

SUPPORTING INFORMATION

Polyethylene Telechelics with POSS Termini: Synthesis, Morphologies and Shape Memory Properties

Bingjie Zhao, Honggang Mei and Sixun Zheng*

Department of Polymer Science and Engineering and the State Key Laboratory of Metal Matrix Composites, Shanghai Jiao Tong University, Shanghai 200240, P. R. China

* Corresponding author, email: szheng@sjtu.edu.cn (S. Zheng)

TABLE OF CONTENTS

1. Experimental.....	S-3
1.1 Materials.....	S-3
2. Measurement and Techniques.....	S-3
2.1 Nuclear Magnetic Resonance (NMR) Spectroscopy.....	S-3
2.2 Gel Permeation Chromatography (GPC).....	S-3
2.3 Atomic Force Microscopy (AFM).....	S-4
2.4 Fourier Transform Infrared Spectroscopy (FTIR).....	S-4
2.5 Transmission Electron Microscopy (TEM).....	S-4
2.6 Thermal Gravimetric Analysis (TGA).....	S-4
2.7 Differential Scanning Calorimetry (DSC).....	S-4
2.8 X-ray Powder Diffraction Analyses (XRD).....	S-5
2.9 Rheological Measurements.....	S-5
2.10 Dynamic Mechanical Thermal Analysis (DMTA).....	S-5
2.11 Tensile Tests.....	S-5
3. References.....	S-6
4. Figures.....	S-7

1. EXPERIMENTAL

1.1 Materials

Phenyltrimethoxysilane ($\text{PhSi}(\text{OMe})_3$) was purchased from Zhejiang Chemical Technology Co. Ltd., China and further purified by distillation under reduced pressure. Trichlorosilane, allyloxytrimethylsilane, 6-bromo-1-hexene, NaH and cyclooctene (COE) were supplied by TCI (Shanghai) Development Co., Ltd., China and used as received. p-Toluenesulfonyl hydrazide (TSH) and tripropylamine (TPA) were obtained from Sinopharm Chemical Reagent Co., Ltd. Grubbs second generation catalyst was purchased from Aldrich, Shanghai, China and used as received. 3-Hydroxypropylheptaphenyl POSS was synthesized in this lab as detailed elsewhere [1]. The organic solvents such as tetrahydrofuran (THF), methanol, N, N-dimethylformamide (DMF), toluene, o-xylene and chloroform were of chemically pure grade, obtained from commercial sources. Before use, DMF was distilled over calcium hydride (CaH_2) under decreased pressure.

2. Measurements and Techniques

2.1 Nuclear Magnetic Resonance (NMR) Spectroscopy

The ^1H NMR measurement was carried out on a Varian Mercury Plus 500 MHz NMR spectrometer at 25 °C. Deuterium chloroform (CDCl_3) and Deuterium toluene were used as the solvent. The values of the chemical shifts were measured with the resonance at 7.26 and 2.31 ppm ascribed to the proton of chloroform and toluene in the deuterium solvents as the internal reference.

2.2 Gel Permeation Chromatography (GPC)

Gel permeation chromatography (GPC) was conducted using a Waters 1515 HPLC system equipped with three Waters RH columns (RH1, 3, 4) and a RI detector. The GPC was operated at a flow rate of 1 mL/min using N, N-dimethylformamide (DMF) containing 0.01 M lithium as the eluent. The values of molecular weights were calculated relative to polystyrene standards. Solutions were prepared from DMF (~10 mg/mL) and passed through a 0.45 μm PTFE filter prior to injection.

2.3 Atomic Force Microscopy (AFM)

The polymer films were prepared by spin-coating the *ortho*-xylene solution onto silicon wafers with the thickness of about 25 μm . The solvent was evaporated at 60 $^{\circ}\text{C}$ for 12 hour and *in vacuo* at 40 $^{\circ}\text{C}$ for 12 hours. The morphologies were observed with a CSPM 5500 atomic force microscopy (Benyuan Nano-instruments Ltd, China) and a tapping mode was used to obtain the topology and phase shift images. The tips fabricated from silicon (125 μm in length with *c.a.* 500 kHz resonant frequency) were used and the scanning rate was 2.0 Hz. The scan speeds were 0.3 ~ 1 lines \times s⁻¹ and the maximum range of 10 \times 10 μm^2 was observed.

2.4 Fourier Transform Infrared Spectroscopy (ATR-FTIR)

Attenuation reflection Fourier transform infrared spectroscopy (ATR-FTIR) was performed on a Perkin-Elmer Paragon 1000 spectrometer at room temperature. The spectra were recorded in 64 scans at a resolution of 2 cm^{-1} .

2.5 Transmission Electron Microscopy (TEM)

The specimens used for morphological observation by means of Transmission Electron Microscopy (TEM) were prepared via ultracryotomy method. The thickness of all the samples was about 70 nm. The morphological observation was carried out on a JEOL JEM-2010 transmission electron microscope (TEM) with an accelerating voltage of 120 kV.

2.6 Thermal Gravimetric Analysis (TGA)

The TGA measurements were conducted on a TA Instruments Q5000 thermal gravimetric analyzer in air atmosphere from room temperature to 800 $^{\circ}\text{C}$ at the heating rate of 20 $^{\circ}\text{C}/\text{min}$.

2.7 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) was performed on a TA Instruments

Q2000 differential scanning calorimeter. All samples had erased thermal history.

2.8 X-ray Powder Diffraction Analyses (XRD)

X-ray powder diffraction analyses (XRD) were performed on a Bruker D8 Advance X-ray diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$).

2.9 Rheological Measurements

Shear rheometry experiments were performed on a DHR-2 stress-controlled rheometer (TA, USA). The linear viscoelastic (LVE) regime of each circular specimen with the dimension of $20 \times 20 \text{ mm}^2$ was determined by applying strain sweeps at constant frequency of 1Hz. Then, isothermal frequency sweeps were carried out at 150 °C. The temperature control was better than $\pm 0.1 \text{ }^\circ\text{C}$.

2.10 Tensile Tests

Tensile tests were performed with a WDW-2 electron universal testing machine (Songdun Instruments Co. Ltd., Shanghai, China). The experiments were carried out with an elongation rate of $100 \text{ mm} \times \text{min}^{-1}$ at room temperature. For each sample, five specimens were tested and then averaged results were reported.

2.11 Dynamic Mechanical Thermal Analysis (DMTA)

One-way shape memory behavior was also investigated on the DMA Q800 apparatus. The measurements were composed of four steps with five circles: i) deformation: a rectangular specimen was elongated by increasing the applied load from 0 to 1.0 MPa at a rate of $0.1 \text{ MPa} \times \text{min}^{-1}$ at 150 °C; ii) fixing: under the constant load the specimen was then cooled at $3 \text{ }^\circ\text{C} \times \text{min}^{-1}$ to 60 °C to fix the temporary shape; iii) unloading: the load was removed at a constant rate of $0.1 \text{ MPa} \times \text{min}^{-1}$, revealing the quality of fixing through the resulting final strain; iv) recovery.

3. REFERENCES

1. Y. Cao, S. Xu, L. Li and S. Zheng, *J. Polym. Sci., Part B: Polym. Phys.*, 2017, **55**, 587-600.

4. FIGURES

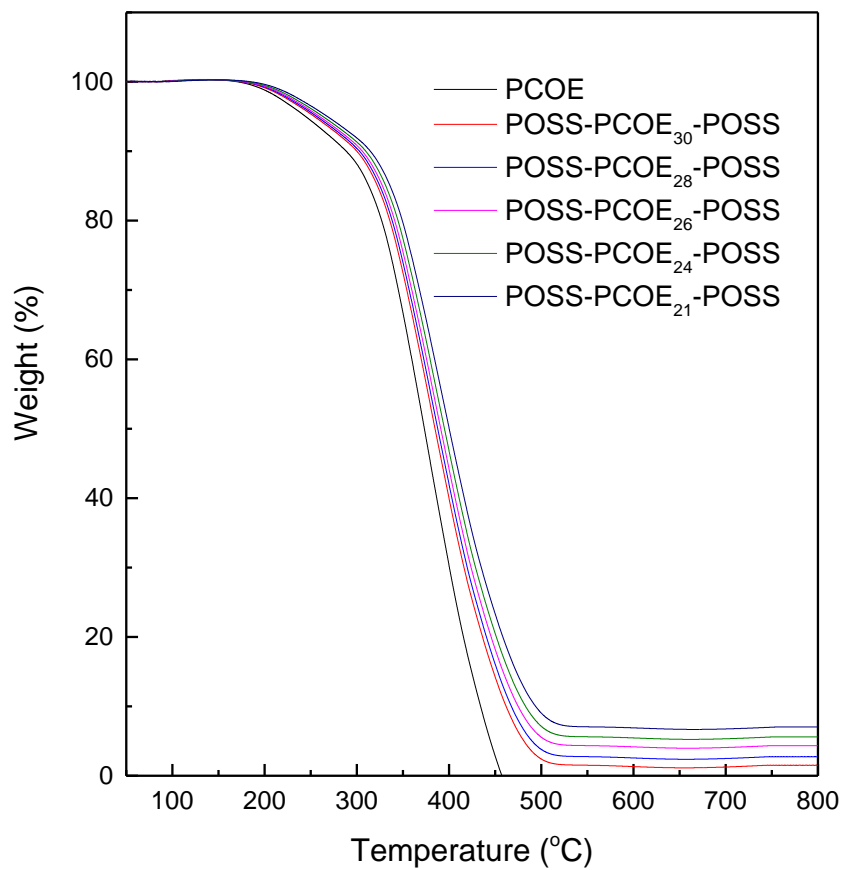


Figure S1 TGA curves of PCOE-POSS-PCOE samples

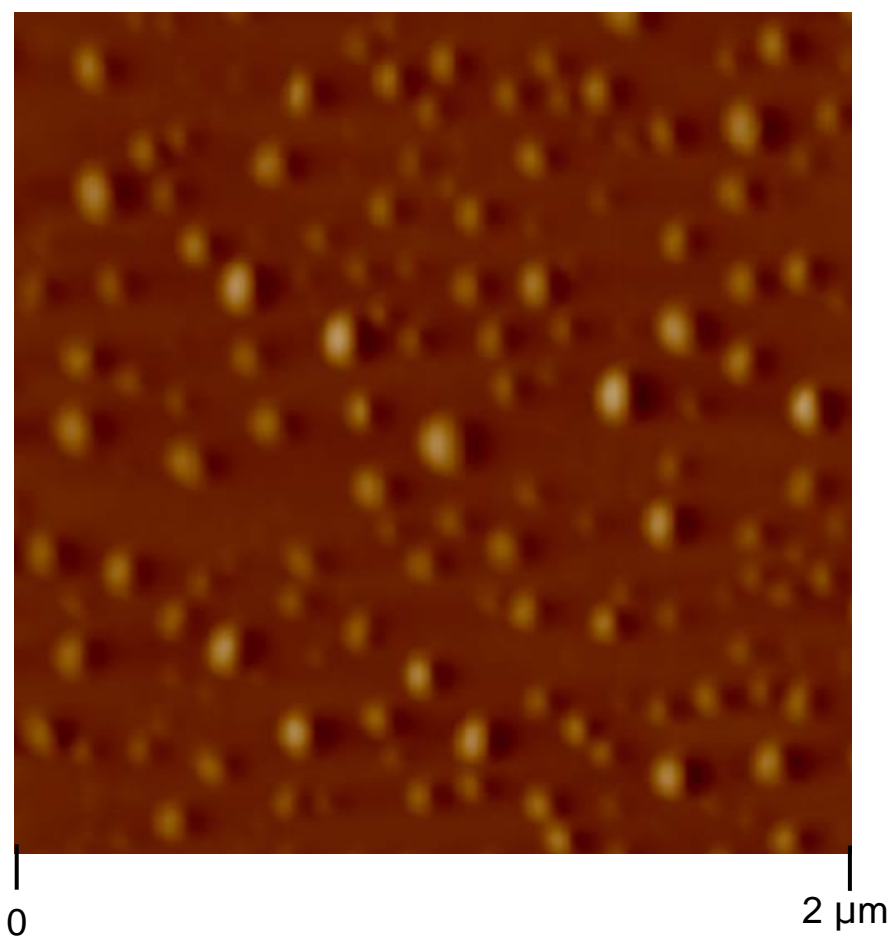


Figure S2 AFM image of POSS-PCOE₂₆-POSS

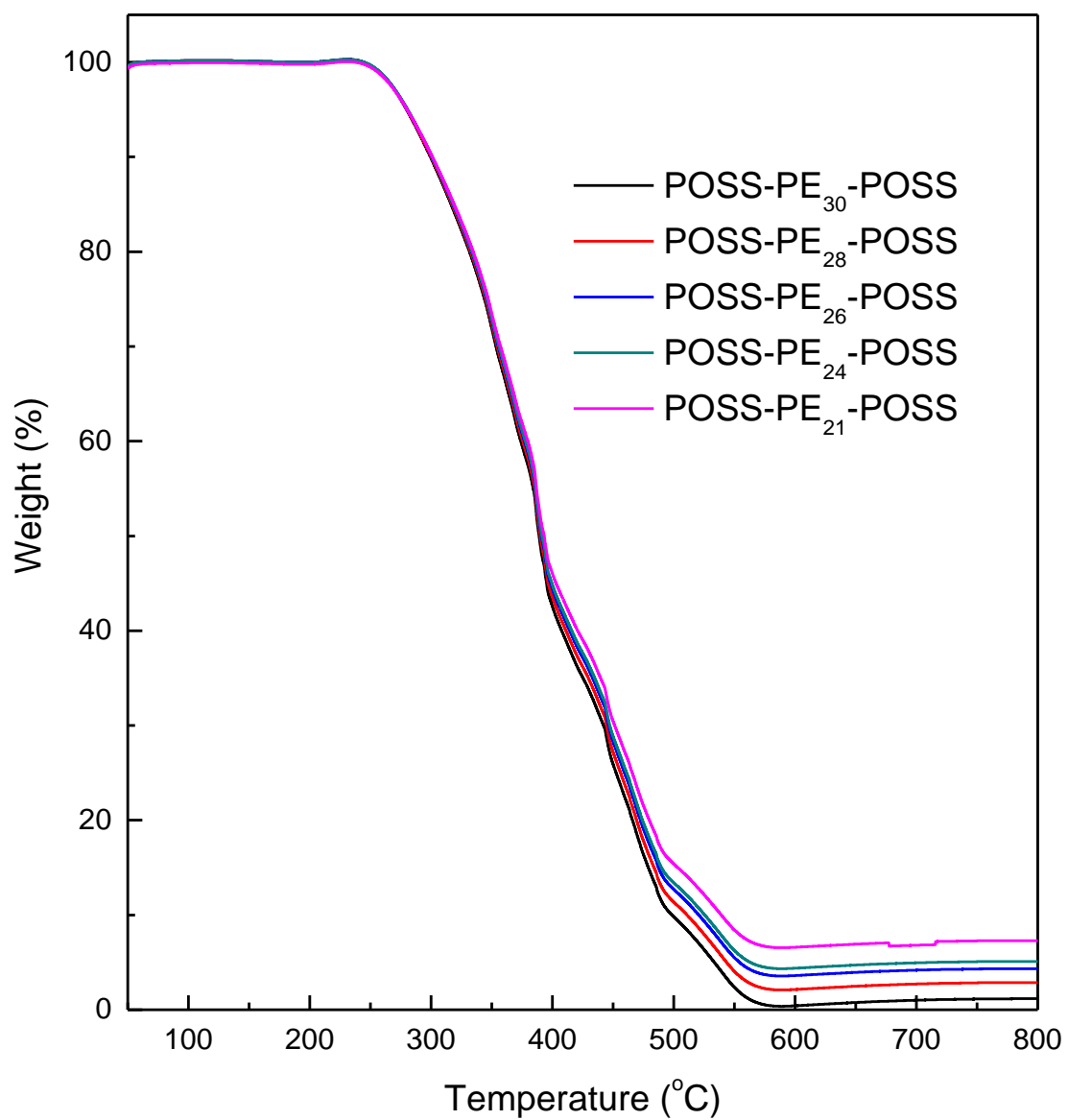


Figure S3 TGA curves of the POSS-PE-POSS samples

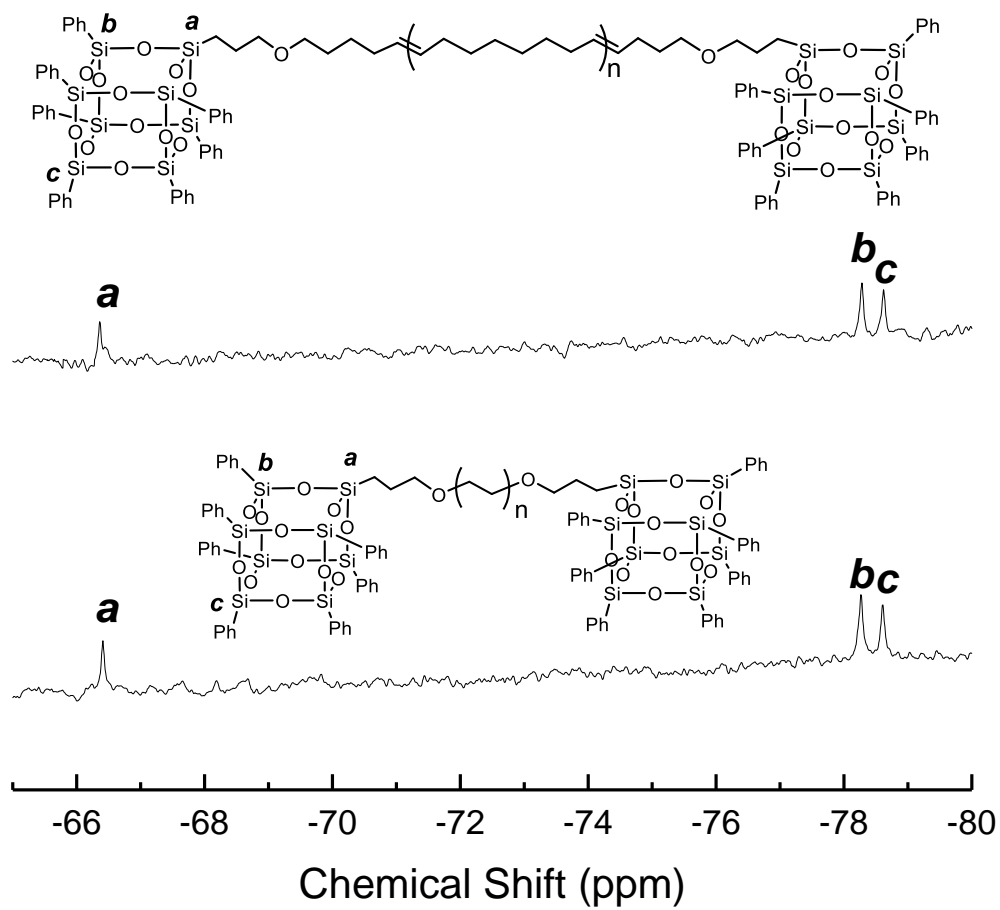


Figure S4 ^{29}Si NMR spectra of POSS-PCOE₂₆-POSS and POSS-PE₂₆-POSS

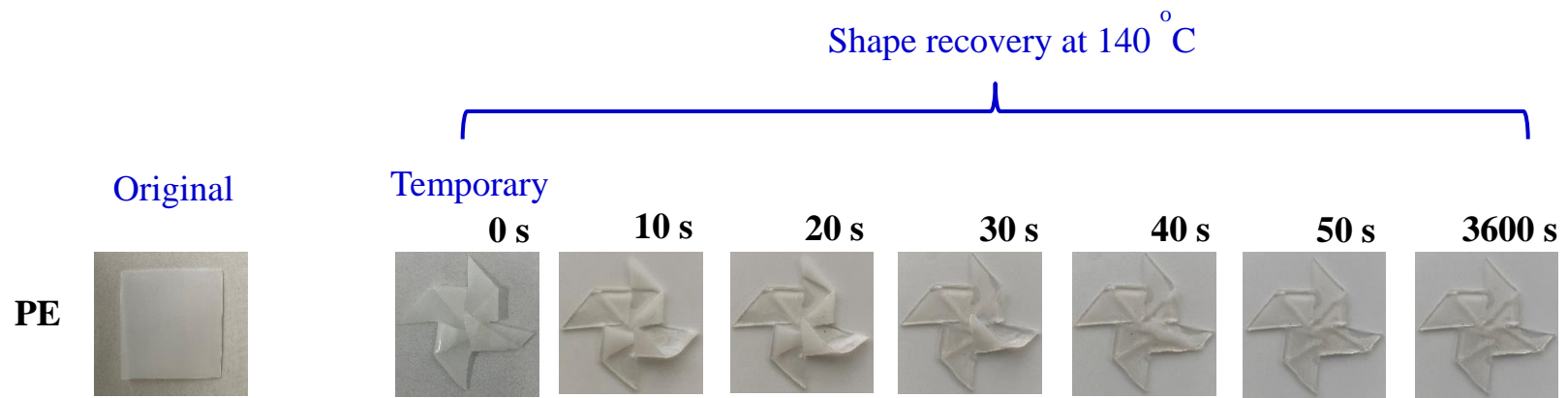


Figure S5 Shape recovery process of PE at 140 °C