

Supporting Information for:

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

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

^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.

^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

Materials

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

Dibutyltin 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.¹ HDPE (DGDB-2480, Melt Flow Index (190°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.

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°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 $^{29}\text{Si}/^{13}\text{C}$ NMR and high-temperature $^1\text{H}/^{13}\text{C}$ NMR 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 (\bar{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.

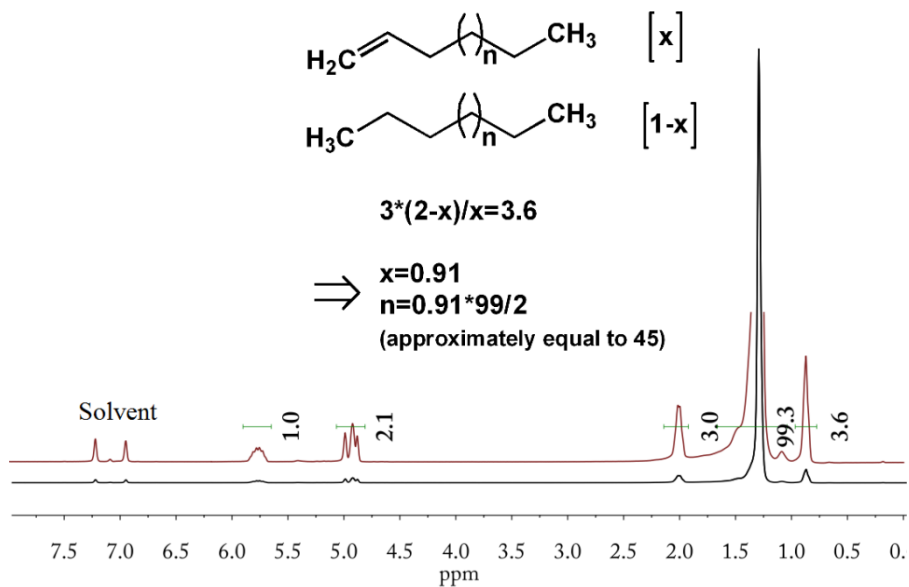


Figure S1. ^1H NMR spectrum of v-PE1 (1,2-Dichlorobenzene- d_4)

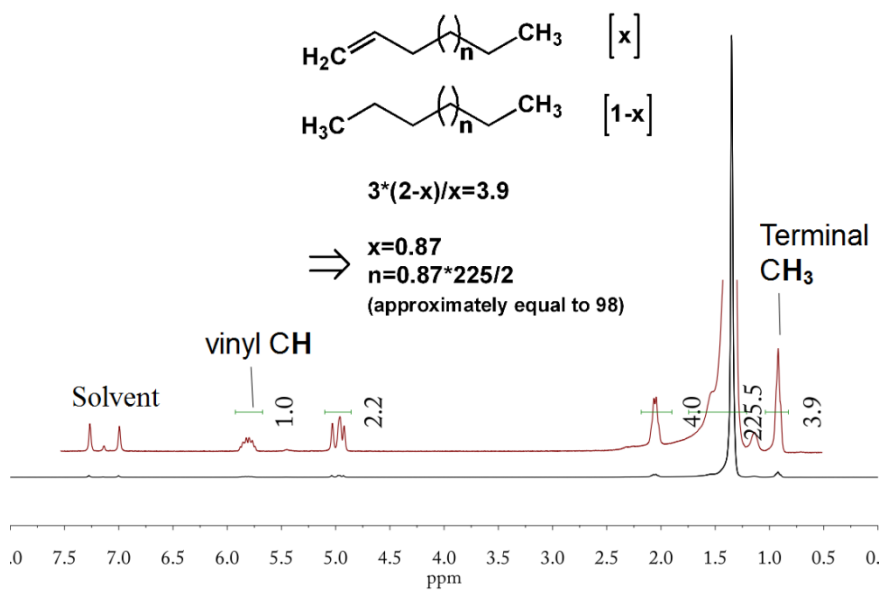


Figure S2. ^1H NMR spectrum of v-PE2 (1,2-Dichlorobenzene- d_4)

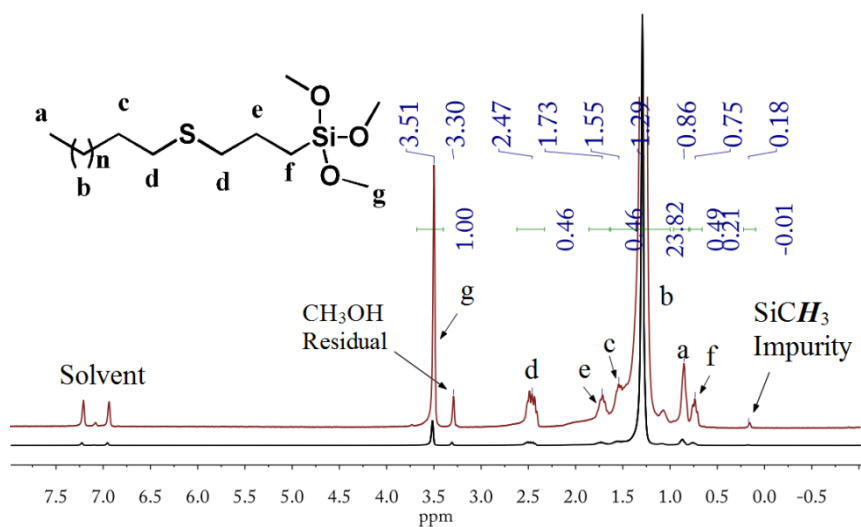


Figure S3. ¹H NMR spectrum of TMS-PE2 (1,2-Dichlorobenzene-d₄)

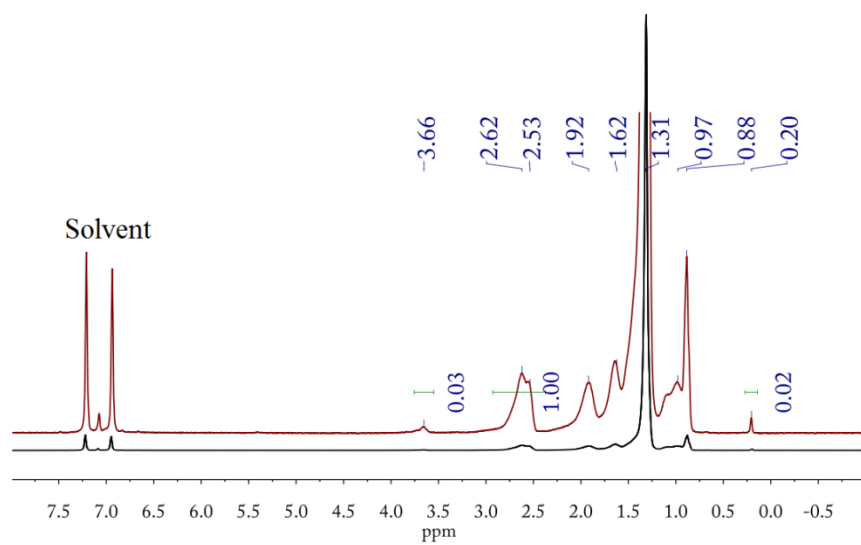


Figure S4. ¹H NMR spectrum of sPE1a (1,2-Dichlorobenzene-d₄)

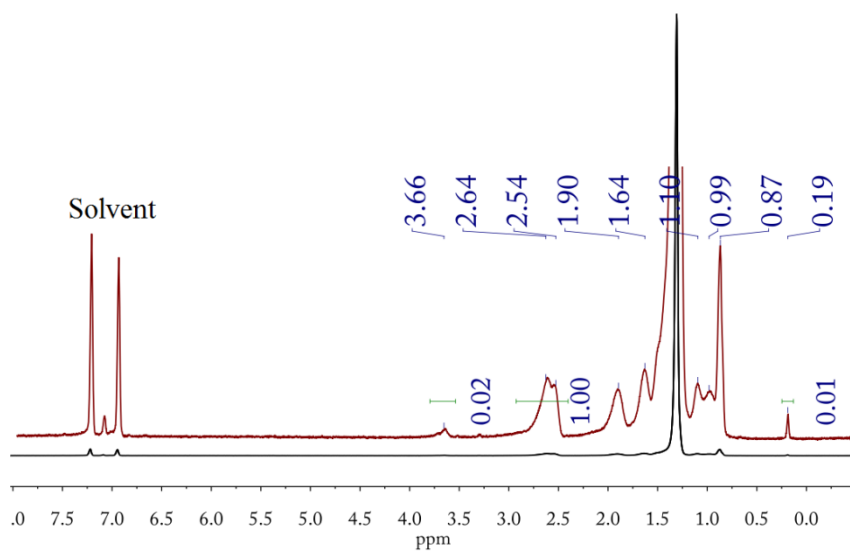


Figure S5. ^1H NMR spectrum of sPE2 (1,2-Dichlorobenzene- d_4)

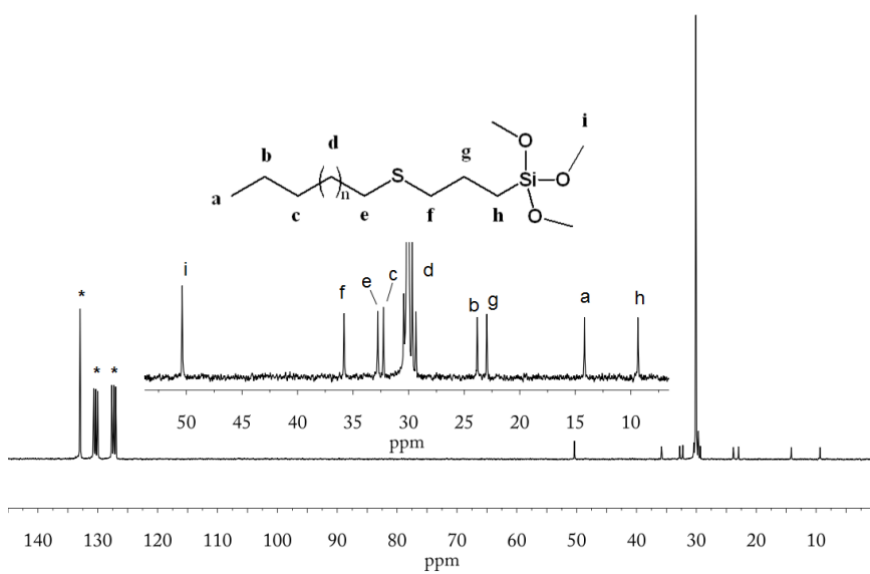


Figure S6. ^{13}C NMR spectrum of TMS-PE1 (1,2-Dichlorobenzene- d_4)

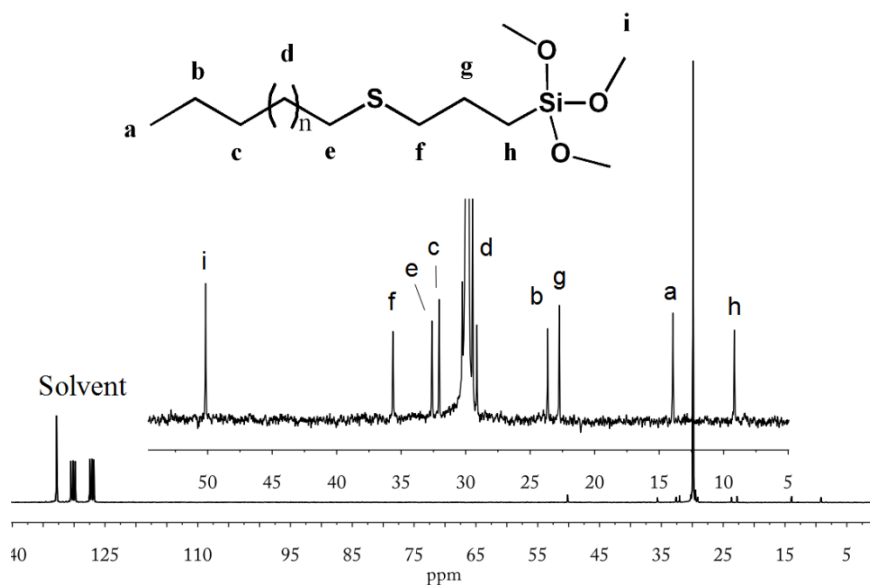


Figure S7. ¹³C NMR spectrum of TMS-PE2 (1,2-Dichlorobenzene-d4)

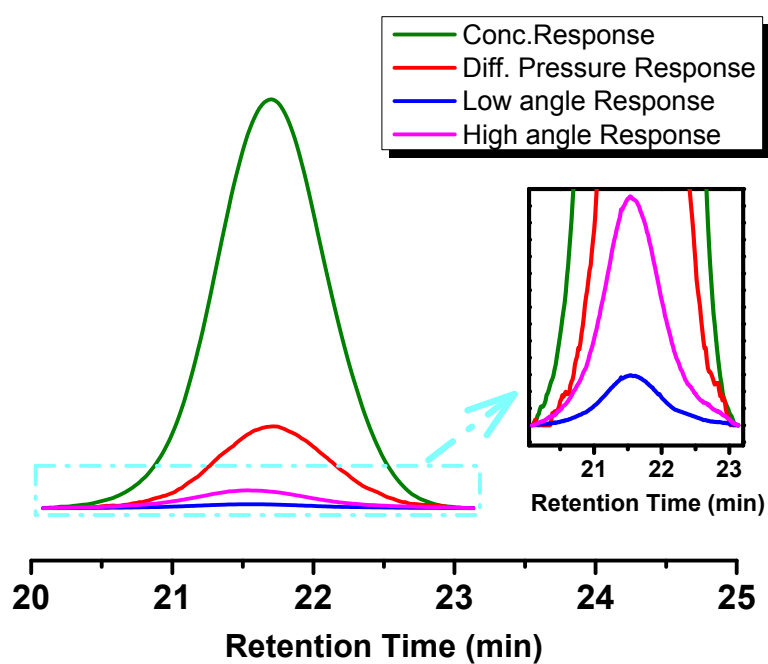


Figure S8. GPC traces of sPE1

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.

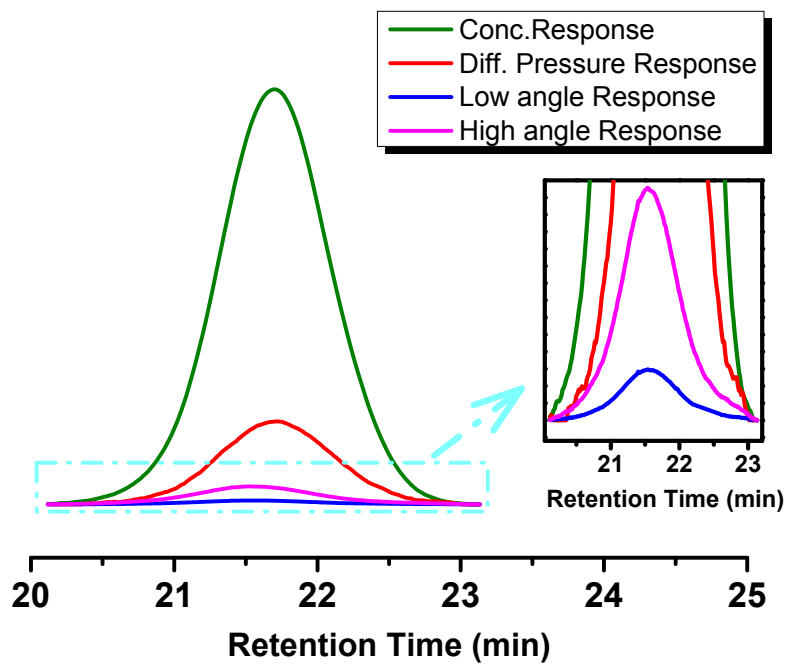


Figure S9. GPC traces of sPE1a

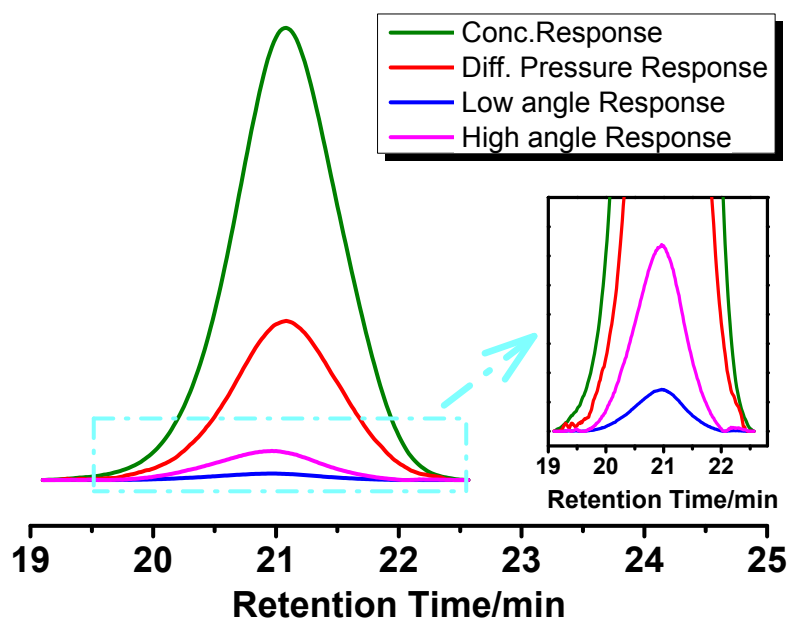


Figure S10. GPC traces of sPE2

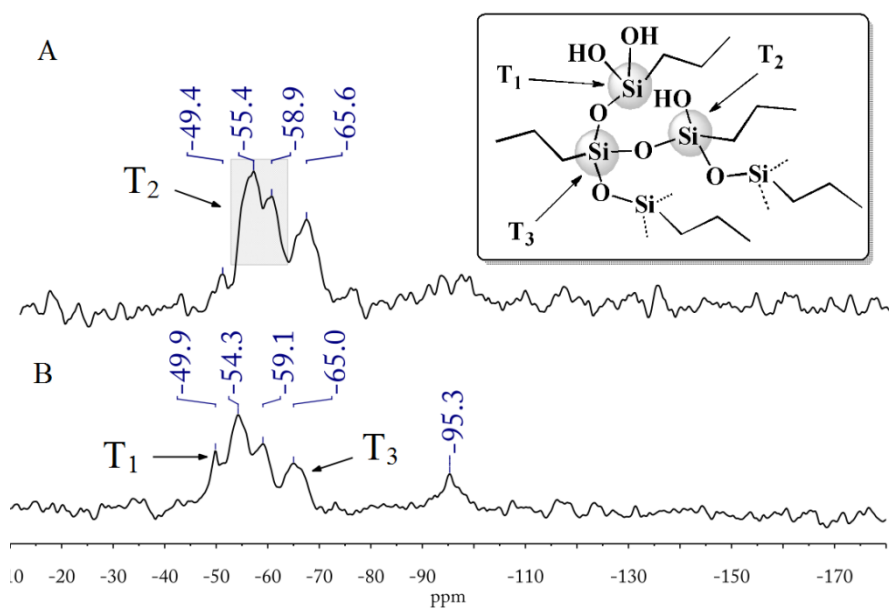


Figure S11. CP-MAS Solid ^{29}Si NMR of sPE1 (upper) and sPE1a (lower) (130 mg, 5 kHz, 4 mm MAS BB/BB/ ^1H , NS 20000)

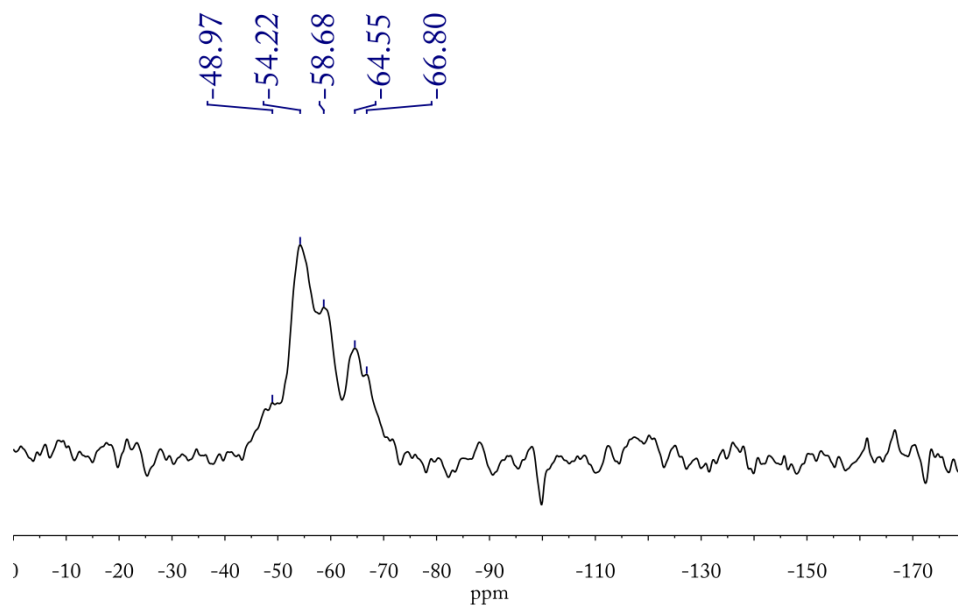


Figure S12. CP-MAS Solid ^{29}Si NMR of sPE2 (150 mg, 5 kHz, 7 mm MAS BB/1H, NS 20480)

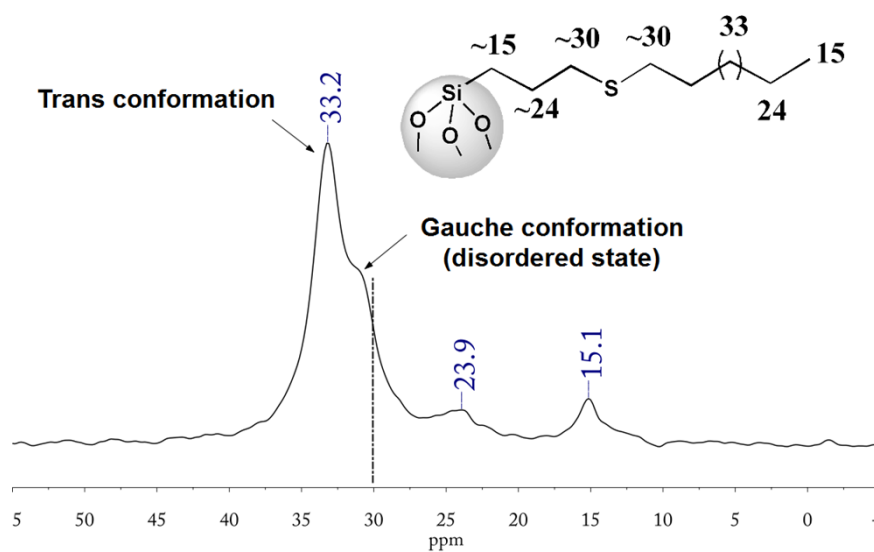


Figure S13. CP-MAS Solid ^{13}C NMR of sPE1 (130 mg, 5 kHz, 4.0 mm MAS BB/BB/1H, NS 1914)

(Spectrum is shown along with the peak assignments based on previous studies.²⁻⁶)

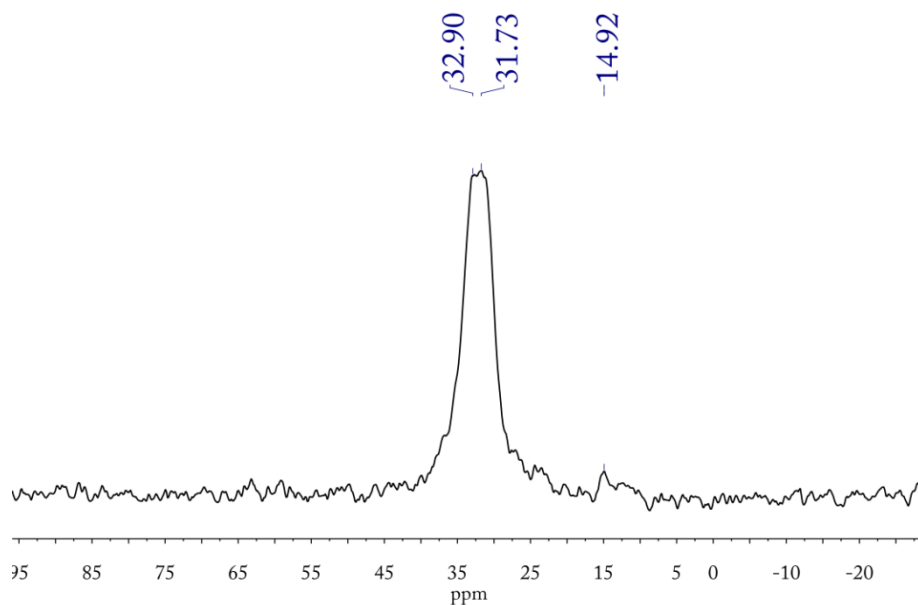


Figure S14. CP-MAS Solid ^{13}C NMR of sPE2 (150 mg, 5 kHz, 7.0 mm MAS BB/1H, NS 3688)

The longer alkyl chain in sPE2 mainly possesses trans conformation (33-32 ppm) since it is more likely to crystallize for longer alkyl chain and therefore reduce its mobility.

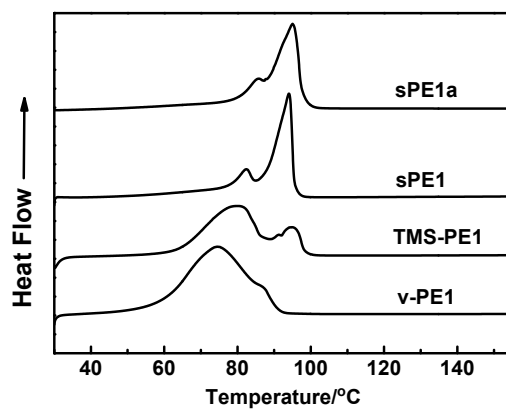


Figure S15. DSC curves of v-PE1, TMS-PE1, sPE1 and sPE1a

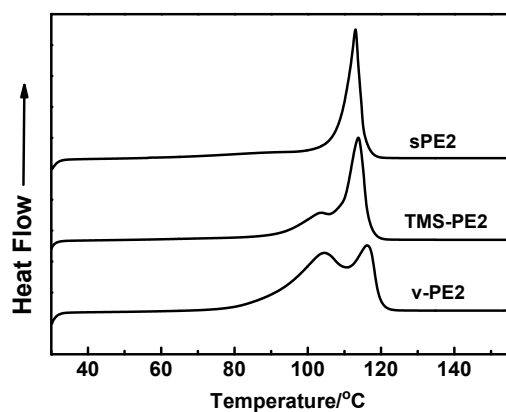


Figure S16. DSC curves of v-PE2, TMS-PE2 and sPE2

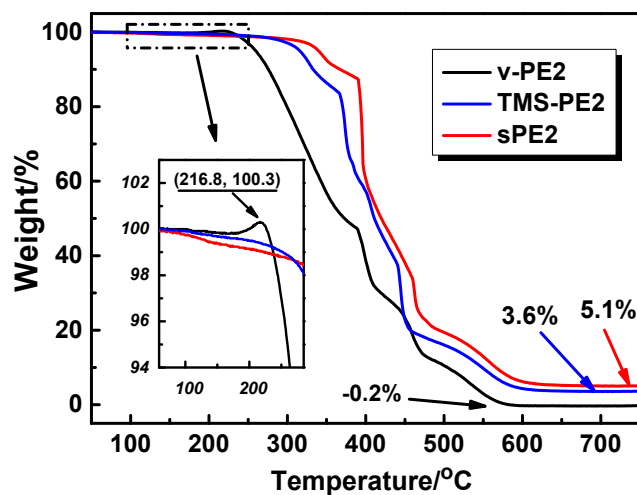


Figure S17. TGA curves of v-PE2, TMS-PE2 and sPE2 in air (10°C/min)

(Inner Picture: Expansion of O₂ uptake region of v-PE2)

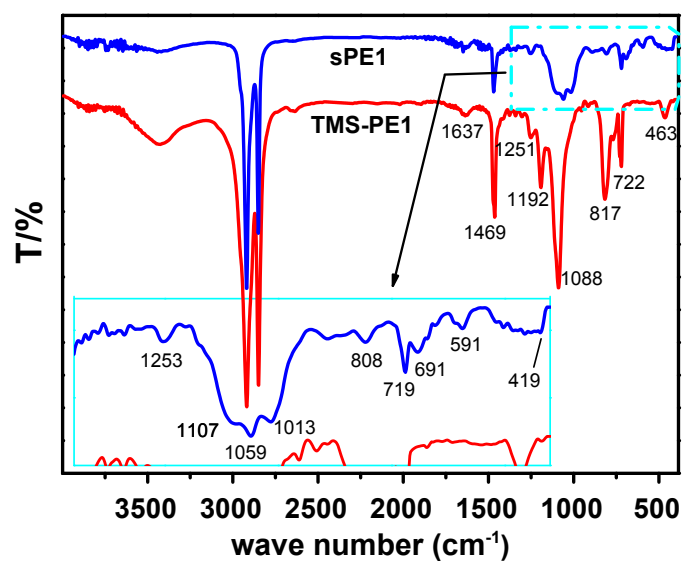


Figure S18. FT-IR spectrums of TMS-PE1 (red) and sPE1 (blue)

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, ($1200\text{-}1000\text{ cm}^{-1}$) Si-O-Si stretching, (817 cm^{-1}) Si-O symmetric stretching, ($719/722\text{ cm}^{-1}$) C-C out of plane bending, (463 cm^{-1}) and ($400\text{-}550\text{ cm}^{-1}$) 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 $1200\text{-}1000\text{ cm}^{-1}$ corresponding to Si-O-Si stretching emerged in spectrum of sPE1.

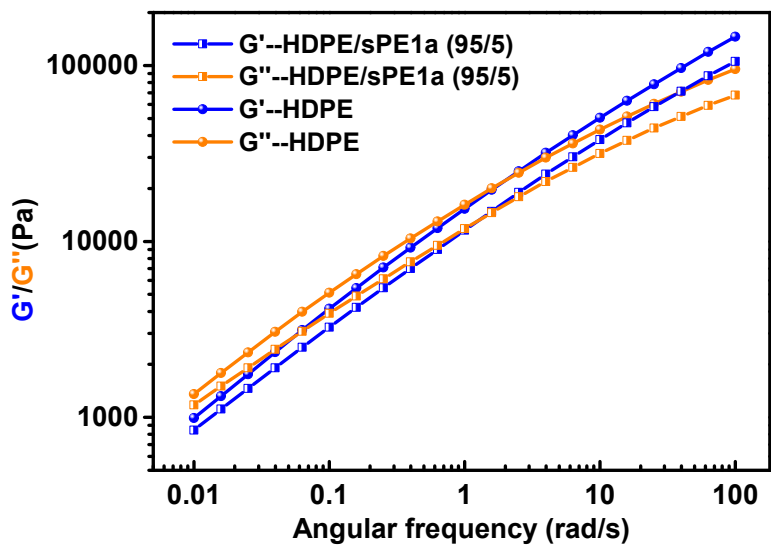


Figure S19. Storage modulus (G') and loss modulus (G'') versus angular frequency curves at 200°C for HDPE and HDPE/sPE1a blend

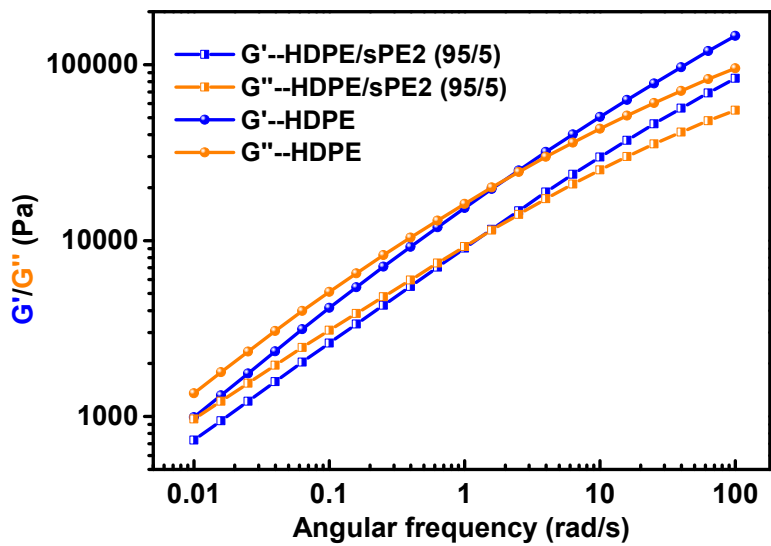


Figure S20. Storage modulus (G') and loss modulus (G'') versus angular frequency curves at 200°C for HDPE and HDPE/sPE2 blend

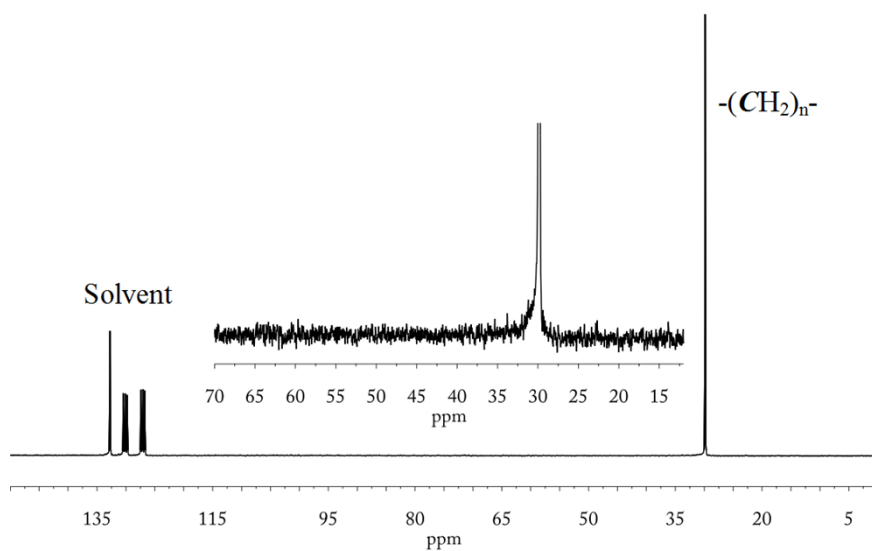


Figure S21. ^{13}C NMR spectrum of LPE (100 mg in 0.5 ml 1,2-Dichlorobenzene- d_4 , 3,000 scans)

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

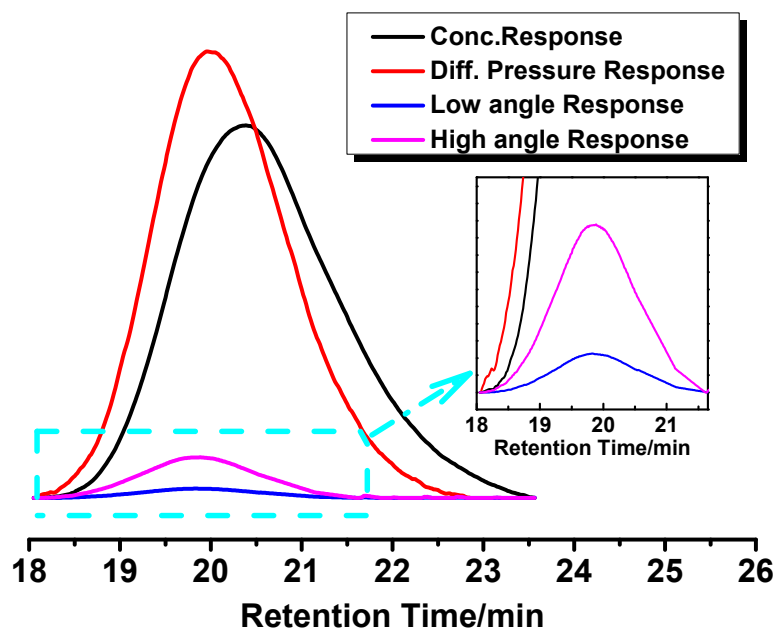


Figure S22. GPC curves of LPE

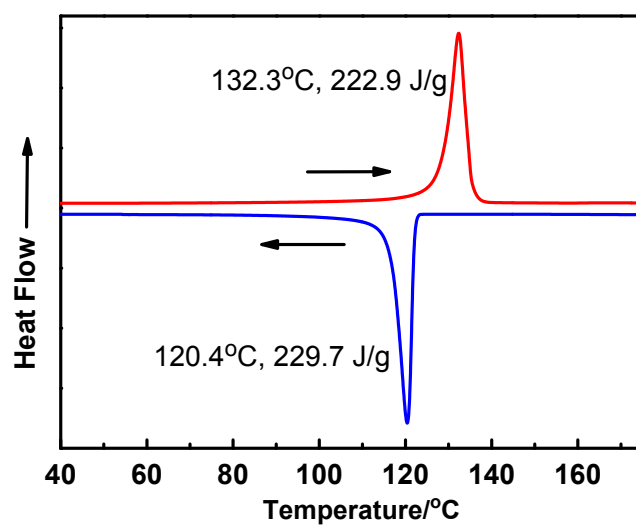


Figure S23. DSC curves of LPE

References

- 1 Y. Zhang, H. Li, J.-Y. Dong and Y. Hu, *Polym. Chem.*, 2014, **5**, 105-115.
- 2 A. Crisci, M. Tucker, J. Dumesic and S. Scott, *Top Catal.*, 2010, **53**, 1185-1192.
- 3 L. Ni, A. Chemtob, C. Croutxe-Barghorn, J. Brendle, L. Vidal and S. Rigolet, *J. Mater. Chem.*, 2012, **22**, 643-652.
- 4 M. Pursch, R. Brindle, A. Ellwanger, L. C. Sander, C. M. Bell, H. Händel and K. Albert, *Solid State Nucl. Mag.*, 1997, **9**, 191-201.
- 5 J. Cheng, M. Fone and M. W. Ellsworth, *Solid State Nucl. Mag.*, 1996, **7**, 135-140.
- 6 W. Gao and L. Reven, *Langmuir*, 1995, **11**, 1860-1863.