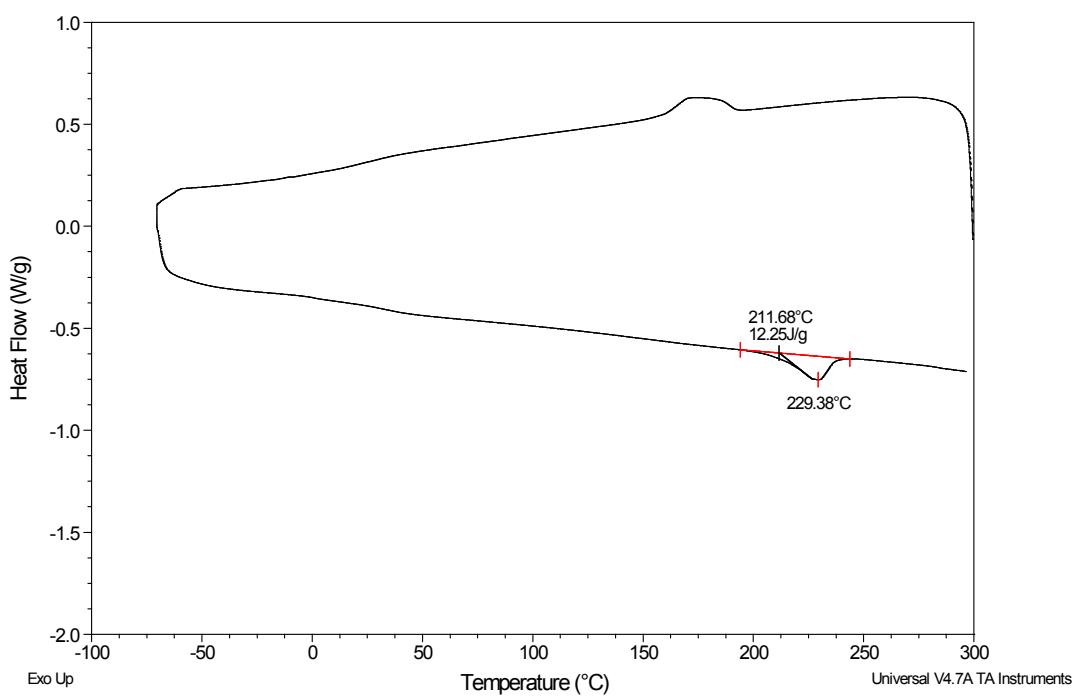


Fig. S28 DSC curve of a propylene–ethylene–styrene terpolymer prepared by **4**/[Ph_3C][$\text{B}(\text{C}_6\text{F}_5)_4$] (St content = 30%, E content = 45%, Table 3, run 13).