Supporting Information for:

Synthesis of Low Dispersity Star-like Polyethylene: a Combination of Click Chemistry and Sol-gel Process

Yongjie Zhang\textsuperscript{a,b}, Huayi Li\textsuperscript{a,*}, Zenan Xu\textsuperscript{a,b}, Wensheng Bu\textsuperscript{a}, Chenyang Liu\textsuperscript{a}, Jin-Yong Dong\textsuperscript{a,*}, Youliang Hu\textsuperscript{a}

\textsuperscript{a} Beijing National Laboratory of Molecular Sciences, CAS Key Laboratory of Engineering Plastics, Joint Laboratory of Polymer Science and Materials, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, PR China.

\textsuperscript{b} University of Chinese Academy of Sciences, Beijing 100049, PR China.

* Corresponding authors: Huayi Li (lihuayi@iccas.ac.cn) or Jin-Yong Dong (jydong@iccas.ac.cn)

Materials and methods

\textit{Materials}

Toluene was deoxygenated by nitrogen purge before refluxing for 48 h, and then distilled over sodium. High-purity nitrogen was used as received.

Dibulytin maleate (DBTM, 95%) and 1,1'-Azobis(cyclohexanecarbonitrile) (ABCN, 98%), from Aladdin Industrial Inc., (3-mercaptopropyl)trimethoxysilane (MPTMS, 95%) from J&K Scientific, were used as received. vinyl-terminated polyethylene was synthesized as described before.\textsuperscript{1} HDPE (DGDB-2480, Melt Flow Index (190\textdegree C/2.16kg)=0.1 g/10 min) was purchased from SINOPEC Qilu Company.

All synthesis procedures with air-sensitive compounds were performed under inert gas atmosphere using a syringe and standard Schlenk techniques.

\textit{Synthesis of TMS-PE1}

To a solution of v-PE1 (7 g, 1.1 mmol, 1 eq.) in 150 ml toluene, MPTMS (10 g, 4.6 eq.) and ABCN (2 g, 0.7 eq.) were added. The mixture was then heated to 85\textdegree C. After stirring for 12 h, the reaction mixture was precipitated in methanol, and filtered, and the product was
washed with methanol and dried under vacuum at 40°C to give TMS-PE. 8.3 g light yellow solid was obtained.

**Synthesis of TMS-PE2**

To a solution of v-PE2 (4.6 g, 3.3 mmol, 1 eq.) in 150 ml toluene, MPTMS (6 g, 9 eq.) and ABCN (0.73 g, 0.9 eq.) were added. The mixture was then heated to 90°C. After stirring for 12 h, the reaction mixture was precipitated in methanol, and filtered, and the product was washed with methanol and dried under vacuum at 40°C to give TMS-PE. 5.1 g light yellow solid was obtained.

**Synthesis of sPE1**

To a solution of TMS-PE1 (0.9 g, 1.1 mmol, 1 eq.) in 10 ml toluene, solution of DBTM in toluene (0.1 eq.) and deionized water (0.1 ml, 55 mol, 50 e.q.) were added. The mixture was then heated to 120°C. After stirring for 22 h, the reaction mixture was precipitated in methanol, and filtered, and the product was washed with methanol and dried under vacuum at 40°C to give sPE1a. 0.72 g white fine powder was obtained.

**Synthesis of sPE1a**

To a solution of TMS-PE1 (3.6 g, 4.4 mmol, 1 eq.) in 40 ml toluene, solution of DBTM in toluene (0.1 eq.) and deionized water (0.4 ml, 220 mmol, 50 e.q.) were added. The mixture was then heated to 120°C. After stirring for 22 h, the reaction mixture was precipitated in methanol, and filtered, and the product was washed with methanol and dried under vacuum at 40°C to give sPE1b. 3.2 g white fine powder was obtained.

**Synthesis of sPE2**

To a solution of TMS-PE2 (2.5 g, 1.6 mmol, 1 eq.) in 30 ml toluene, solution of DBTM in toluene (0.1 eq.) and deionized water (0.15 ml, 83 mmol, 53 e.q.) were added. The mixture was then heated to 120°C. After stirring for 22 h, the reaction mixture was precipitated in
methanol, and filtered, and the product was washed with methanol and dried under vacuum at 40°C to give sPE2. 2.15 g white solid was obtained.

**Preparation of HDPE/sPE blends**

HDPE/sPE blends were prepared via solution mixing method in xylene at 130°C.

**Analysis**

Solid \(^{29}\)Si/\(^{13}\)C NMR and high-temperature \(^{1}\)H/\(^{13}\)CNMR spectrums were recorded on Bruker III 400 and Bruker DMX 300 instruments, respectively. In solid NMR analyses, 4 mm MAS BB/BB/1H (sPE1 and sPE1a) and 7 mm MAS BB/1H (sPE2) probes were used with spinning speeds up to 5.0 kHz. The melting temperature of the polymers was measured by Differential Scanning Calorimetry (DSC) using a TA Instrument Q2000 with a heating rate of 10°C/min. The molecular weight (MW) and dispersity (D) values of polymers were determined by Gel Permeation Chromatography (GPC) using an Alliance PL-GPC 220 instrument equipped with a refractive index detector (890 nm), a PL-GPC 220 viscometer (four-bridge capillary viscometer), a PL-GPC 220 light scattering detector (Rayleigh scattering angles, 15° and 90°; laser wavelength, 658 nm) and three PLgel 10 μm MIXED-B columns. The measurement was performed at 150°C with 1,2,4-trichlorobenzene as the eluent at a flow rate of 1.0 ml/min. Narrow-molecular-weight-distribution polystyrene samples were used as standards for calibration (\(M_p\) ranging from 580 to 6,870,000 g/mol). TG analyses were performed at a heating rate of 10°C/min in air atmosphere from 50 to 800°C on Perkin-Elmer TGA-7 instrument. FT-IR analyses were performed on a Bruker Tensor 27 FT-IR Instrument. Melt rheological behavior measurements of HDPE and HDPE/sPE blends were performed with a TA ARES-G2 rheometer at 200°C in the oscillatory mode (dynamic frequency sweep, 5 % strain, 0.1-100 rad/s). A parallel plate geometry of 25 mm diameter and a gap of 1.5 mm was used for the tests.
Figure S1. $^1$H NMR spectrum of v-PE1 (1,2-Dichlorobenzene-d4)

Figure S2. $^1$H NMR spectrum of v-PE2 (1,2-Dichlorobenzene-d4)
Figure S3. $^1$H NMR spectrum of TMS-PE2 (1,2-Dichlorobenzene-d4)

Figure S4. $^1$H NMR spectrum of sPE1a (1,2-Dichlorobenzene-d4)
Figure S5. $^1$H NMR spectrum of sPE2 (1,2-Dichlorobenzene-d4)

Figure S6. $^{13}$C NMR spectrum of TMS-PE1 (1,2-Dichlorobenzene-d4)
Figure S7. $^{13}$C NMR spectrum of TMS-PE2 (1,2-Dichlorobenzene-d4)

Figure S8. GPC traces of sPE1

Conc. Response (concentration response) stands for response from refractive index detector;
Diff. Pressure Response (differential pressure response) stands for response from viscometer;
High and Low angle Response stand for response from light scattering detector at 90° and 10°, respectively. Same as below.

Figure S9. GPC traces of sPE1a
Figure S10. GPC traces of sPE2

Figure S11. CP-MAS Solid $^{29}$Si NMR of sPE1 (upper) and sPE1a (lower) (130 mg, 5 kHz, 4 mm MAS BB/BB/$^1$H, NS 20000)
Figure S12. CP-MAS Solid $^{29}$Si NMR of sPE2 (150 mg, 5 kHz, 7 mm MAS BB/1H, NS 20480)

Figure S13. CP-MAS Solid $^{13}$C NMR of sPE1 (130 mg, 5 kHz, 4.0 mm MAS BB/BB/1H, NS 1914)

(Spectrum is shown along with the peak assignments based on previous studies.$^{2-6}$)
The longer alkyl chain in sPE2 mainly possesses trans conformation (33-32 ppm) since it is more likely to crystalize for longer alkyl chain and therefore reduce its mobility.
Figure S16. DSC curves of v-PE2, TMS-PE2 and sPE2

Figure S17. TGA curves of v-PE2, TMS-PE2 and sPE2 in air (10°C/min)

(Inner Picture: Expansion of O₂ uptake region of v-PE2)
Figure S18. FT-IR spectrums of TMS-PE1 (red) and sPE1 (blue)

Peaks: (3429 cm\(^{-1}\)) O-H stretching, (2918 cm\(^{-1}\)) and (2850 cm\(^{-1}\)) C-H stretching, (1469 cm\(^{-1}\)) C-H bending (CH\(_2\)), (1088 cm\(^{-1}\)) Si-O-C asymmetric stretching, (1200-1000 cm\(^{-1}\)) Si-O-Si stretching, (817 cm\(^{-1}\)) Si-O symmetric stretching, (719/722 cm\(^{-1}\)) C-C out of plane bending, (463 cm\(^{-1}\)) and (400-550 cm\(^{-1}\)) Si-O bending.

Characteristic absorption of Si-O-CH\(_3\) at 1088 cm\(^{-1}\) in former TMS-PE1 became much weaker in spectrum of sPE1 and a group of absorption peaks at 1200-1000 cm\(^{-1}\) corresponding to Si-O-Si stretching emerged in spectrum of sPE1.
Figure S19. Storage modulus (G’) and loss modulus (G’’) versus angular frequency curves at 200°C for HDPE and HDPE/sPE1a blend

Figure S20. Storage modulus (G’) and loss modulus (G’’) versus angular frequency curves at 200°C for HDPE and HDPE/sPE2 blend
Figure S21. $^{13}$C NMR spectrum of LPE (100 mg in 0.5 ml 1,2-Dichlorobenzene-d4, 3,000 scans)

Linear structure of LPE is well proved by $^{13}$C NMR spectrum.

Figure S22. GPC curves of LPE
Figure S23. DSC curves of LPE

References


