

Supplementary Materials for:

**Titanium complex with an [OSSO]-type bis(phenolate) ligand for ethylene
copolymerization with vinyl polar monomer**

Yuqiong Zhu¹, Sihan Li¹, Huaqing Liang¹, Xiuli Xie¹, Fangming Zhu^{1, 2}

¹GDHPPCLab, School of Chemistry, Sun Yat-Sen University, 510275, China

²Key Lab for Polymer Composite and Functional Materials of Ministry of Education,
School of Chemistry, Sun Yat-Sen University, Guangzhou, 510275, China

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Experimental Procedures

Synthesis of *p*-TBDMSOS. A 500 mL flask equipped with a magnetic stirrer was charged with 14.46 g (120 mmol) of *p*-hydroxybenzaldehyde and 100 mL of CH₂Cl₂. Then 16.8 mL (120 mmol) of trimethylamine was introduced into the suspension solution and stirred until it become clear. Then 100 mL solution of CH₂Cl₂ containing 18.04 g (120 mmol) *tert*-butyldimethylsilyl was added dropwise into the solution and stirred 2 h at room temperature. The reactant was quenched by adding 100 mL water. The organic phase was separated and washed three times by pure water and brine respectively, dried by anhydrous MgSO₄, filtered and concentrated to yield yellow oily production, which was regard as *p-tert*-butyldimethylsilyxybenzaldehyde. Yield 26.8 g (95%).¹

THF (50 mL) was added to dissolve methyltriphenylphosphonium bromide (10.18 g, 28.5 mmol) in a 250 mL flask equipped with a magnetic stirrer. *n*-BuLi (2.5 M solution in hexane, 11.2 mL) in 50 mL THF was introduced dropwise via syringe into the solution above under ice bathe and the mixture was stirred 10 min. A solution of *p-tert*-butyldimethylsilyxybenzaldehyde (7.09 g, 30 mmol) in 50 mL THF was added dropwise with a dropping funnel and then stirred for 4 h after heating up to the room temperature. After the reaction, the reactant was quenched with NH₄Cl (1.6 g) and filtered to obtain the solution. Then it was purified by concentrating and column chromatography with hexane as the eluent. The final production was a colorless oil with high yield of 5.63 g (90 %).

Spectra Data

¹H NMR and ¹³C NMR

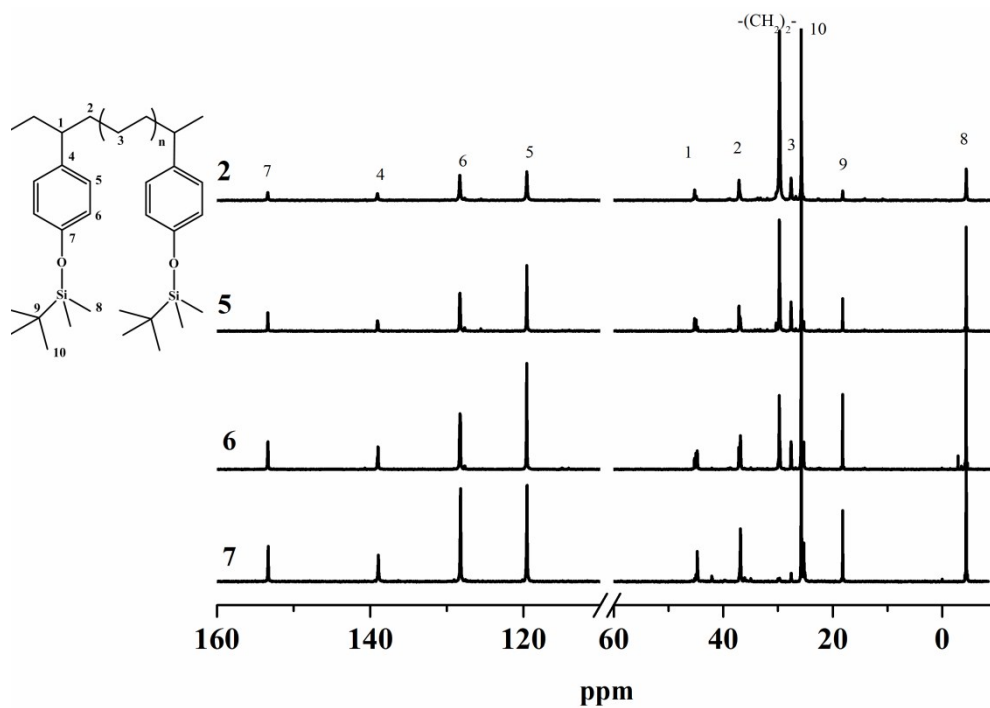


Fig. 1. The ^{13}C NMR spectra of poly(E-co-(*p*-TBDMSOS)) obtained from Runs 2, 5, 6 and 7 in

Table 1.

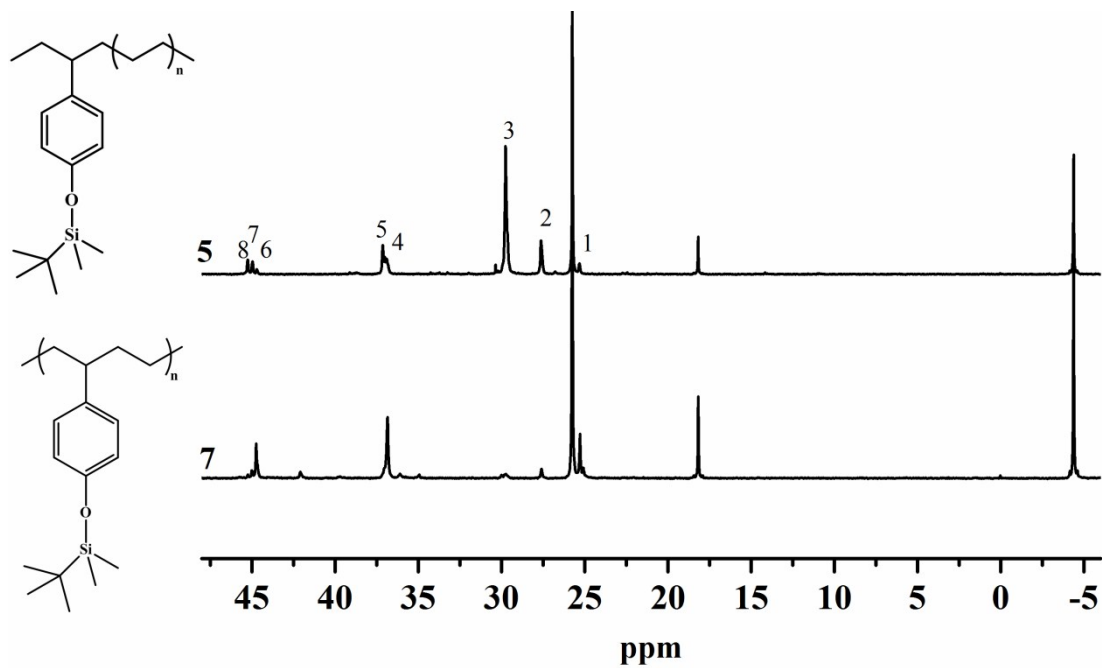


Fig. 2. Aliphatic regions of ^{13}C NMR spectra of poly(E-co-(*p*-TBDMSOS))

Table 1. The ^{13}C NMR chemical shift of poly(E-co-(*p*-TBDMSOS)) in Fig. 2

Carbon	Chemical Shift (ppm)	Sequence
1($\text{S}_{\beta\beta}$)	25.3	SES
2($\text{S}_{\beta\delta}$)	27.6	SEES, SEE
3($\text{S}_{\gamma\gamma}$, $\text{S}_{\delta\delta}$, $\text{S}_{\gamma\delta}$)	29.7	SEES, EEE, SEE
4($\text{S}_{\alpha\gamma}$)	36.9	SES
5($\text{S}_{\alpha\delta}$)	37.1	SEES
6($\text{T}_{\delta\delta}$)	44.7	SES
7($\text{T}_{\delta\delta}$)	45.0	SEES
8($\text{T}_{\delta\delta}$)	45.2	SEE

DSC and GPC data

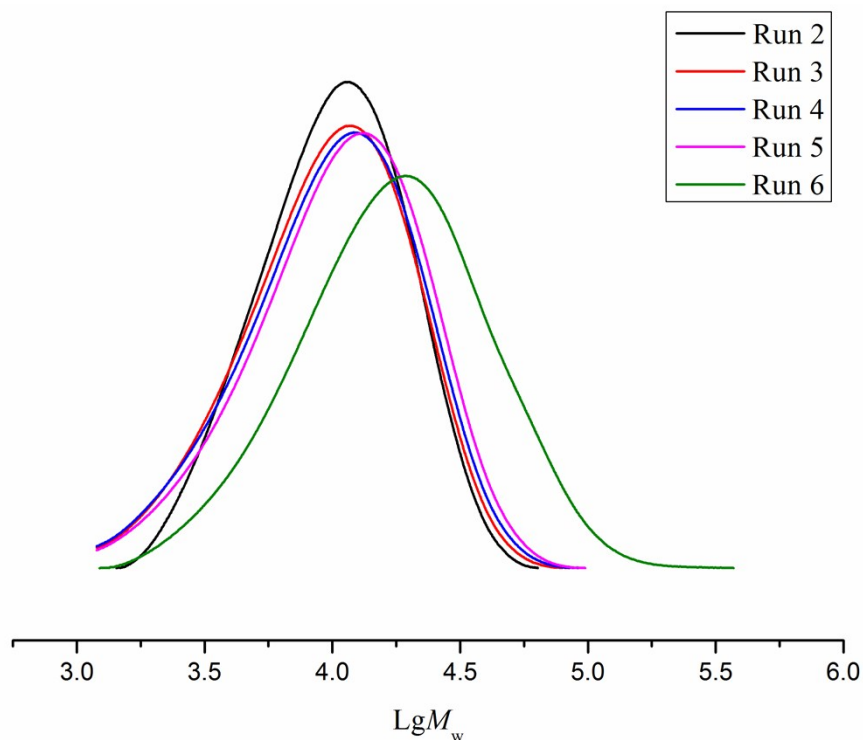


Fig. 3. GPC curves for copolymerization of E/*p*-TBDMSOS of Runs 2, 3, 4, 5 and 6.

3. References

- (1) Kim, Y.; Do, Y. Preparation of Syndiotactic Poly(4-*tert*-butyldimethylsilyloxystyrene) and

Poly(4-hydroxystyrene). *Macromol. Rapid Commun.* **2000**, 21, 1148–1155.