

Support information

Syndioselective Coordination Polymerization of the Unmasking Polar
Methoxystyrenes Using Pyridenylmethylene Fluorenyl Yttrium Precursor

Dongtao Liu,^{a,#} Rong Wang,^{b,#} Meiyang Wang,^c Chunji Wu,^a Zichuan Wang,^a Changguang Yao,^a Bo Liu,^a Xinhua Wan,^{*b} Dongmei Cui^{*a}

^a State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China.

^b Beijing National Laboratory for Molecular Sciences, Key Laboratory of Polymer Chemistry and Physics of Ministry of Education, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

^c Institute of Theoretical Chemistry, State Key Laboratory of Theoretical and Computational Chemistry, Jilin University, Changchun 130022, People's Republic of China.

The first two authors contributed equally to this paper.

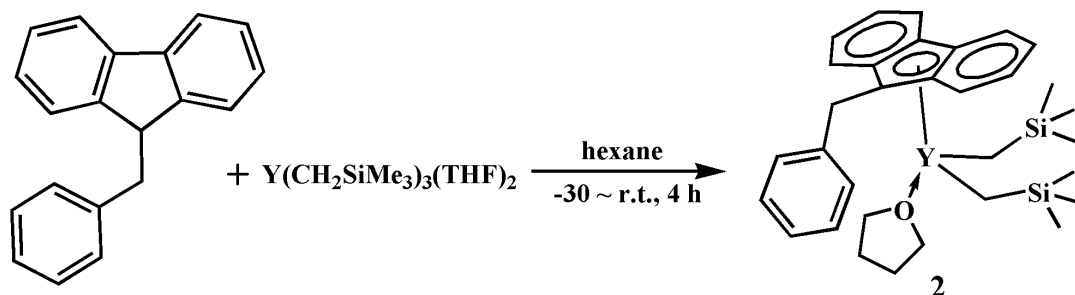
Corresponding to E-mail: dmcui@ciac.ac.cn and xhwan@pku.edu.cn

Experimental Section

General Considerations. All manipulations were performed under a dry and oxygen-free argon atmosphere using standard high vacuum Schlenk techniques or in a glove box. All solvents were purified via a solvent purification system. The *ortho*-methoxystyrene (*o*MOS), *meta*-methoxystyrene (*m*MOS), *para*-methoxystyrene (*p*MOS), and styrene (St) were purchased from Aldrich and dried over CaH₂ under stirring for 48 hours and distilled before use. Aluminum alkyls were purchased from Aldrich and used without further purification. The pyridyl methylene fluorenyl yttrium complex **1**¹ and phenyl methylene fluorenyl ligand² were prepared according to the reported methods. Organometallic samples for NMR spectroscopic measurements were prepared in the glove box by use of NMR tubes sealed by paraffin film. ¹H, ¹³C NMR spectra were recorded on a Bruker AV400 (FT, 400 MHz for ¹H; 100 MHz for ¹³C) or AV500 (FT, 500 MHz for ¹H; 125 MHz for ¹³C). NMR assignments were confirmed by ¹H-¹³C HMQC experiments when necessary. The molecular weight (*M_n*) and molecular weight distribution of the polymers were measured by means of gel permeation chromatography (GPC) on a PL-GPC 220 type high-temperature chromatography equipped with three PL-gel 10 μm Mixed-B LS type columns at 150 °C. Differential scanning calorimetry (DSC) analyses were carried out on a DSC 1 from METTLER-TOLEDO Instruments under a nitrogen atmosphere at a heating rate of 10 °C/min. The thermal history difference in the polymers was eliminated by first heating the specimen to 300 °C, cooling at 10 °C/min to 25 °C, and then recording the second DSC scan.

Synthesis of Complex (Ph-CH₂-Flu)Y(CH₂SiMe₃)₂(THF) (2). Under a nitrogen atmosphere, to a hexane solution (5 mL) of Y(CH₂SiMe₃)₃(THF)₂ (0.495 g, 1.0 mmol), 1 equiv of Ph-CH₂-FluH (0.256 g, 1.0 mmol) was added slowly at -30 °C. The mixture was stirred for 4 h to afford a dark red solution. Evaporation of the solvent left **2** as yellow solids (Scheme S1)(0.21 g, 35%). ¹H NMR (500 MHz, C₆D₆, 25 °C): δ -1.00 (br, 4H, Y-CH₂SiMe₃), 0.21 (s, 18H, CH₂SiMe₃), 1.22 (br, 4H, THF), 3.52 (br, 4H, THF), 4.69 (s, 2H,

Flu-CH₂-Ph), 6.95–7.03 (m, 7H, Flu, Ph), 7.15 (2H, Flu), 7.63 (d, ³J_{H-H} = 8.5 Hz, 2H, Flu), 7.93 (d, ³J_{H-H} = 8.0 Hz, 2H, Flu). ¹³C NMR (125 MHz, C₆D₆, 25 °C): δ 4.74 (s, 6C, CH₂SiMe₃), 25.45 (br, 2C, THF), 39.09 (d, 2C, J_{Y-C} = 43.7 Hz, Y-CH₂SiMe₃), 70.48 (br, 2C, THF), 97.37 (s, 1C, Flu-CH₂-Ph), 118.50, 118.80, 120.14, 122.65, 125.88, 126.45, 128.90, 129.02, 132.68, 142.55 (19C, Flu, Ph).



Scheme S1. Synthesis of complex 2

Typical Procedure for Polymerization of *p*MOS. A detailed polymerization procedure is described as following (Table 1, run 2): Under a nitrogen atmosphere and room temperature, complex 1 (5.9 mg, 1.0×10⁻⁵ mol, 0.8 mL toluene) and 10 equiv. of Al^{*i*}Bu₃ (0.2 ml, 1.0×10⁻⁴ mol, 0.5 M in toluene) were added into a 10 mL flask. Then 1 equiv of [Ph₃C][B(C₆F₅)₄] (9.2 mg, 1.0×10⁻⁵ mol) was added under stirring to give a yellow solution after several minutes. Upon the addition of *p*MOS (0.20 g, 1.5 mmol), polymerization was initiated and carried out for 30 min. The reaction mixture was poured into a large quantity of methanol and then dried under vacuum at 50 °C to a constant weight (0.15 g, 75%).

Computational Details

The natural bond orbital (NBO) analysis³ was made using larger basis set 6-311G(d,p) for all the main group atoms.

Reference:

1. Pan, Y. P.; Rong, W. F.; Jian, Z. B.; Cui, D. M., *Macromolecules* **2012**, *45*, 1248.
2. Fleckenstein, C. A.; Plenio, H. *Chem. Eur. J.* **2007**, *13*, 2701.
3. Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. NBO Version 3.1.

Legends

Figure S1. ^1H NMR spectrum of syndiotactic P(*p*MOS) (CDCl_3 , 25°C)

Figure S2 ^1H - ^{13}C COSY spectrum of syndiotactic P(*p*MOS) (CDCl_3 , 25°C)

Figure S3. ^{13}C NMR spectrum of syndiotactic P(*p*MOS) (CDCl_3 , 25°C)

Figure S4. ^1H NMR spectrum of syndiotactic P(*m*MOS) (CDCl_3 , 25°C)

Figure S5 ^1H - ^{13}C COSY spectrum of syndiotactic P(*m*MOS) (CDCl_3 , 25°C)

Figure S6. ^{13}C NMR spectrum of syndiotactic P(*m*MOS) (CDCl_3 , 25°C)

Figure S7. ^{13}C NMR spectrum of syndiotactic P(*o*MOS) ($\text{C}_2\text{Cl}_4\text{D}_2$, 120°C)

Figure S8. The possible mechanisms for the syndioselective polymerizations of *o*MOS (a), *m*MOS (b) and *p*MOS (c) by complex **1**/ Al^iBu_3 / $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$.

Figure S9. NBO charge of the monomers. (a) St; (b) *o*MOS; (c) *m*MOS; (d) *p*MOS

Figure S10. Probable insertion mechanism of methoxystyrenes.

Table S1. Polymerization of methoxystyrenes by complex **2**.

Figure S11. GPC curve of syndiotactic P(*p*MOS) (Table 1, entry 2).

Figure S12. GPC curve of syndiotactic P(*m*MOS) (Table 1, entry 4).

Figure S13. GPC curve of syndiotactic P(*o*MOS) (Table 1, entry 6).

Figure S14. DSC curve of syndiotactic P(*o*MOS) (Table 1, entry 6)

Figure S15. DSC curve of syndiotactic P(*m*MOS) (Table 1, entry 4)

Figure S16. DSC curve of syndiotactic P(*p*MOS) (Table 1, entry 2)

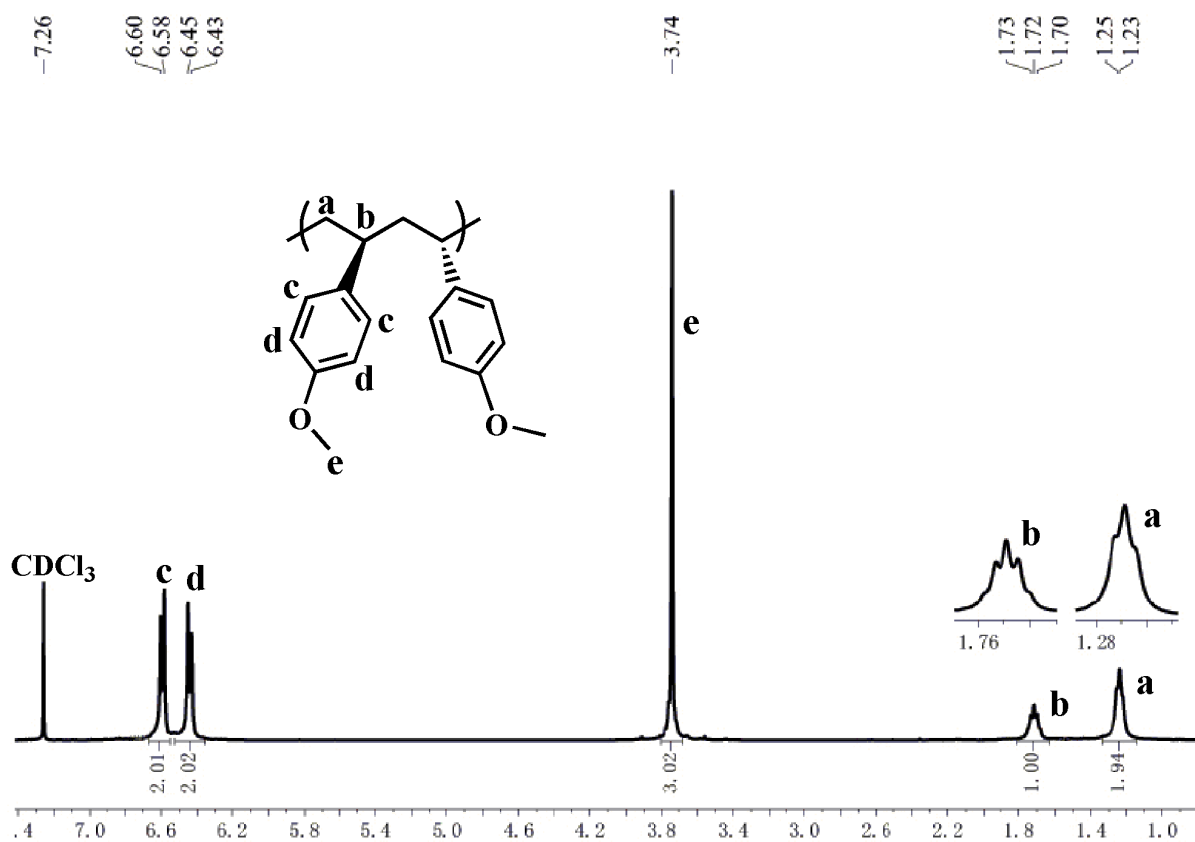


Figure S1. ^1H NMR spectrum of syndiotactic P(*p*MOS) (CDCl_3 , 25°C)

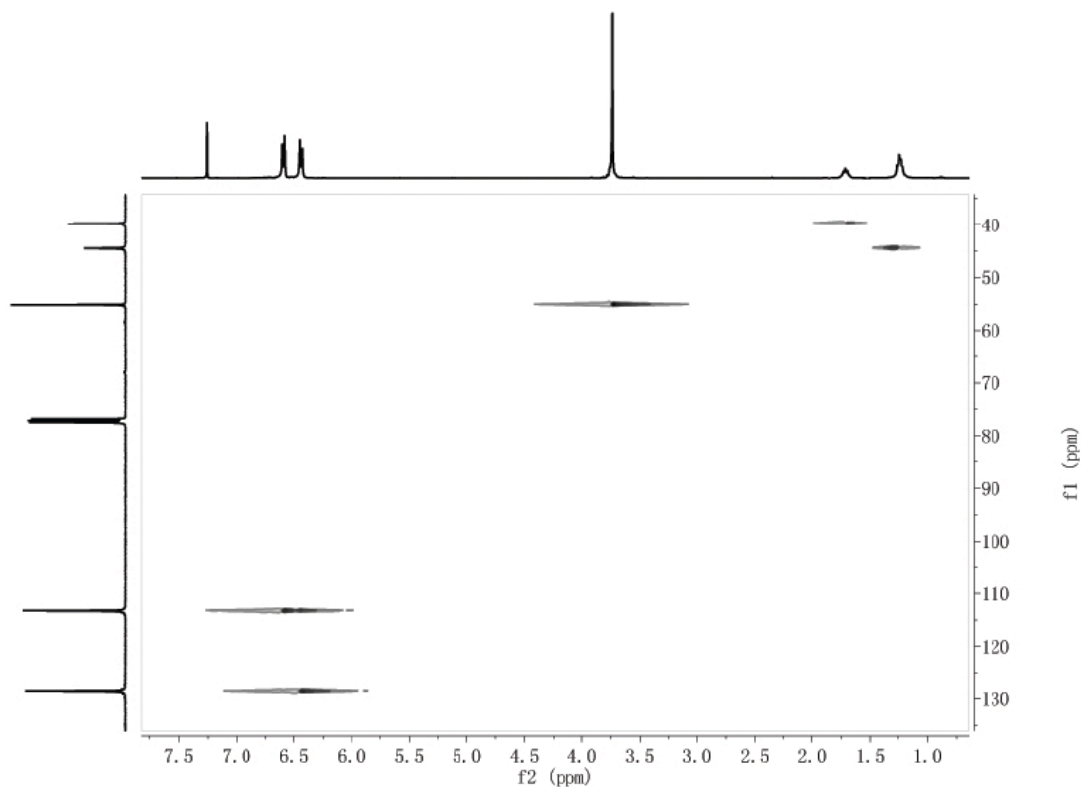


Figure S2 ^1H - ^{13}C COSY spectrum of syndiotactic P(*p*MOS) (CDCl_3 , 25°C)

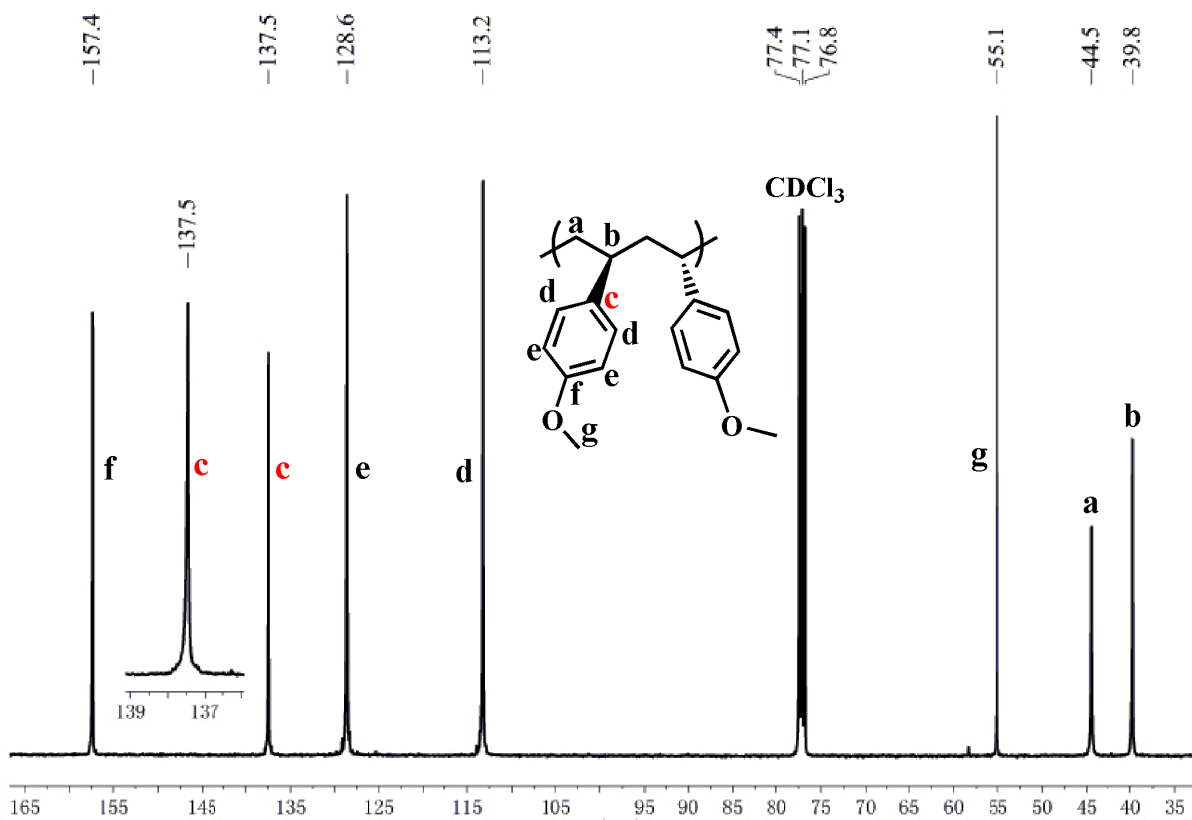


Figure S3. ^{13}C NMR spectrum of syndiotactic P(*p*MOS) (CDCl_3 , 25°C)

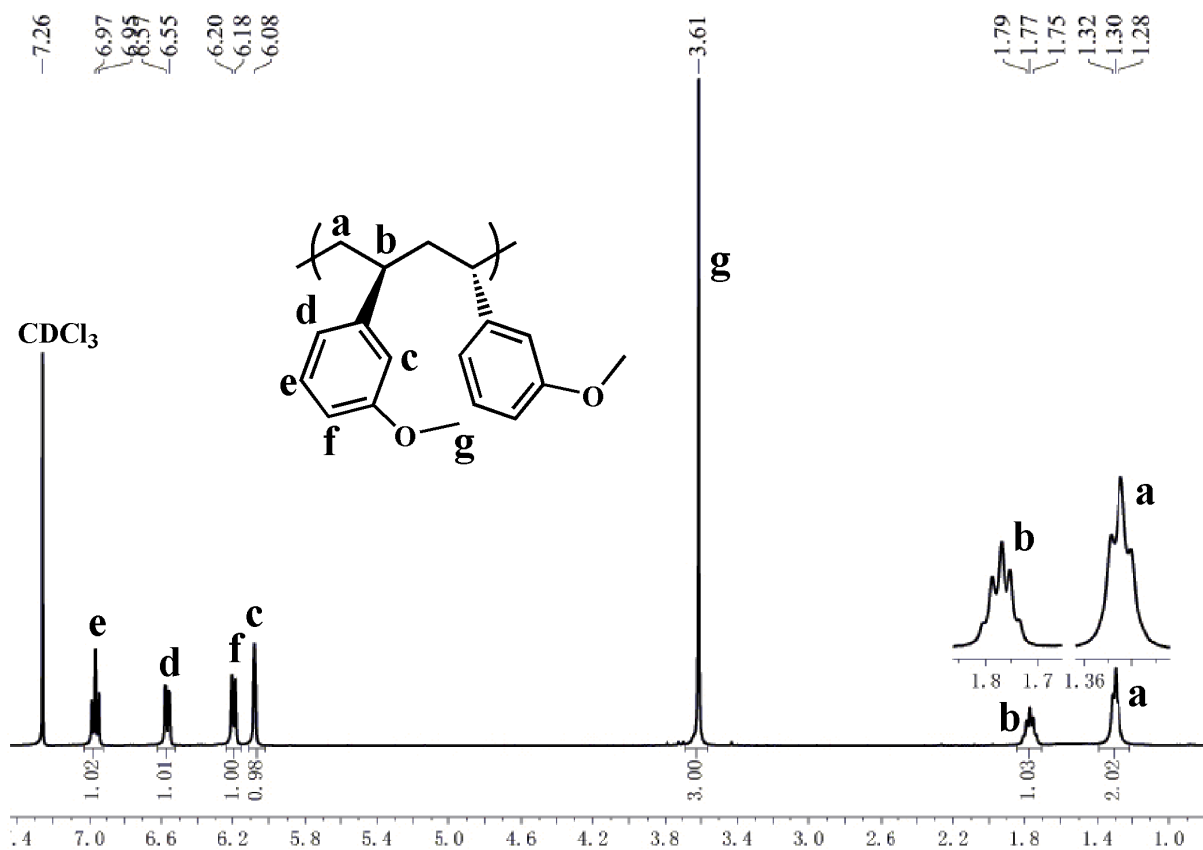


Figure S4. ¹H NMR spectrum of syndiotactic P(*m*MOS) (CDCl₃, 25 °C)

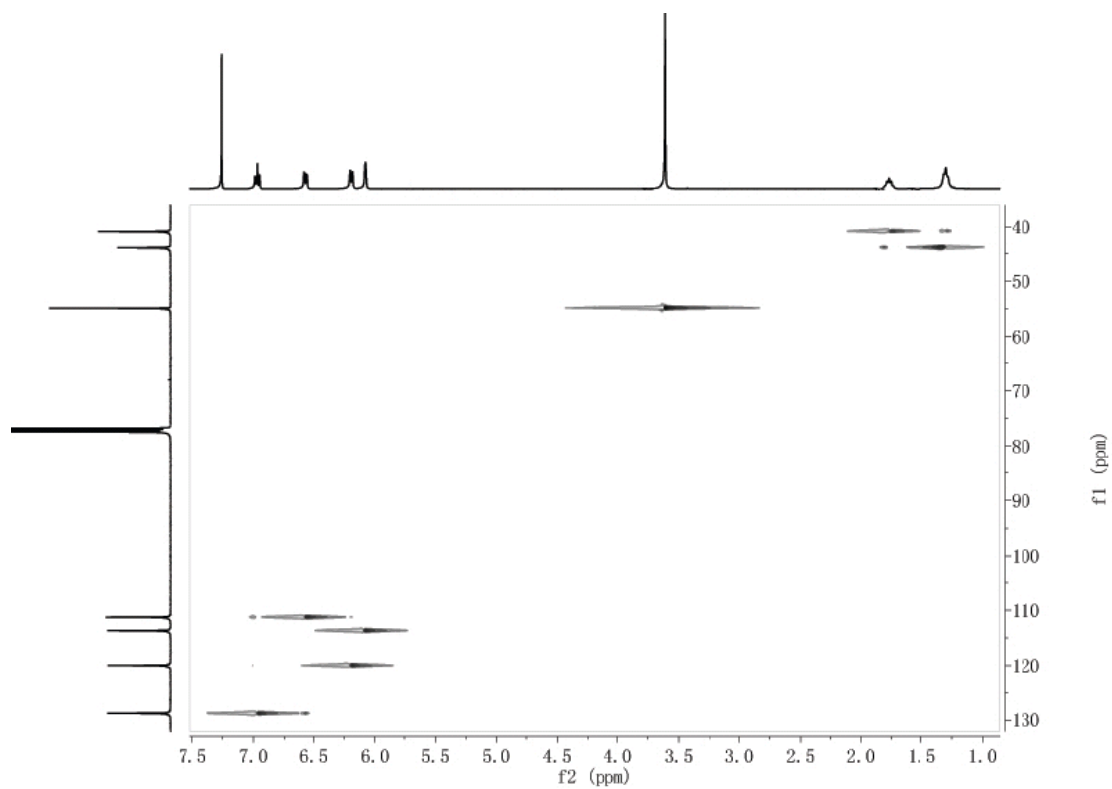


Figure S5 ¹H-¹³C COSY spectrum of syndiotactic P(*m*MOS) (CDCl₃, 25 °C)

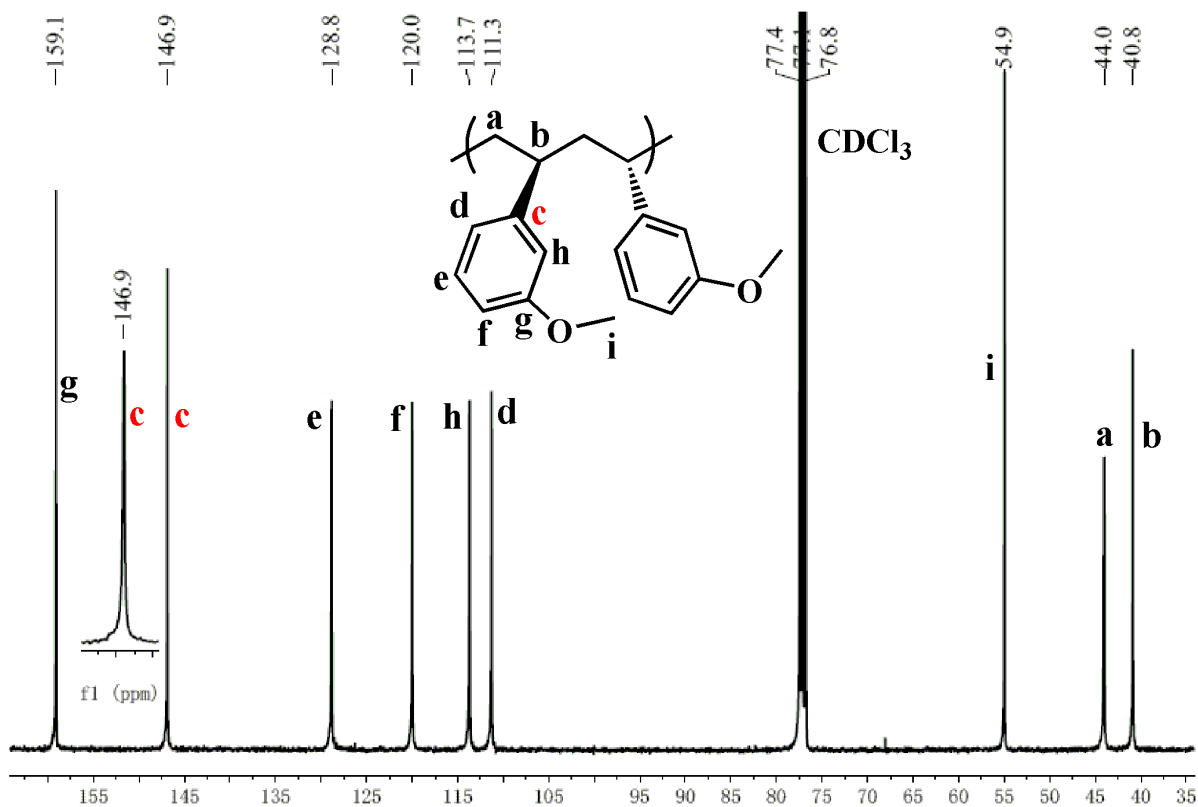


Figure S6. ¹³C NMR spectrum of syndiotactic P(*m*MOS) (CDCl₃, 25°C)

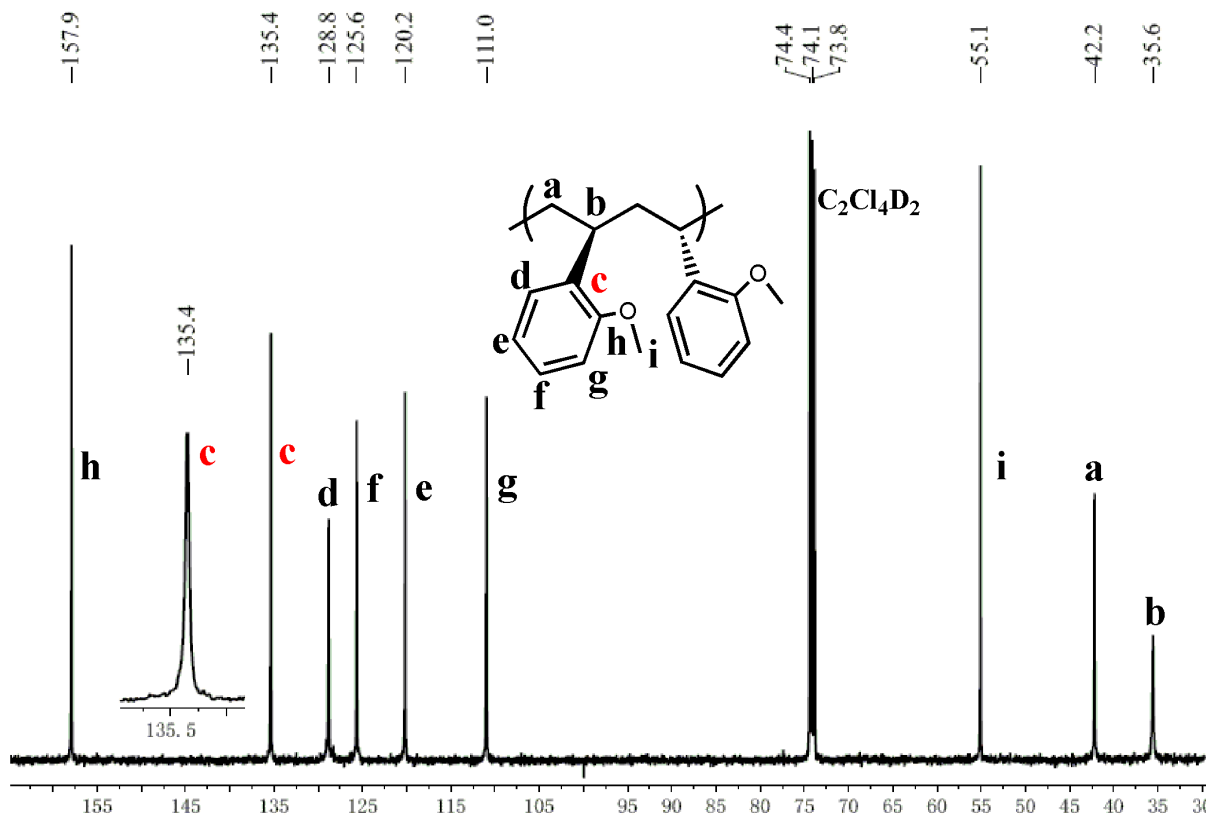


Figure S7. ¹³C NMR spectrum of syndiotactic P(*o*MOS) (C₂Cl₄D₂, 120°C)

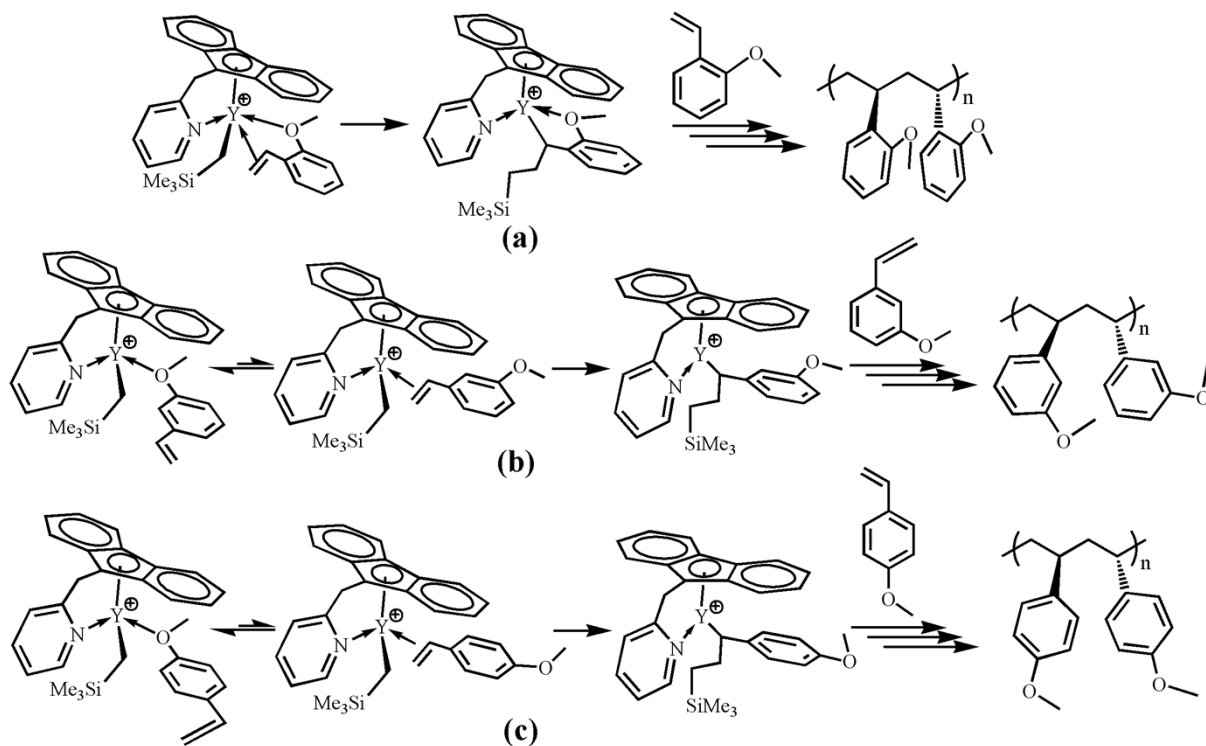
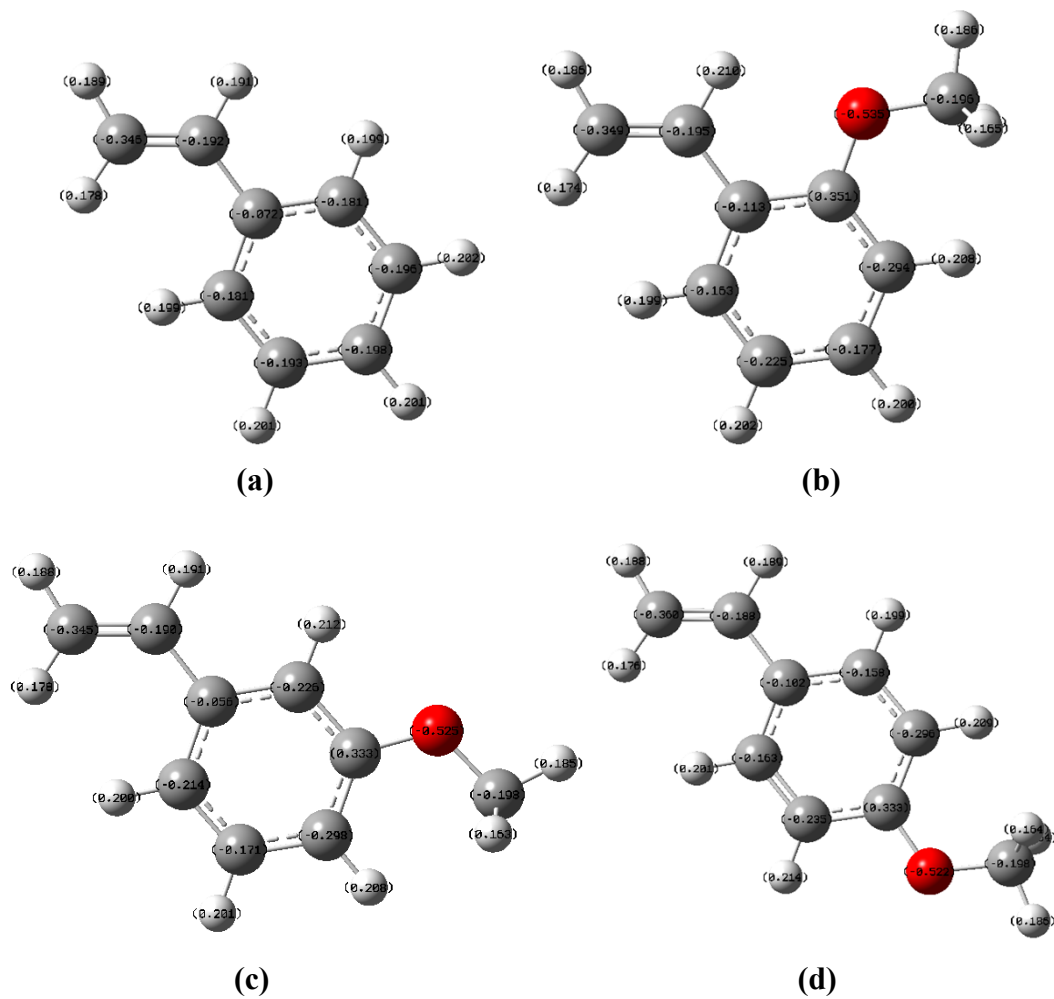


Figure S8. The possible mechanisms for the syndiospecific polymerizations of *o*MOS (a), *m*MOS (b) and *p*MOS (c) by complex 1/Al^{*i*}Bu₃/[Ph₃C][B(C₆F₅)₄].



	St	<i>o</i> MOS	<i>m</i> MOS	<i>p</i> MOS
CH (vinyl group)	-0.192	-0.195	-0.190	-0.188
CH ₂ (vinyl group)	-0.345	-0.349	-0.345	-0.360

Figure S9. NBO charge of the monomers. (a) St; (b) *o*MOS; (c) *m*MOS; (d) *p*MOS

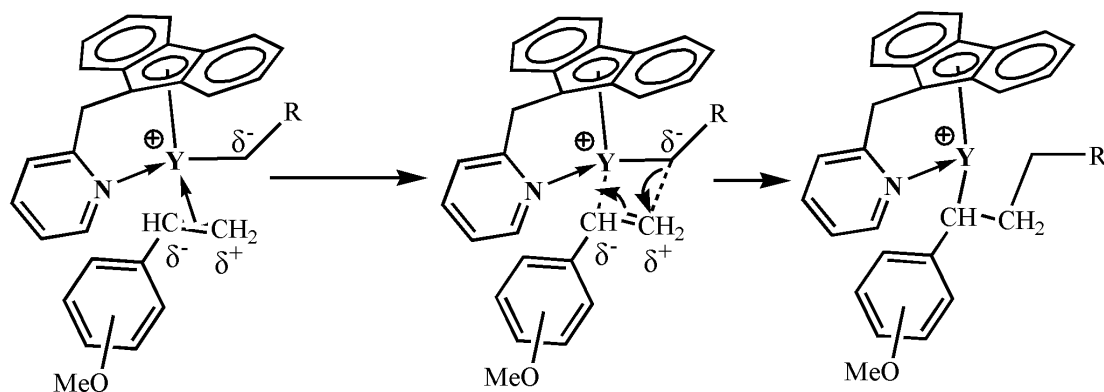


Figure S10. Probable insertion mechanism of methoxystyrenes.

Table S1. Polymerization of methoxystyrenes by complex **2**.

entry	Monomer	[M]/[Y]	time (min)	Yield (g)	M_n^b ($/10^{-4}$)	M_w/M_n^b	T_g/T_m^c ($^{\circ}\text{C}$)
1	<i>p</i> MOS	300	120	trace	-	-	-
2	<i>m</i> MOS	300	120	trace	-	-	-
3	<i>o</i> MOS	300	120	0.38	5.99	1.26	85/234

^a General condition: 10^{-5} mol of Y complex; in toluene; [Al] = AlⁱBu₃; [Al]/[Y] = 10; [Ph₃C][B(C₆F₅)₄] / [Y] = 1; [monomer]₀ = 2.0 mol/L. ^b Determined by GPC in 1,2,4-trichlorobenzene at 150 $^{\circ}\text{C}$ against polystyrene standard. ^c Determined by DSC.

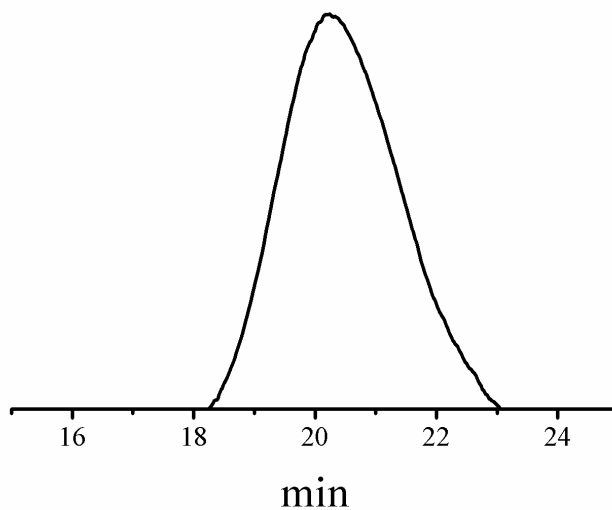


Figure S11. GPC curve of syndiotactic P(*p*MOS) (Table 1, entry 2).

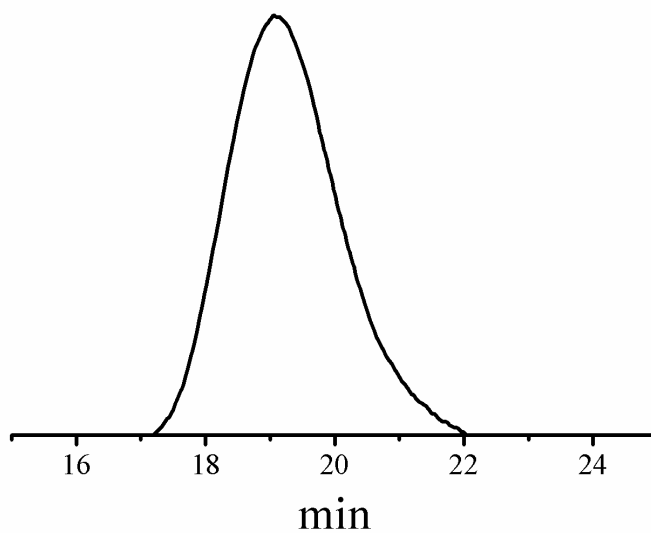


Figure S12. GPC curve of syndiotactic P(*m*MOS) (Table 1, entry 4).

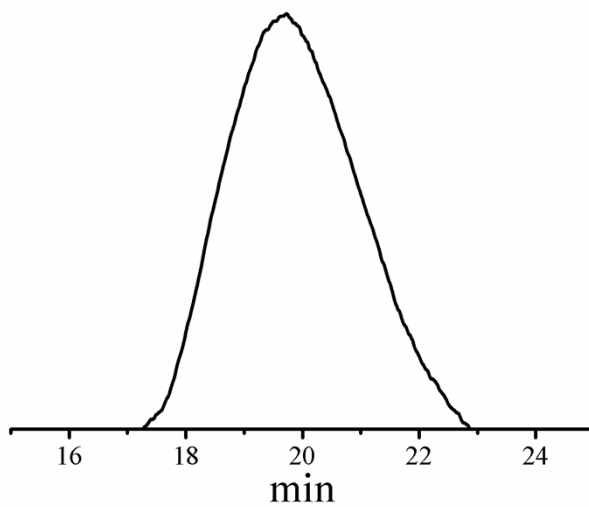


Figure S13. GPC curve of syndiotactic P(*o*MOS) (Table 1, entry 6).

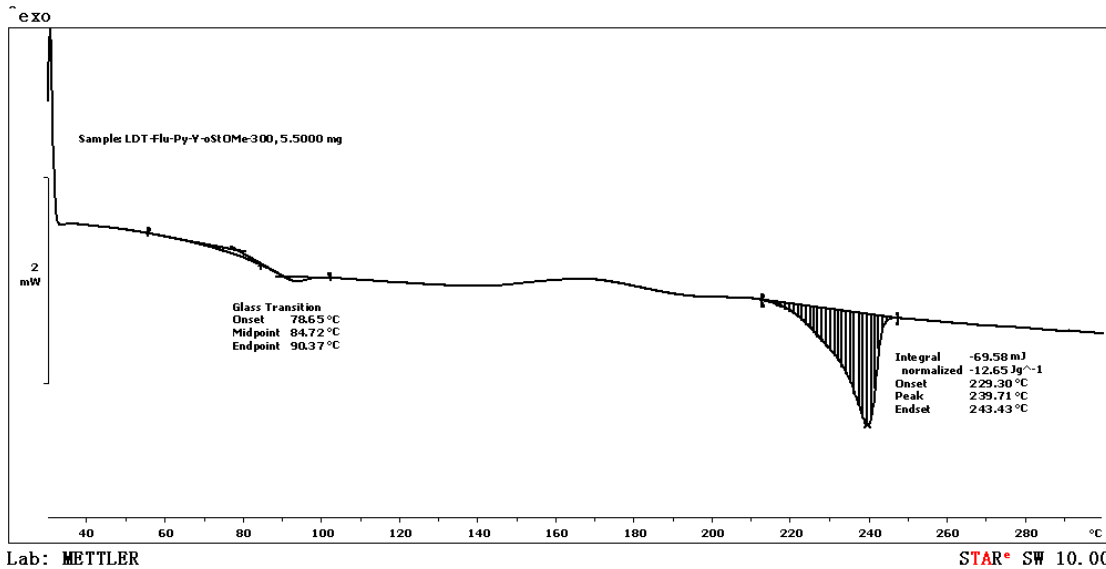


Figure S14. DSC curve of syndiotactic P(oMOS) (Table 1, entry 6)

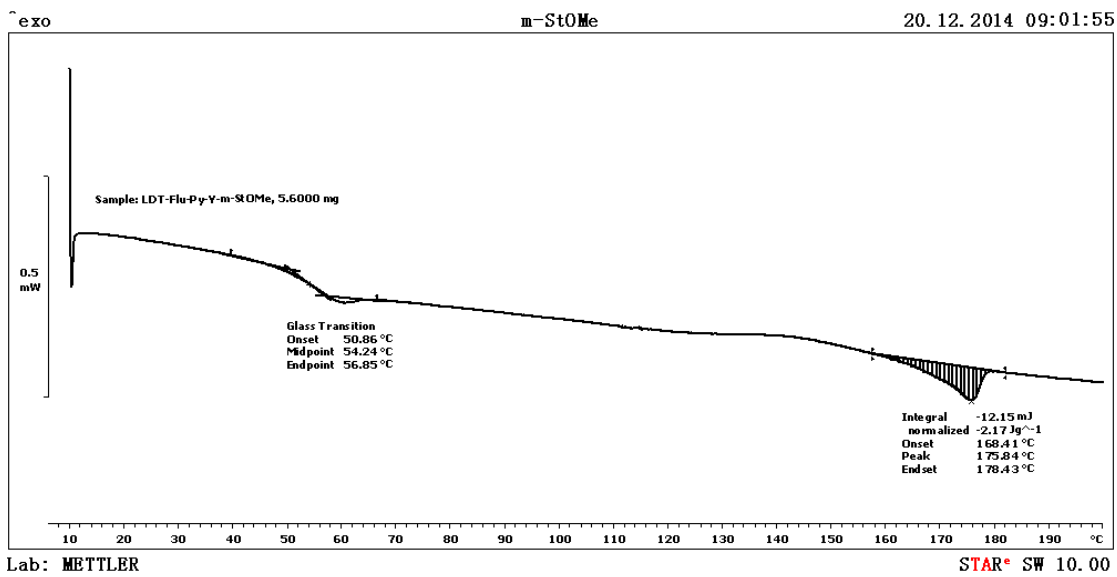


Figure S15. DSC curve of syndiotactic P(mMOS) (Table 1, entry 4)

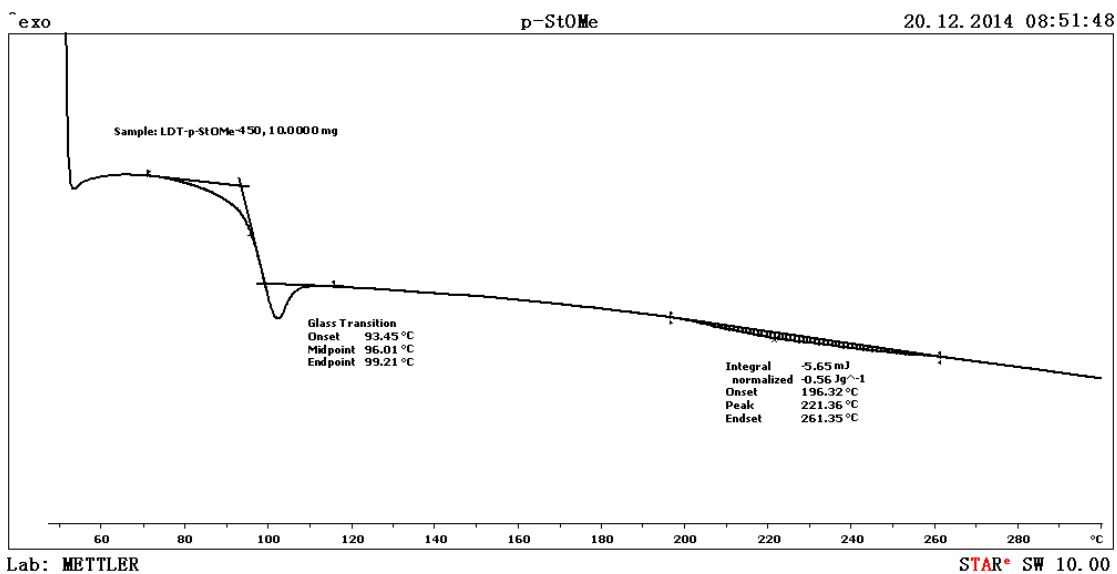


Figure S16. DSC curve of syndiotactic P(*p*MOS) (Table 1, entry 2)