Syndiospecific polymerization of styrene by half-titanocene catalysts with fluorinated phenoxy ligands in the presence of low MAO cocatalyst

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Characterization of catalysts

The ^{1}H NMR and ^{19}F NMR spectrum of $Cp^*Ti(OC_6F_5)_3$ are listed as follow.

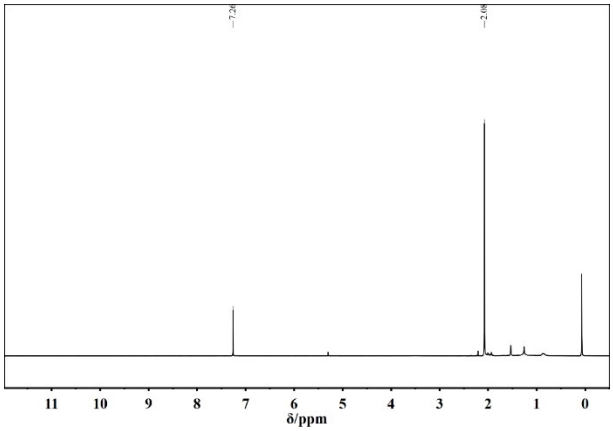

Figure S1 The ^{1}H NMR spectrum of $Cp^*Ti(OC_6F_5)_3$ (**c2**).

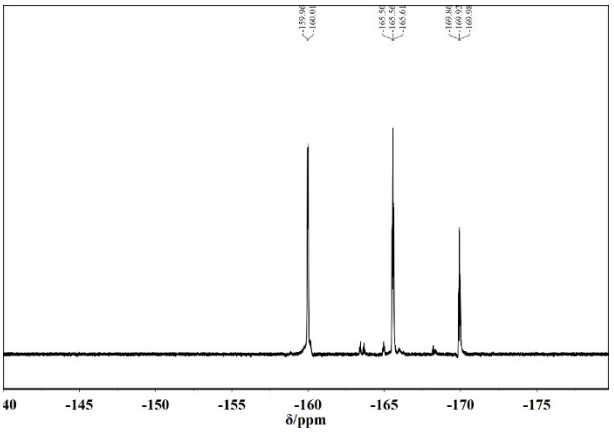

Figure S2 The ^{19}F NMR spectrum of $Cp^*Ti(OC_6F_5)_3$ (**c2**).

The ^{1}H NMR and ^{19}F NMR spectrum of Cp*Ti(O-2,6-$C_6H_3F_2$)$_3$ are listed as follow.

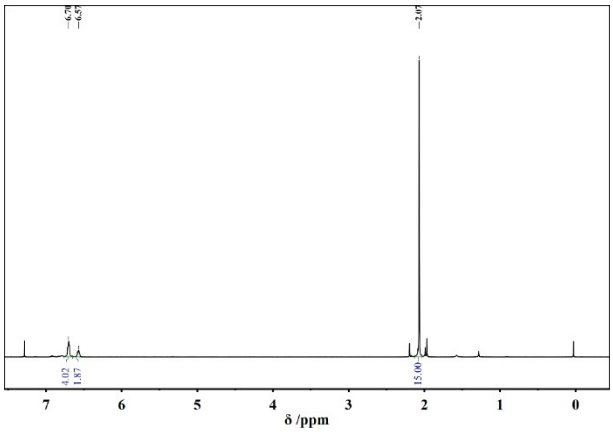

Figure S3 The ^{1}H NMR spectrum of Cp*Ti(O-2,6-$C_6H_3F_2$)$_3$ (**c1**).

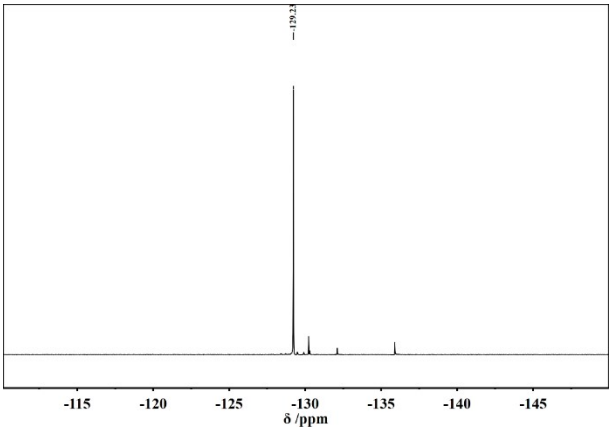

Figure S4 The ^{19}F NMR spectrum of Cp*Ti(O-2,6-$C_6H_3F_2$)$_3$ (**c1**).

Characterization of sPS

Table S1 Styrene polymerization with half-titanocene **c1** depended on additional toluene[a]

Run	Cat	T (°C)	t (h)	Al_{MAO} /Ti	Al_{TIBA} /Ti	Polymer[b] (g)	Syndiotactic Index[b] (%)	Activity[c]	M_w[d] (10^5 g/mol)	PDI[d]	T_m[e] (°C)
26	**c1**	80	3	100	500	8.21	96	456	1.80	1.98	271
27	**c1**	80	3	100	500	6.05	95	336	2.40	1.71	270
28	**c1**	80	3	100	500	4.07	95	226	1.88	1.85	270

[a]Polymerization conditions: catalyst, 6.0 μmol in 2.0 mL DCM; styrene, 20 mL, additional toluene; run 26, 5 mL; run 27, 10 mL; run 28, 20 mL

[b]Estimated by the extraction experiment

[c]Activity in kg-sPS·mol-cat^{-1}·hr^{-1}

[d]GPC data

[e]DSC data

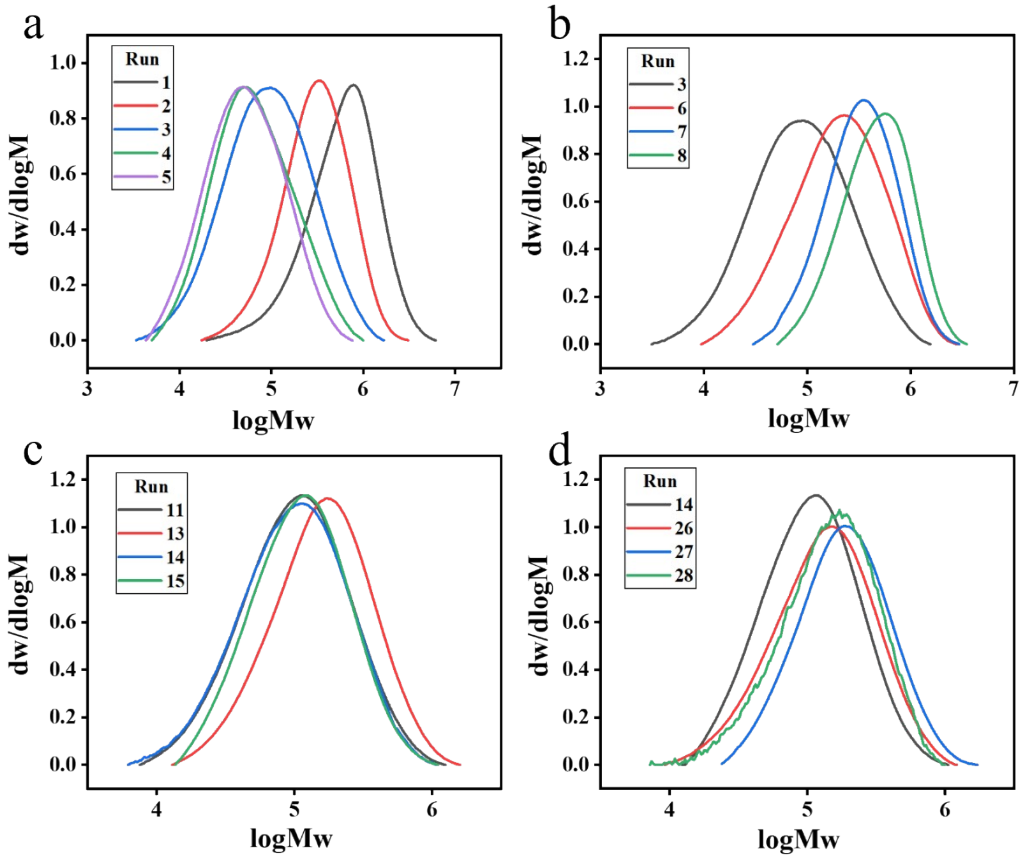

Figure S5 Molecular wight dependence on (a) polymerization temperature (b) the Al/Ti ratio of MAO (c) the Al/Ti ratio of TIBA (d) additional toluene

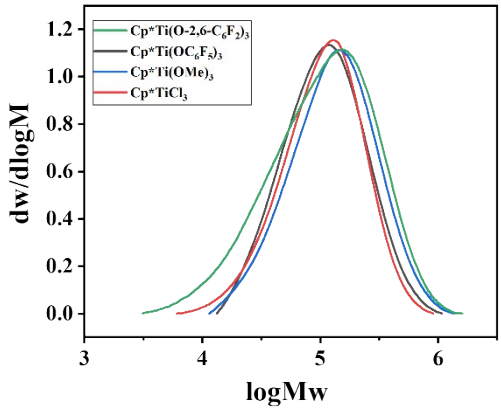

Figure S6 The GPC curves of sPS synthesized by different catalysts from run14, 18, 21, 25.

The DSC curves of sPS synthesized by different catalysts are listed as follow.

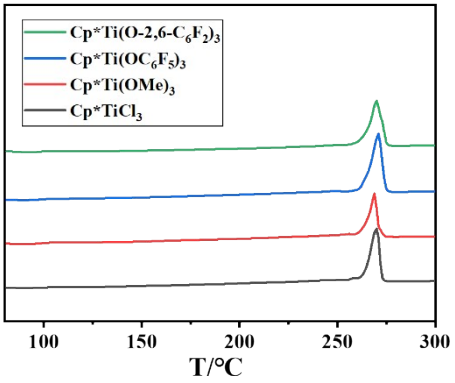

Figure S7 The DSC curves of sPS synthesized by different catalysts from run14, 18, 21, 25.