

Electronic Supplementary Information

Terpolymerization of Ethylene, Propylene with Isoprene via THF-Containing Half-Sandwich Scandium Catalysts: A New Kind of Ethylene-Propylene-Diene Rubber and its Functionalization

Rui Tan,^{a,b} Zhenghai Shi,^{a,b} Fang Guo,^{a,b} Lv He,^{a,b} Li Han^{a,b} and Yang Li^{*a,b}

^a State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, China.

^b Liaoning Key Laboratory of Polymer Science and Engineering, Dalian 116024, China.

* E-mail: liyang@dlut.edu.cn

Experiment Section

Propylene/isoprene copolymerization (Table S1, Run 6)

In a glovebox, a toluene solution (15 mL) of isoprene (272.4 mg, 4 mmol) was added into a stainless steel autoclave (100ml). The autoclave was sealed, taken outside and connected to a well-purged propylene line. Propylene (0.2 MPa) was introduced into the autoclave quickly and was saturated by stirring for 1 min. A toluene solution (5 mL) of [1,3-(Me₂Si)₂C₉H₅]Sc(CH₂SiMe₃)₂(THF) (11.1 mg, 20 μmol) and [Ph₃C][B(C₆F₅)₄] (18.5 mg, 20 μmol) was then added through a springer into the autoclave under vigorous stirring. The total pressure in the reactor was controlled at 0.1 MPa. After 5 min, the polymerization was terminated by methanol. The copolymer was collected by adding another 100 mL of methanol, dried at 30 °C under vacuum to a constant weight. The propylene (P) and isoprene (Ip) contents of the propylene-isoprene copolymers were calculated according to the following formulas:

$$\text{Ip mol\%} = (6 I_1 + 3 I_2) / (6 I_1 + 3 I_2 + 2 I_3) \times 100$$

$$3,4\text{-Ip mol\%} = 2 I_1 / (2 I_1 + I_2) \times 100$$

$$1,4\text{-Ip mol\%} = 100 - 3,4\text{-Ip mol\%}$$

$$\text{P mol\%} = 100 - \text{Ip mol\%}$$

Where I_1 is the integration of the resonances from 4.90 to 5.20 ppm (one unsaturated protons of the 1,4-isoprene unit), I_2 is the integration of the resonances from 4.50 to 4.85 ppm (two unsaturated protons of the 3,4-isoprene unit), I_3 is the integration of the resonances from 0.40 to 0.90 ppm (three methyl protons of the propylene unit).

Ethylene/isoprene copolymerization (Table S1, Run 13)

In a glovebox, a toluene solution (15 mL) of isoprene (681.1 mg, 10 mmol) was charged into a stainless steel autoclave (100 mL). The autoclave was sealed, taken outside and connected to a well-purged ethylene line. Ethylene (0.1 MPa) was introduced into the autoclave quickly and was saturated by stirring for 1 min. A toluene solution (5 mL) of [1,3-(Me₂Si)₂C₉H₅]Sc(CH₂SiMe₃)₂(THF) (11.1 mg, 20 μmol) and [Ph₃C][B(C₆F₅)₄] (18.5 mg, 20 μmol) was then added through a springer into the autoclave under vigorous stirring. The total pressure in the reactor was controlled at 0.1 MPa, the polymerization was terminated after 2 min by methanol. The copolymer was collected by filtered, washed with methanol and dried at 30 °C under vacuum to a constant weight. The isoprene and ethylene contents of the ethylene-isoprene copolymers were calculated according to the literature.²

Table S1 Ethylene, propylene and isoprene polymerization catalyzed by $(C_5Me_4SiMe_3)Sc(CH_2SiMe_3)_2(THF)$ (**1**) and $[1,3-(Me_2Si)_2C_9H_5]Sc(CH_2SiMe_3)_2(THF)$ (**2**) / $[Ph_3C][B(C_6F_5)_4]$.^a

Run	[Sc]	Pressure ^e (MPa)	P/E	Ip (mmol)	Time (min)	Yield ^d (g)	Activity ^b	Composition ^c (mol%)			M_n^d ($\times 10^4$)	M_w / M_n^d	$T_g(T_m)^e$ ($^{\circ}C$)
								Ip(1,4/3,4)	E	P			
1 ^f	1	0.2	1/0		2	0.59	886	—	—	100	1.2	1.98	-9
2	2	0.2	1/0		2	1.52	2280	—	—	100	2.0	1.91	-4
3 ^g	1			10	60	0.18	9	5/54/41	—	—	24.5	1.31	-38
4	2			20	5	1.35	810	75/0/25	—	—	14.5	1.23	-45
5	1	0.2	1/0	4	5	0.05	30	34(60/40)	—	66	n.d.	n.d.	-25
6	2	0.2	1/0	4	5	0.27	162	23(74/26)	—	77	2.3	1.65	-15
7	1	0.2	2/1		2	1.82	2730	—	58	42	n.d. ^h	n.d.	-(104)
8 ^f	1	0.2	5/1		2	1.53	2295	—	50	50	2.8	1.79	-41
9	2	0.2	2/1		2	2.25	3375	—	47	53	n.d.	n.d.	-44
10	2	0.2	5/1		2	2.09	3135	—	40	60	3.2	1.90	-30
11	1	0.1	0/1	5	2	0.54	810	16(45/55)	84	—	n.d.	n.d.	(64,132)
12	1	0.1	0/1	10	2	0.41	615	26(42/58)	74	—	12.4	1.23	-54
13	2	0.1	0/1	10	2	0.42	630	30(69/31)	70	—	n.d.	n.d.	-(131)
14	2	0.1	0/1	20	2	0.43	645	41(69/31)	59	—	24.1	2.11	-47

^a Reaction condition: [Sc], 20 μ mol; $[Ph_3C][B(C_6F_5)_4]$, 20 μ mol; Toluene, 20 mL, 25 $^{\circ}C$; Total pressure, 0.2 MPa. ^b Given in Kg of polymer per (mol Sc h). ^c Determined by 1H -NMR and ^{13}C -NMR. ^d Determined by GPC in THF. ^e Determined by DSC. ^f Reference 1. ^g Reference 2. ^h Not determined.

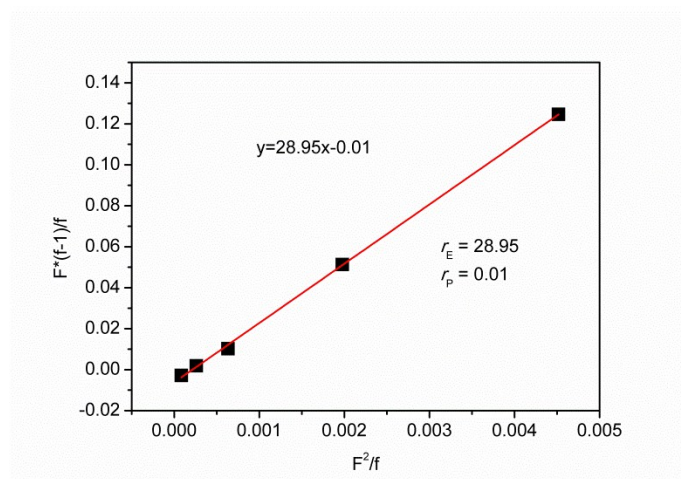


Fig. S1 The Fineman-Ross plot for the copolymerization of ethylene with propylene catalyzed by the complex **1** / $[Ph_3C][B(C_6F_5)_4]$. ($F = [E]/[P]$ in solution, $f = [E]/[P]$ in copolymer)

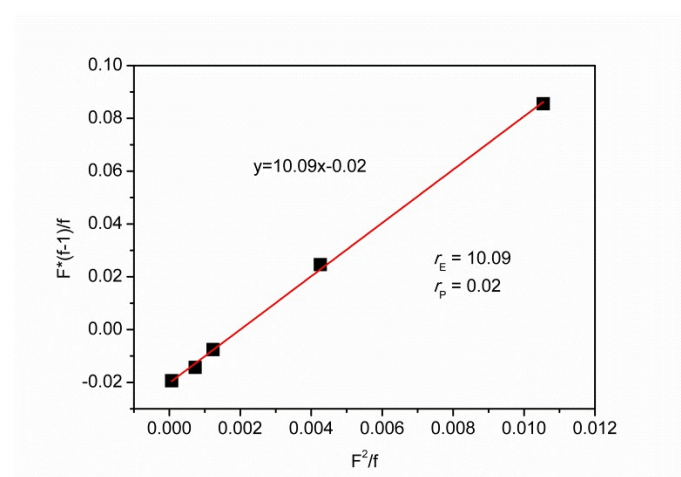


Fig. S2 The Fineman-Ross plot for the copolymerization of ethylene with propylene catalyzed by the complex **2**/[Ph₃C][B(C₆F₅)₄]. ($F = [E]/[P]$ in solution, $f = [E]/[P]$ in copolymer)

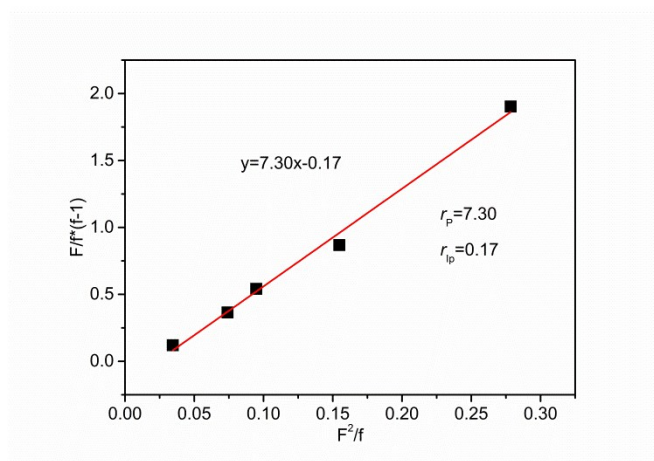


Fig. S3 The Fineman-Ross plot for the copolymerization of propylene with isoprene catalyzed by the complex **1**/[Ph₃C][B(C₆F₅)₄]. ($F = [P]/[Ip]$ in solution, $f = [P]/[Ip]$ in copolymer)

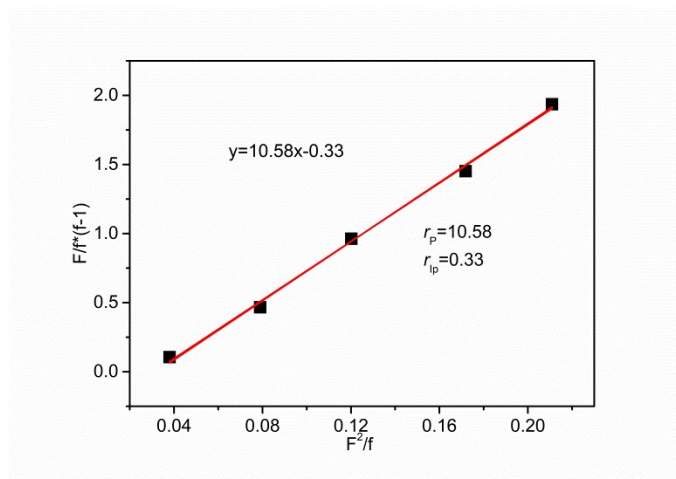


Fig. S4 The Fineman-Ross plot for the copolymerization of propylene with isoprene catalyzed by the complex **1**/[Ph₃C][B(C₆F₅)₄]. ($F = [P]/[Ip]$ in solution, $f = [P]/[Ip]$ in copolymer)

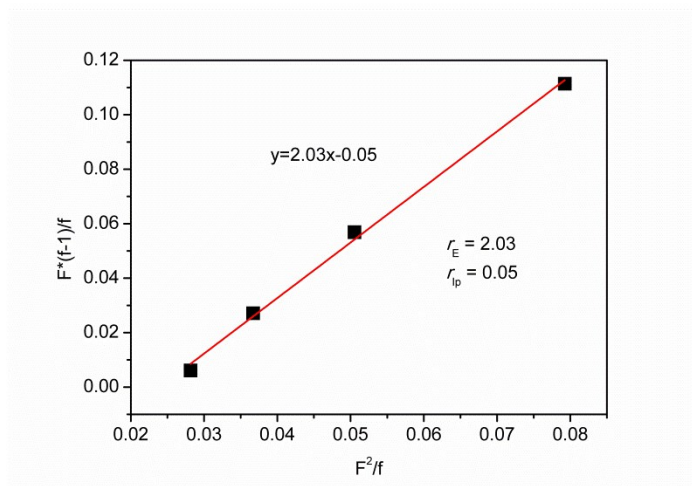


Fig. S5 The Fineman-Ross plot for the copolymerization of ethylene with isoprene catalyzed by the complex **2**/[Ph₃C][B(C₆F₅)₄]. ($F = [E]/[Ip]$ in solution, $f = [E]/[Ip]$ in copolymer)

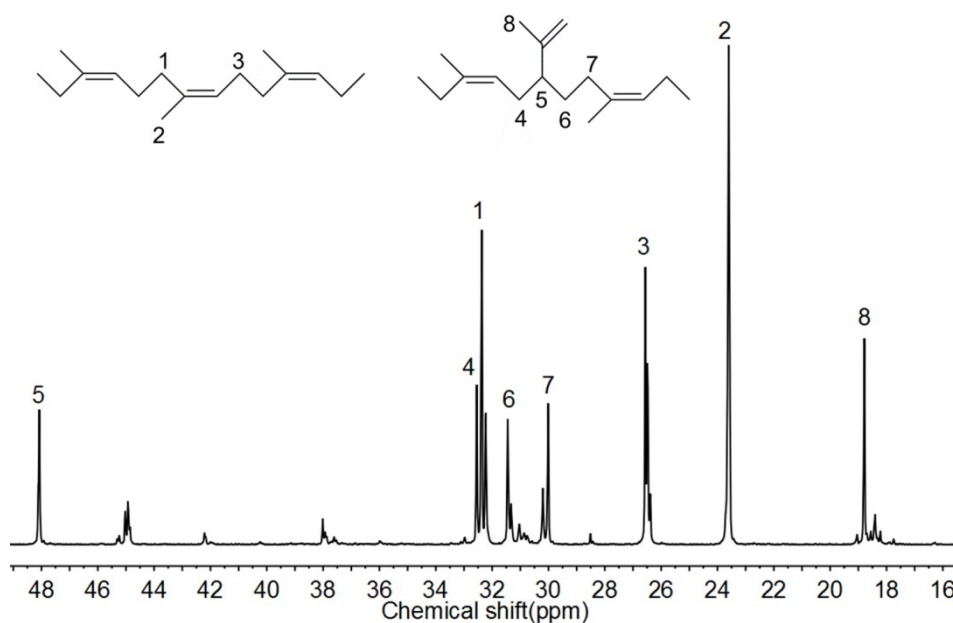


Fig. S6 ^{13}C -NMR spectrum (100 MHz, CDCl_3 , 25 $^\circ\text{C}$) of the polyisoprene prepared by the complex **2**/[Ph_3C][$\text{B}(\text{C}_6\text{F}_5)_4$] (Table S1, Run 4).

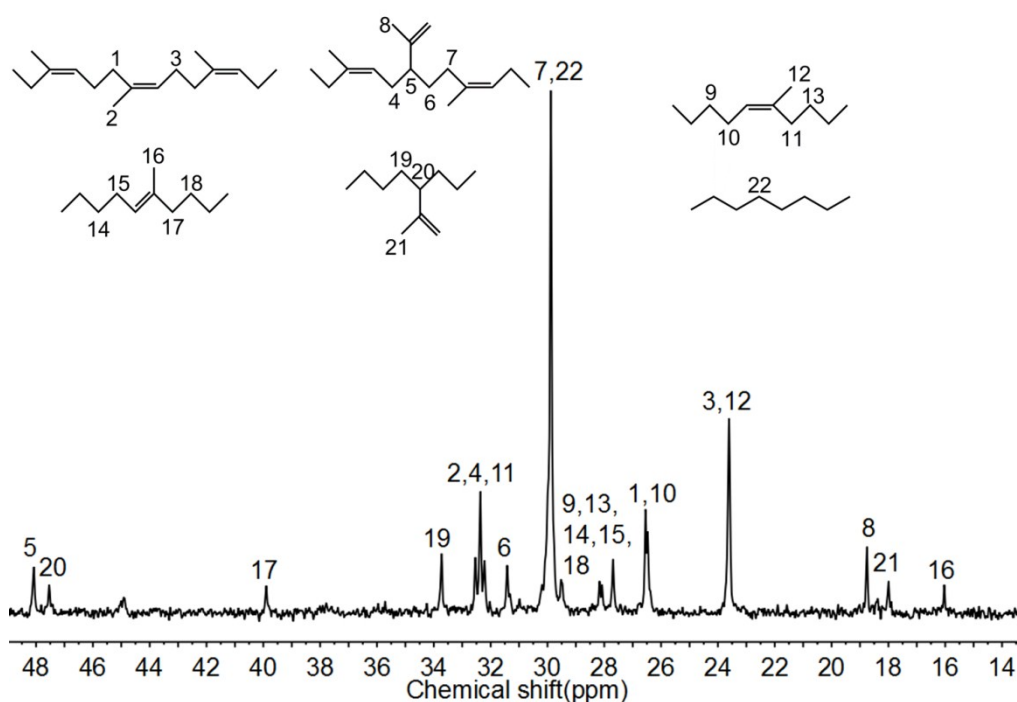


Fig. S7 ^{13}C -NMR spectrum (100 MHz, CDCl_3 , 25 $^\circ\text{C}$) of the ethylene-isoprene copolymer prepared by the complex **2**/[Ph_3C][$\text{B}(\text{C}_6\text{F}_5)_4$] (Ip content = 41 mol%) (Table S1, Run 14).

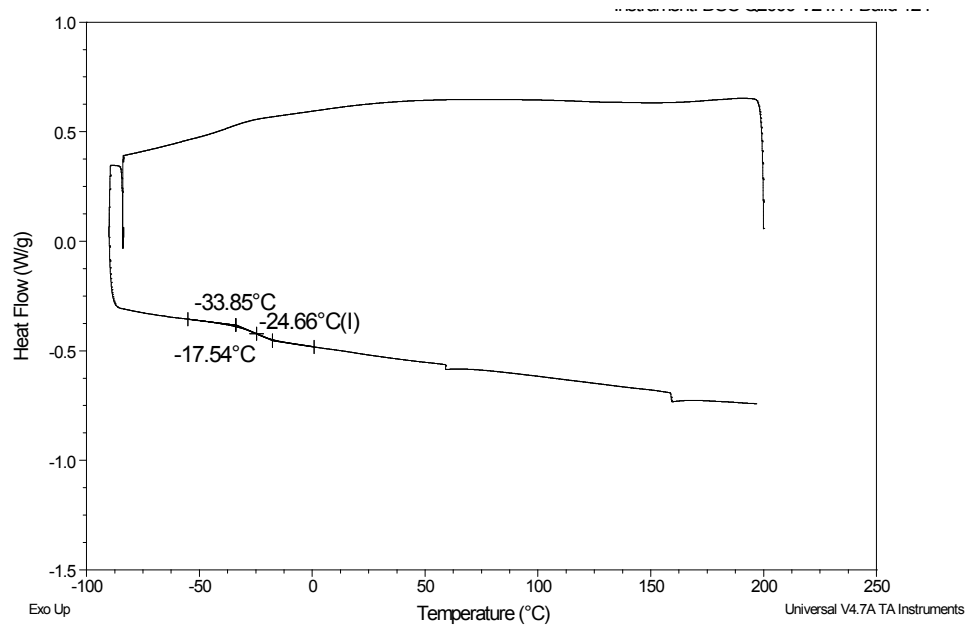


Fig. S8 DSC curve of the propylene-isoprene copolymer prepared by the complex **1**/[Ph₃C][B(C₆F₅)₄] (Ip content = 34 mol%) (Table S1, Run 5).

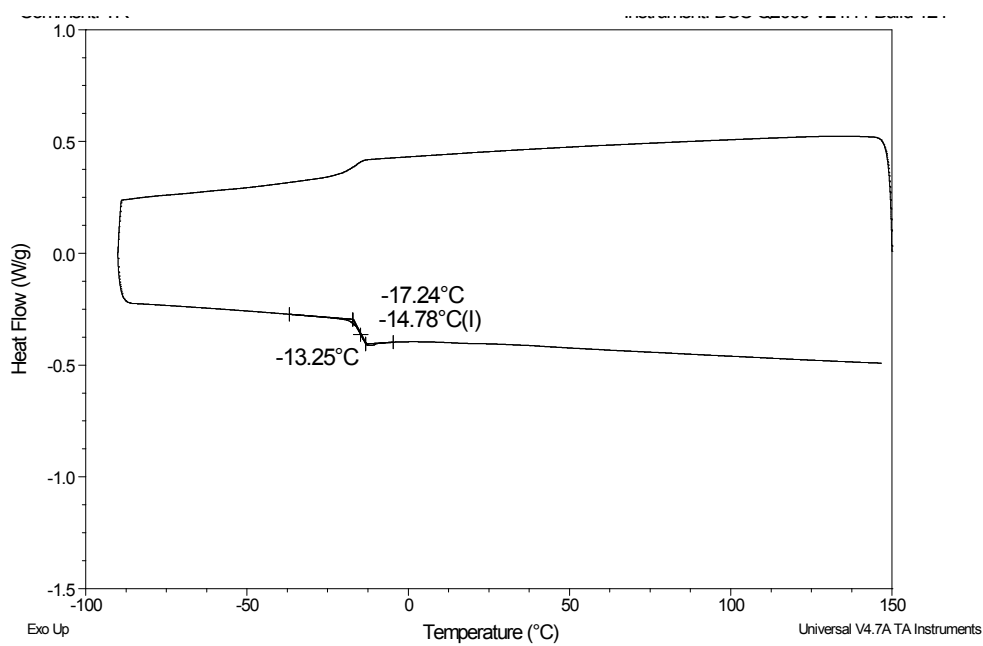


Fig. S9 DSC curve of the propylene-isoprene copolymer prepared by the complex **2**/[Ph₃C][B(C₆F₅)₄] (Isoprene content = 23 mol%) (Table S1, Run 6).

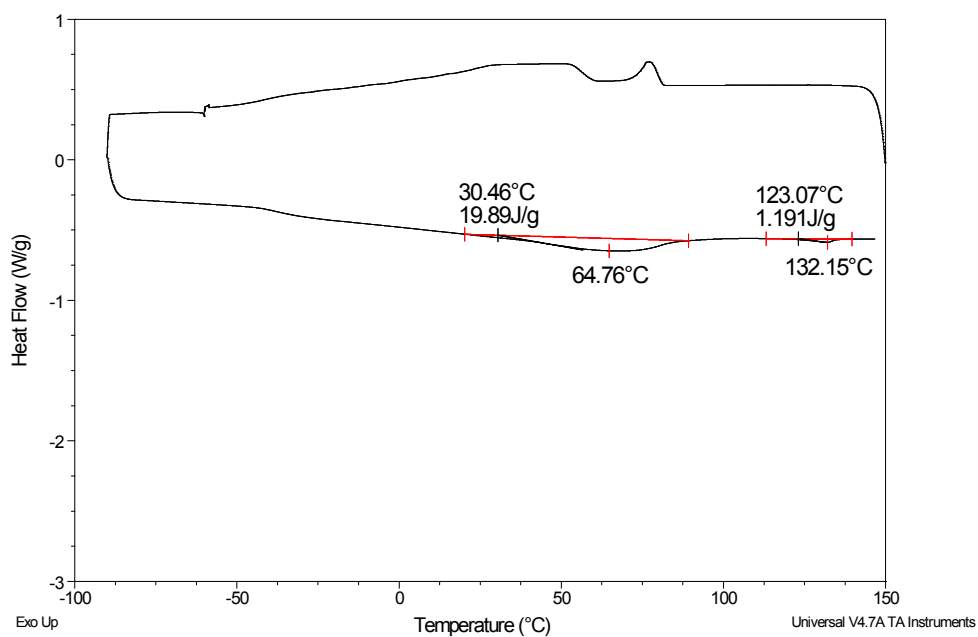


Fig. S10 DSC curve of the ethylene-isoprene copolymer prepared by the complex **1**/[Ph₃C][B(C₆F₅)₄] (Ip content = 16 mol%) (Table S1, Run 11).

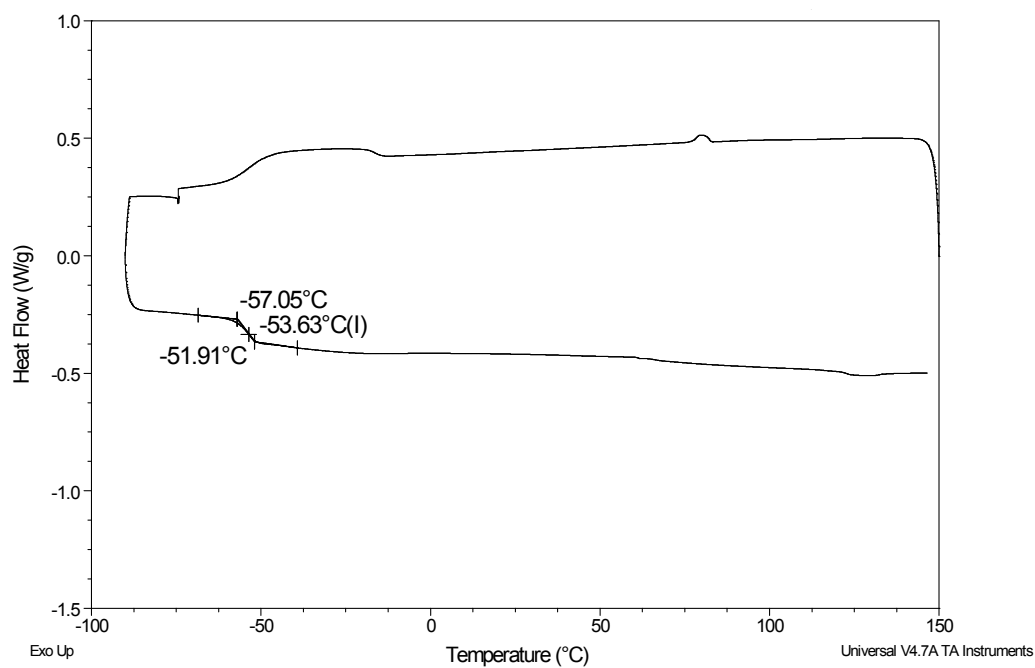


Fig. S11 DSC curve of the ethylene-isoprene copolymer prepared by the complex **1**/[Ph₃C][B(C₆F₅)₄] (Ip content = 26 mol%) (Table S1, Run 12).

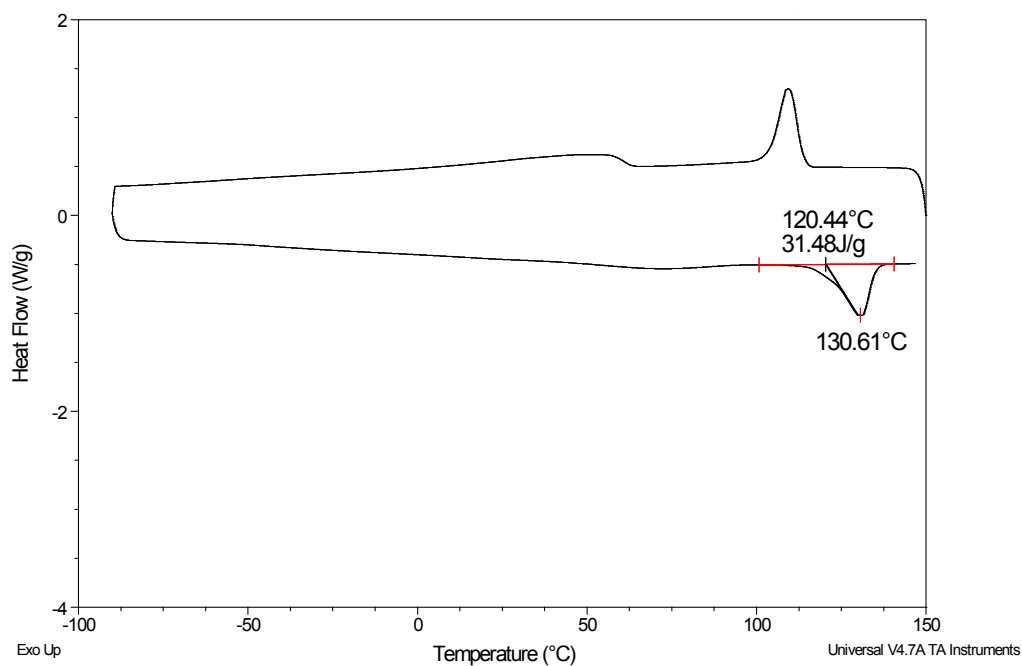


Fig. S12 DSC curve of the ethylene-isoprene copolymer prepared by the complex **2**/[Ph₃C][B(C₆F₅)₄] (Ip content = 30 mol%) (Table 1, Run 13).

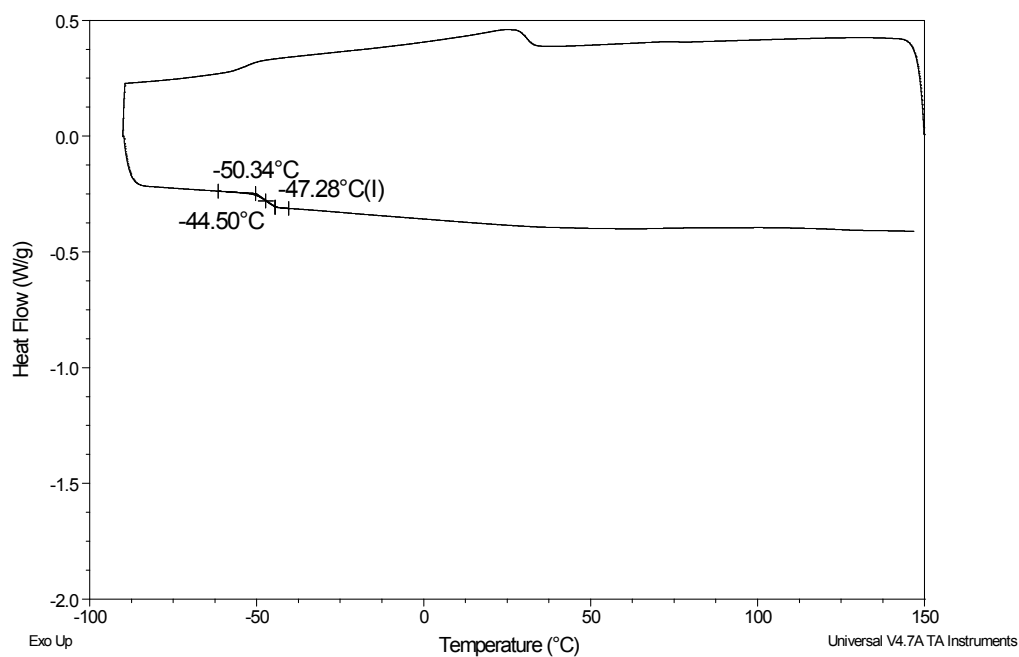


Fig. S13 DSC curve of the ethylene-isoprene copolymer prepared by the complex **2**/[Ph₃C][B(C₆F₅)₄] (Ip content = 41 mol%) (Table S1, Run 14).

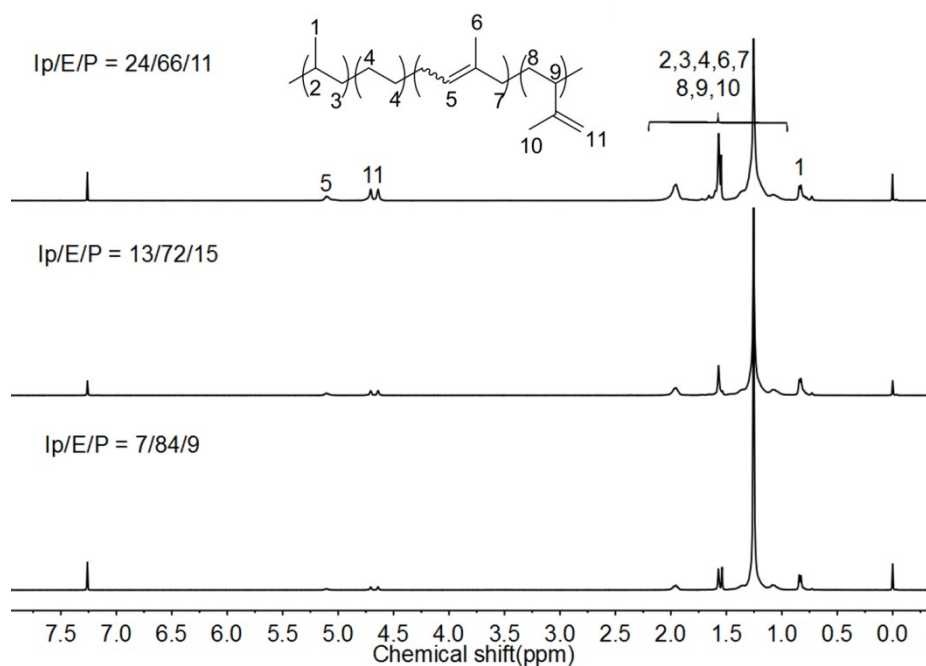


Fig. S14 ^1H -NMR spectra (400 MHz, CDCl_3 , 25 $^\circ\text{C}$) of the ethylene-propylene-isoprene terpolymer prepared by the complex **1**/[Ph_3C][$\text{B}(\text{C}_6\text{F}_5)_4$] (Table 1, Runs 1, 3 and 4).

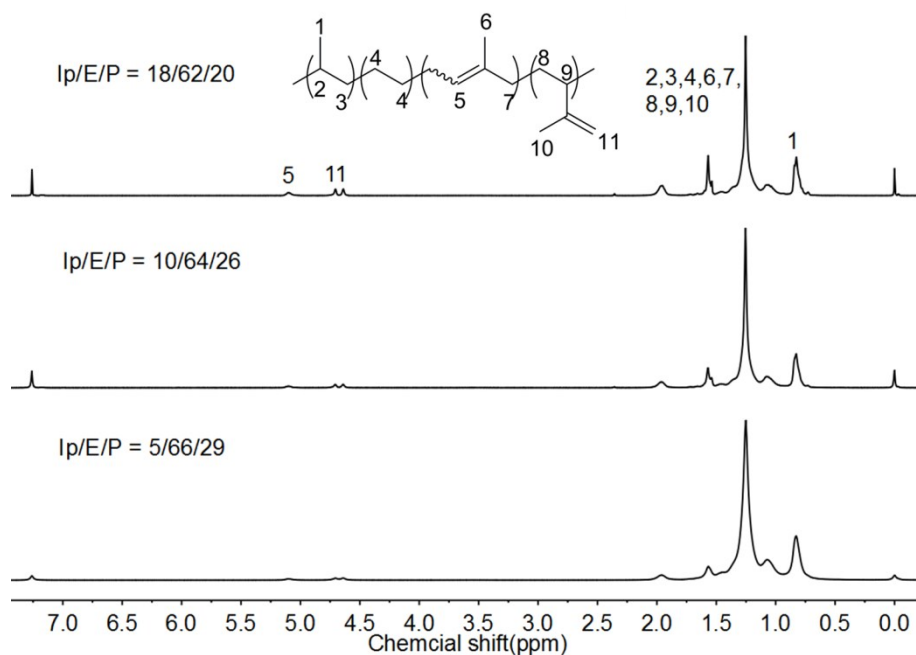


Fig. S15 ^1H -NMR spectra (400 MHz, CDCl_3 , 25 $^\circ\text{C}$) of the ethylene-propylene-isoprene terpolymer prepared by the complex **1**/[Ph_3C][$\text{B}(\text{C}_6\text{F}_5)_4$] (Table 1, Runs 7–9).

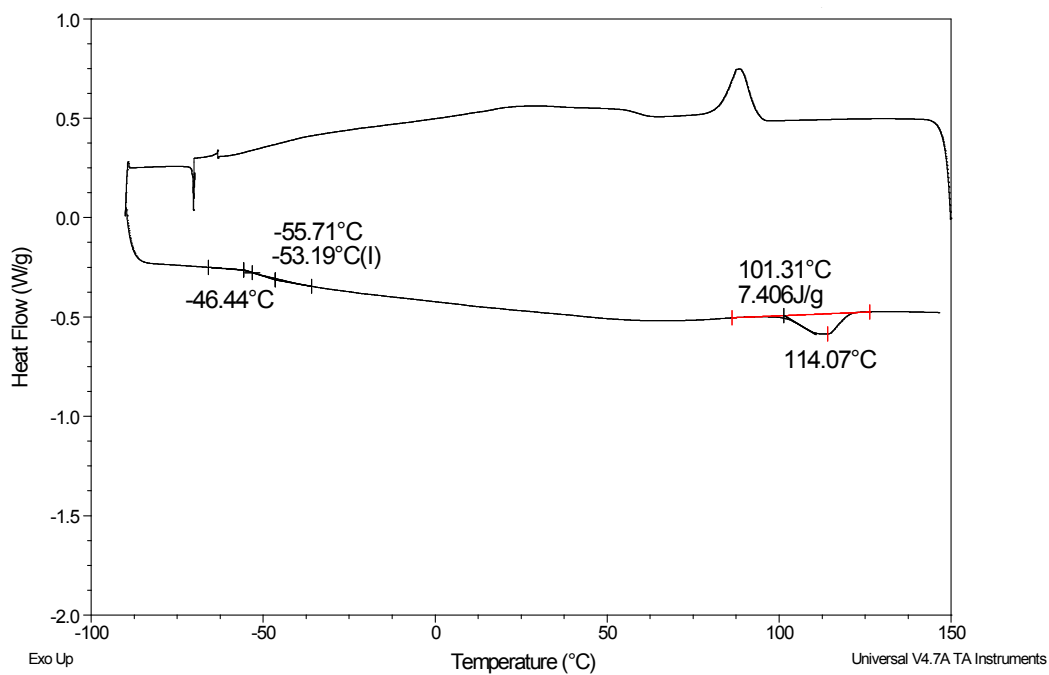


Fig. S16 DSC curve of the ethylene-propylene-isoprene terpolymer prepared by the complex **1**/[Ph₃C][B(C₆F₅)₄] (Ip content = 16 mol%, E content = 77 mol%) (Table 1, Run 2).

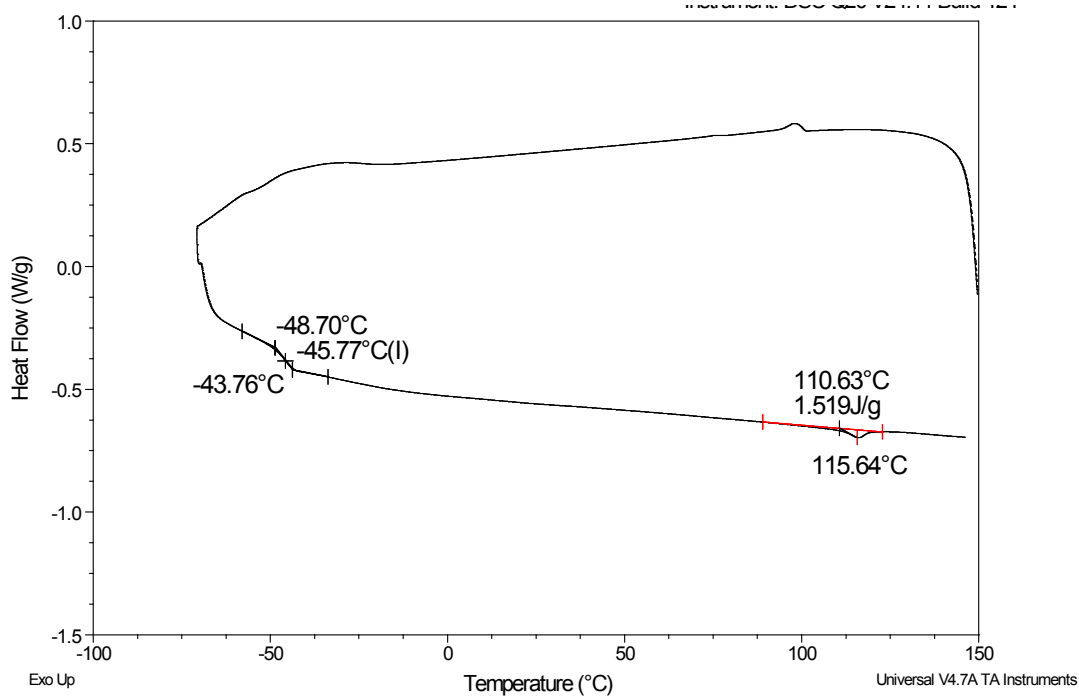


Fig. S17 DSC curve of the ethylene-propylene-isoprene terpolymer prepared by the complex **1**/[Ph₃C][B(C₆F₅)₄] (Ip content = 13 mol%, E content = 72 mol%) (Table 1, Run 3).

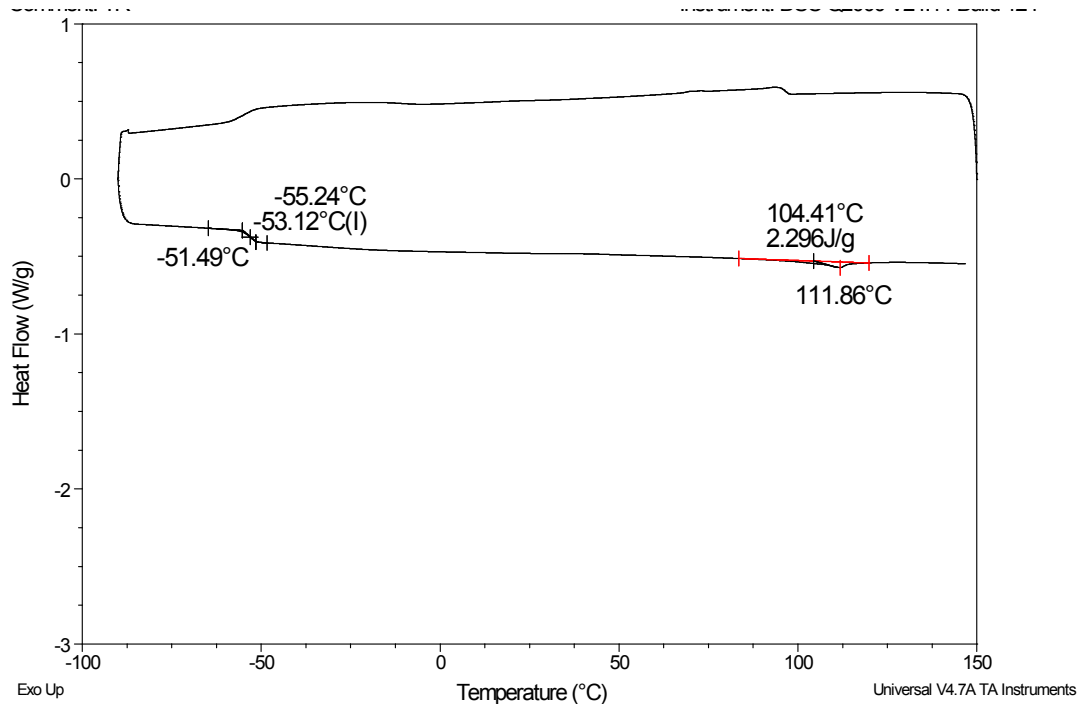


Fig. S18 DSC curve of the ethylene-propylene-isoprene terpolymer prepared by the complex **1**/[Ph₃C][B(C₆F₅)₄] (Ip content = 5 mol%, E content = 66 mol%) (Table 1, Run 7).

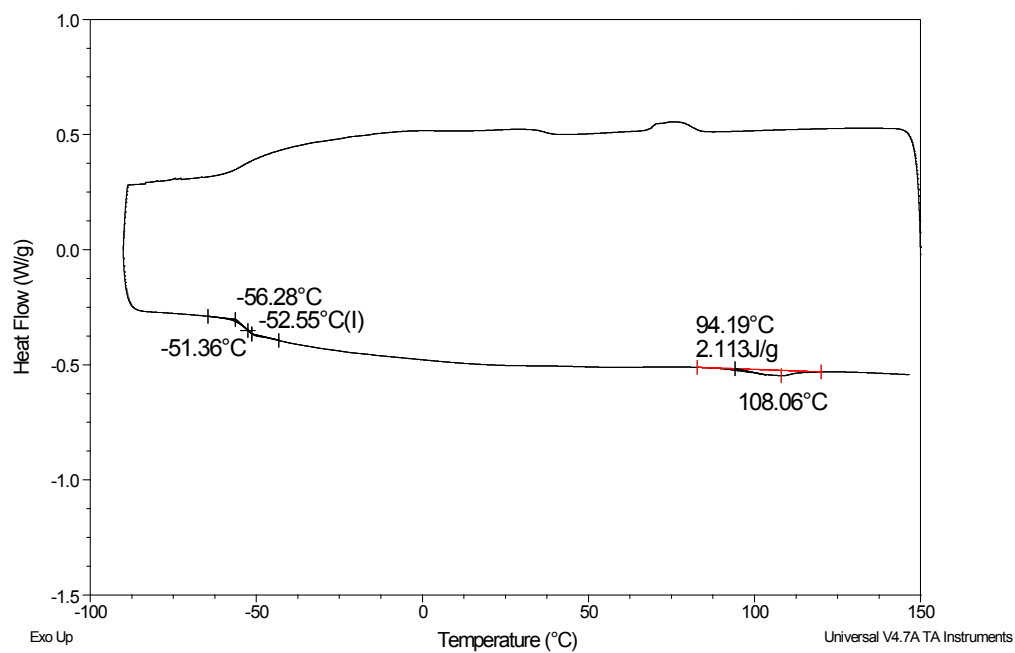


Fig. S19 DSC curve of the ethylene-propylene-isoprene terpolymer prepared by the complex **1**/[Ph₃C][B(C₆F₅)₄] (Ip content = 10 mol%, E content = 64 mol%) (Table 1, Run 8).

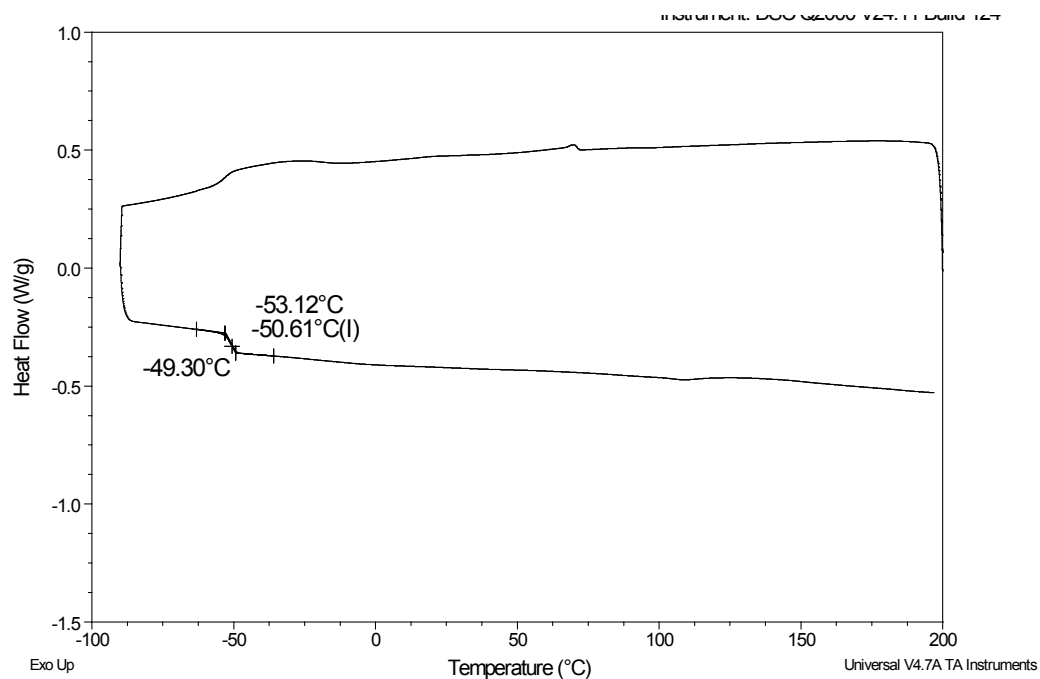


Fig. S20 DSC curve of the ethylene-propylene-isoprene terpolymer prepared by the complex **1**/[Ph₃C][B(C₆F₅)₄] (Ip content = 18 mol%, E content = 62 mol%) (Table 1, Run 9).

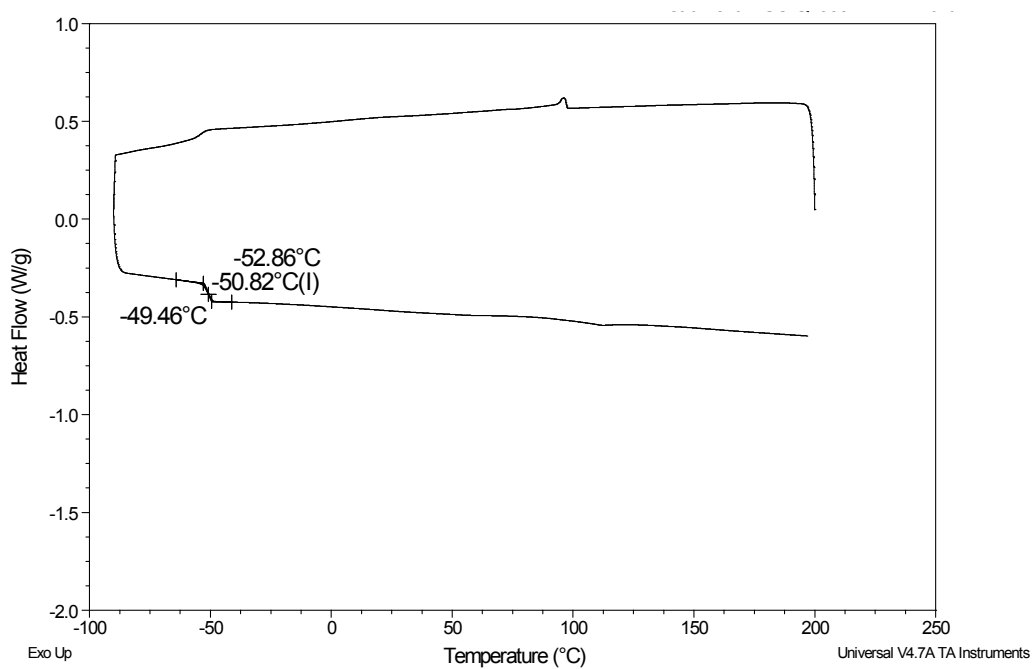


Fig. S21 DSC curve of the ethylene-propylene-isoprene terpolymer prepared by the complex **1**/[Ph₃C][B(C₆F₅)₄] (Ip content = 26 mol%, E content = 60 mol%) (Table 1, Run 10).

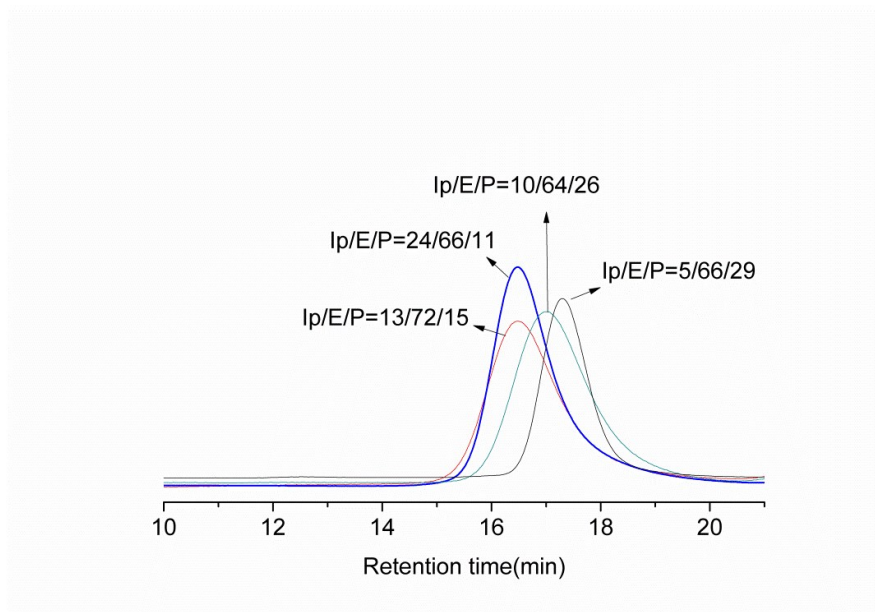


Fig. S22 GPC curves of the ethylene-propylene-isoprene terpolymer prepared by the complex **1**/[Ph₃C][B(C₆F₅)₄] (Table 1, Runs 3, 4, 7 and 8).

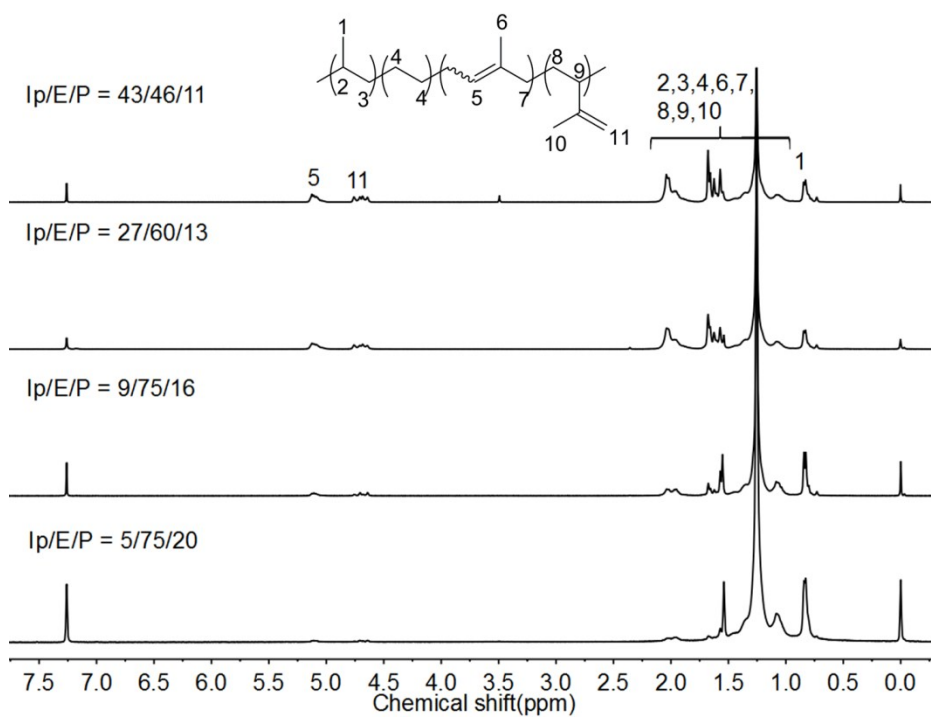


Fig. S23 ¹H-NMR spectra (400 MHz, CDCl₃, 25 °C) of the ethylene-propylene-isoprene terpolymer prepared by the complex **2**/[Ph₃C][B(C₆F₅)₄] (Table 2, Runs 1–4).

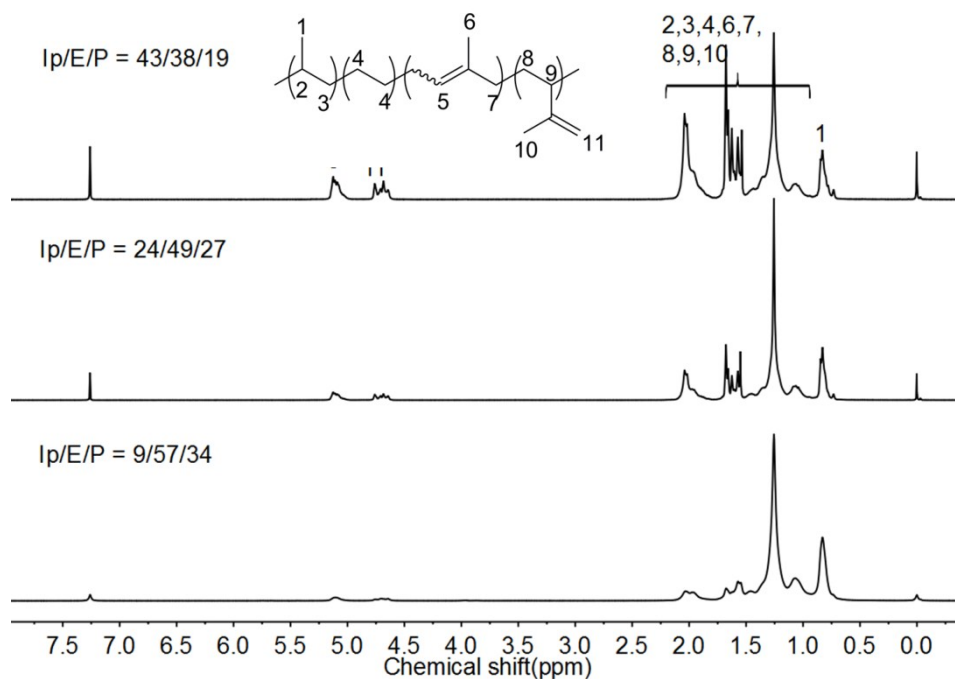


Fig. S24 ^1H -NMR spectra (400 MHz, CDCl_3 , 25 $^\circ\text{C}$) of the ethylene-propylene-isoprene terpolymer prepared by the complex **2**/[Ph_3C][$\text{B}(\text{C}_6\text{F}_5)_4$] (Table 2, Runs 6–8).

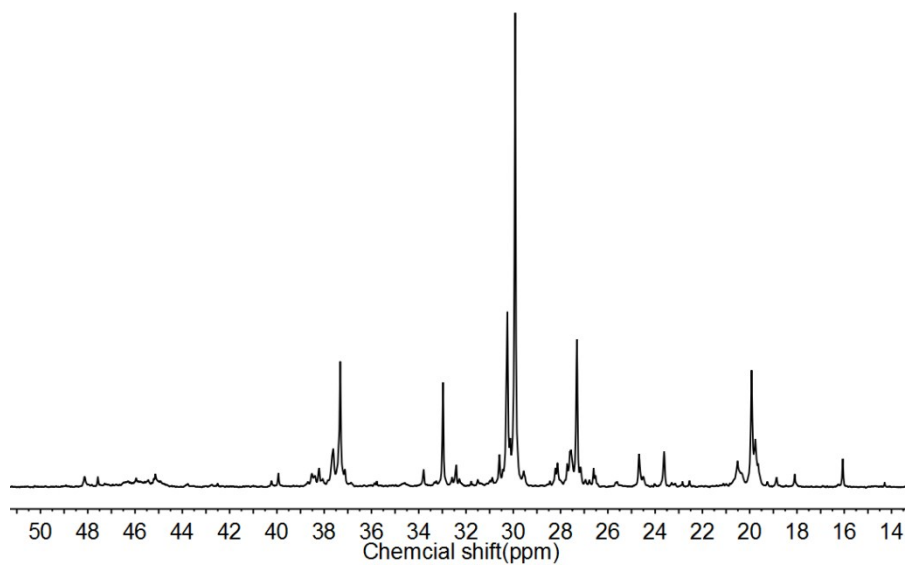


Fig. S25 ^{13}C -NMR spectrum (100 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 25 $^\circ\text{C}$) of ethylene-*ter*-propylene-*ter*-isoprene terpolymers prepared by the complex **2**/[Ph_3C][$\text{B}(\text{C}_6\text{F}_5)_4$] (Ip content = 9 mol%, E content = 57 mol%) (Table 2, Run 6).

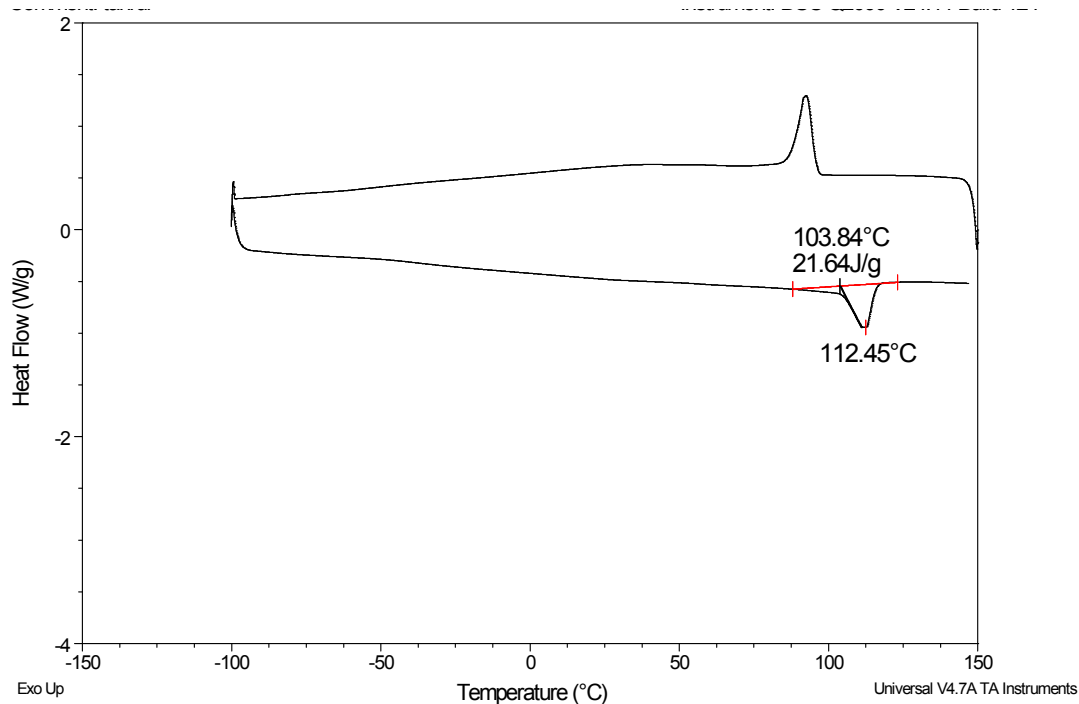


Fig. S26 DSC curve of the ethylene-propylene-isoprene terpolymer prepared by the complex **2**/[Ph₃C][B(C₆F₅)₄] (Ip content = 5 mol%, E content = 75 mol%) (Table 2, Run 1).

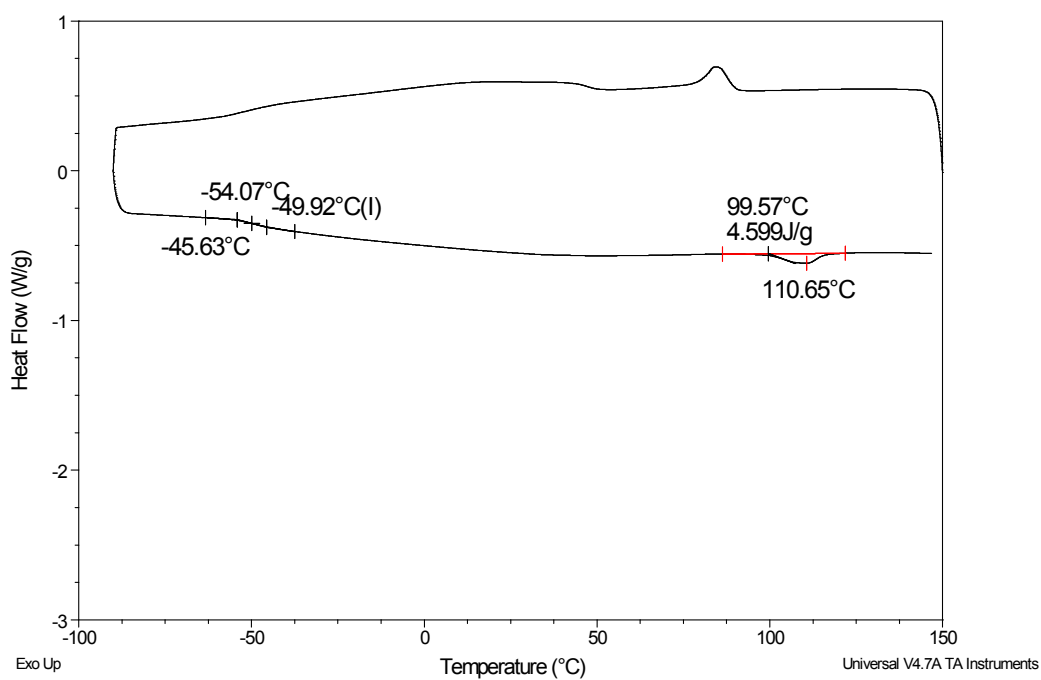


Fig. S27 DSC curve of the ethylene-propylene-isoprene terpolymer prepared by the complex **2**/[Ph₃C][B(C₆F₅)₄] (Ip content = 9 mol%, E content = 75 mol%) (Table 2, Run 2).

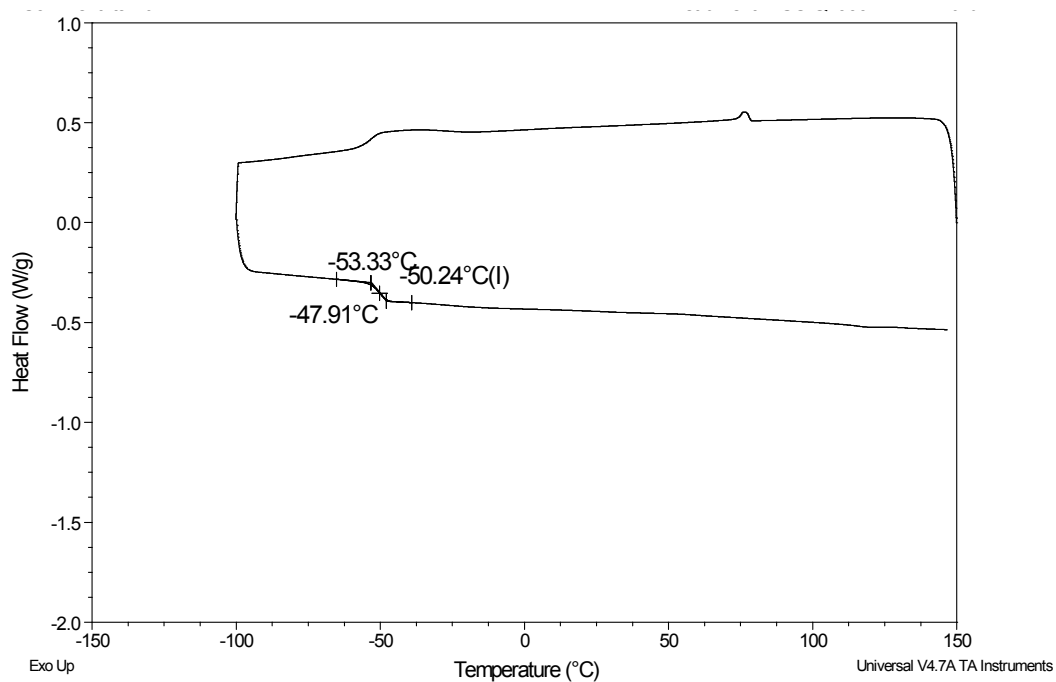


Fig. S28 DSC curve of the ethylene-propylene-isoprene terpolymer prepared by the complex **2**/[Ph₃C][B(C₆F₅)₄] (Ip content = 27 mol%, E content = 60 mol%) (Table 2, Run 3).

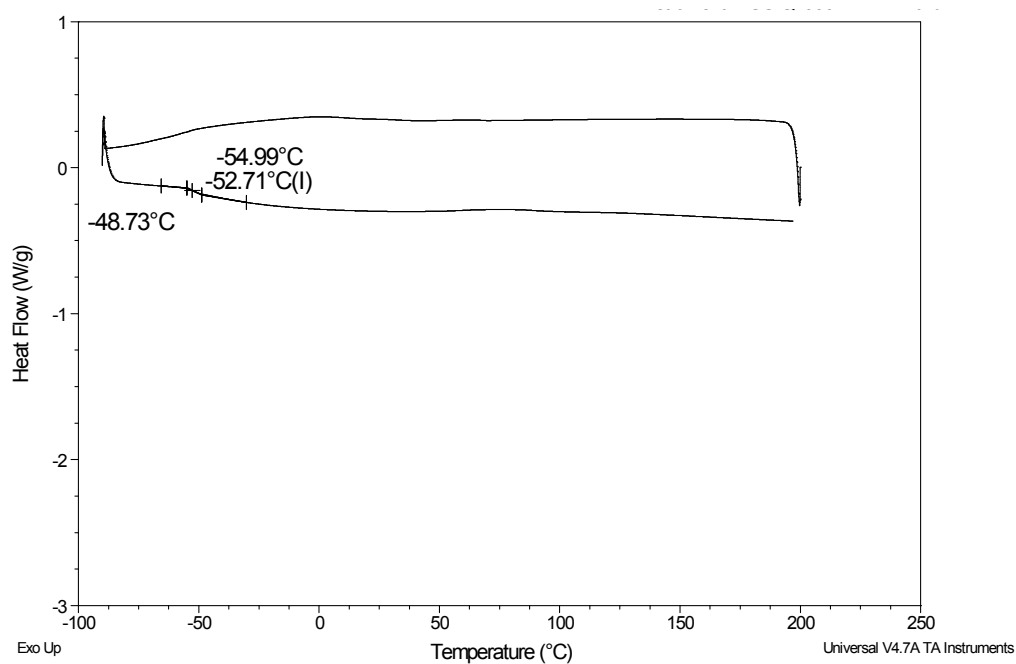


Fig. S29 DSC curve of the ethylene-propylene-isoprene terpolymer prepared by the complex **2**/[Ph₃C][B(C₆F₅)₄] (Ip content = 9 mol%, E content = 57 mol%) (Table 2, Run 6).

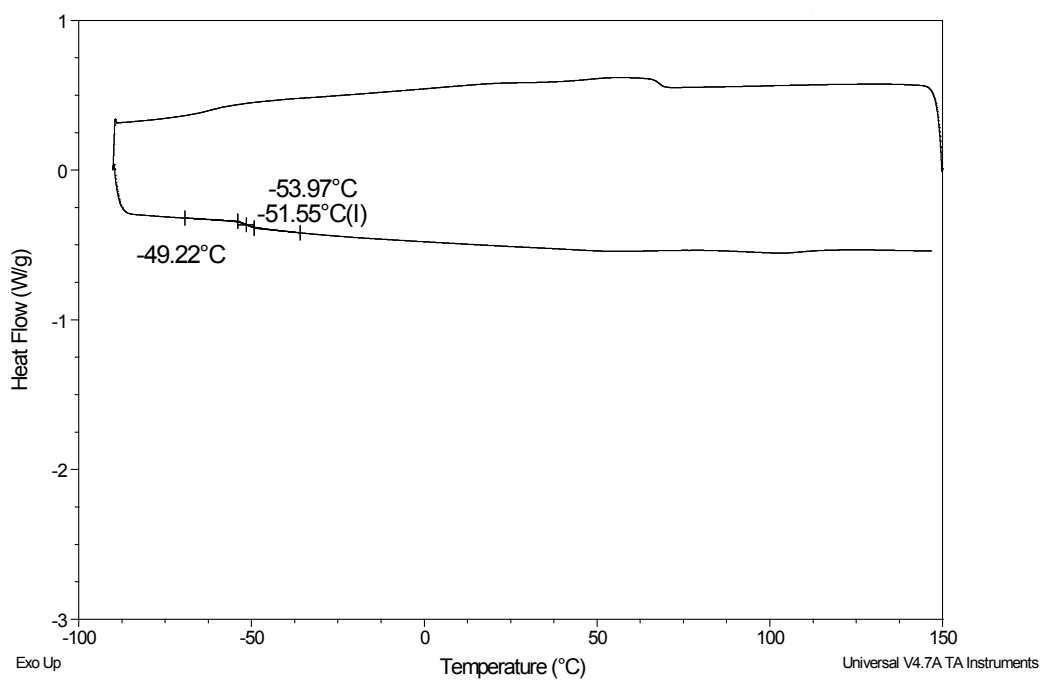


Fig. S30 DSC curve of the ethylene-propylene-isoprene terpolymer prepared by the complex **2**/[Ph₃C][B(C₆F₅)₄] (Ip content = 24 mol%, E content = 49 mol%) (Table 2, Run 7).

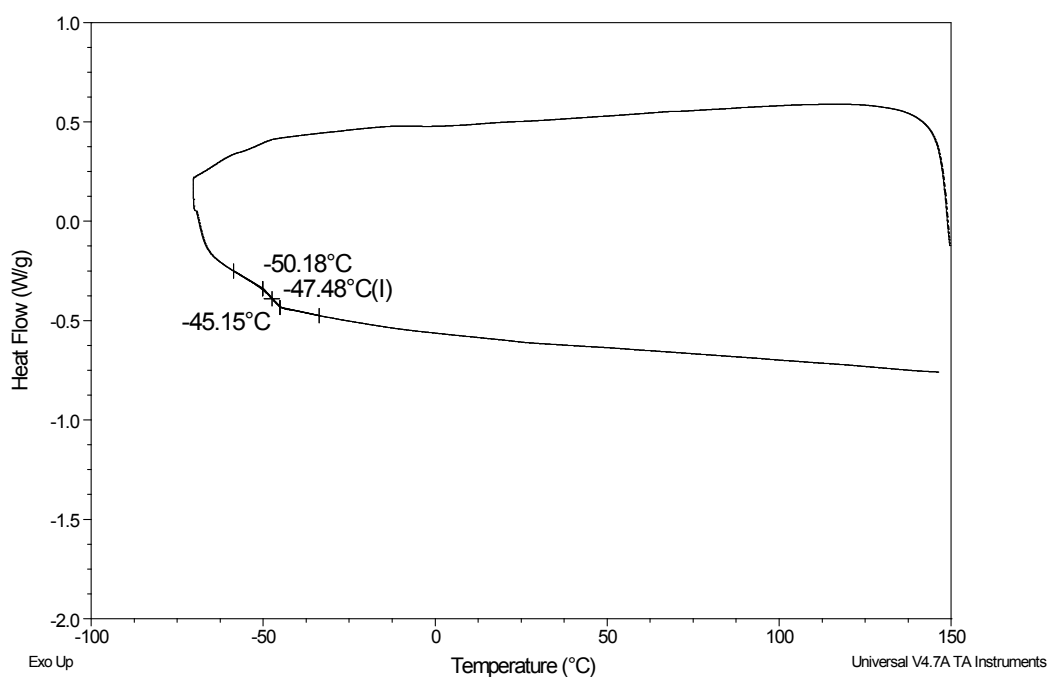


Fig. S31 DSC curve of the ethylene-propylene-isoprene terpolymer prepared by the complex **2**/[Ph₃C][B(C₆F₅)₄] (Ip content = 43 mol%, E content = 38 mol%) (Table 2, Run 8).

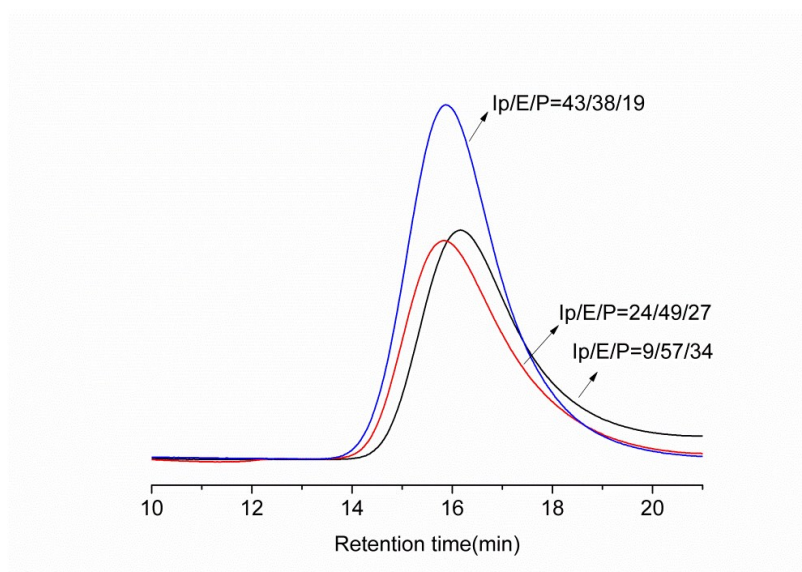


Fig. S32 GPC curves of the ethylene-propylene-isoprene terpolymer prepared by the complex **2**/[Ph₃C][B(C₆F₅)₄] (Table 2, Runs 6–8).

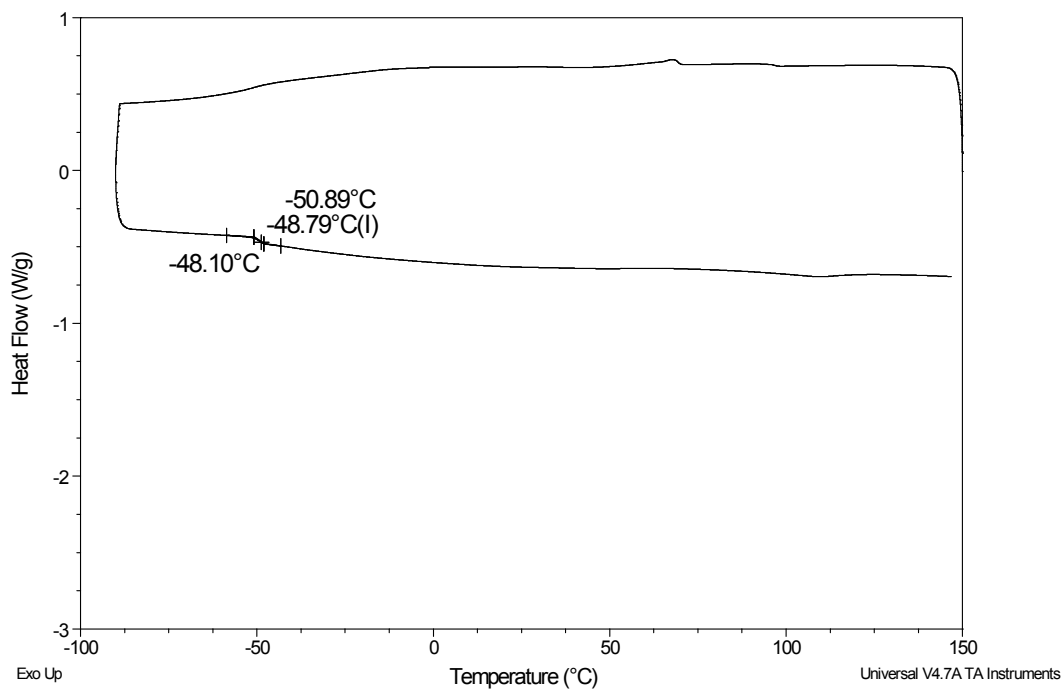


Fig. S33 DSC curve of the epoxidized ethylene-propylene-isoprene terpolymer.

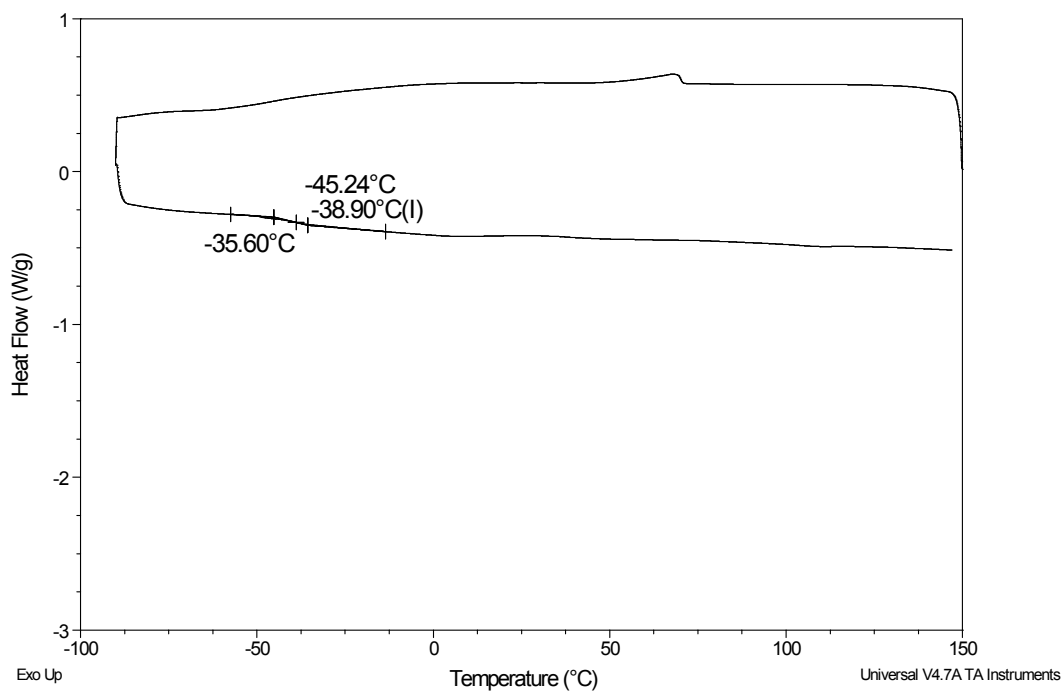


Fig. S34 DSC curve of the hydroxylated-chlorinated ethylene-propylene-isoprene terpolymer.

References

- 1 R. Tan, F. Guo and Y. Li, *Polym. Chem.*, 2017, **8**, 615–623.
- 2 L. Pan, K. Y. Zhang, M. Nishiura and Z. M. Hou, *Angew. Chem. Int. Ed.*, 2011, **50**, 12012–12015.