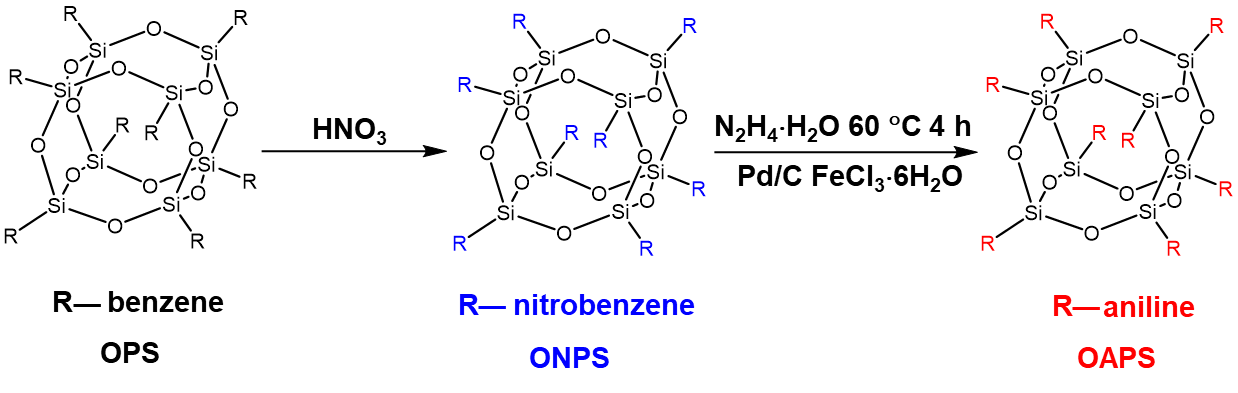
**Supporting Information**

Transparent, High Glass-Transition Temperature, Shape Memory Hybrid Polyimides Based on Polyhedral Oligomeric Silsesquioxane

**1. Synthesis and characterizations of OAPS**

OPS (octaphenylsilsesquioxane) 5 g (4.84 mmol) was added into 30 mL fuming nitric acid in 5 portions with stirring at 0 °C. After stirring for 30 min, the solution was kept at room temperature for 20 h. Then the solution was poured into 25 g ice and yellow precipitate was collected. After washing with water and ethanol, the product was then dried at 30 °C in vacuum oven to yield ONPS (octa(nitrophenyl)silsesquioxane) (5.578 g, 82.3%).

ONPS 3 g (2.14 mmol), 10 wt% Pd/C 0.366 g (0.26 mmol) and FeCl3·6H2O 0.12 g（0.444 mmol）were added into three-necked bottle equipped with a condenser under N2. Distilled THF (12 mL) was added and heated to 60 °C. Then 80% N2H4·H2O 4.8 mL (72 mmol) was added into the solution slowly in 30 min. The reaction was kept for 3 h. The suspension was filtered through diatomite. 20 mL ethyl acetate was added into the filtrate and washed with water 20 mL × 3. The organic layer was dried with 2 g MgSO4 and precipitated by 100 mL hexane. After filtration, the white precipitation was dissolved into 20 mL 3:5 THF/EA and reprecipitated into 100 mL hexane. The product was then dried under vacuum at 30 °C to yield OAPS (1.511 g, 61.2%).

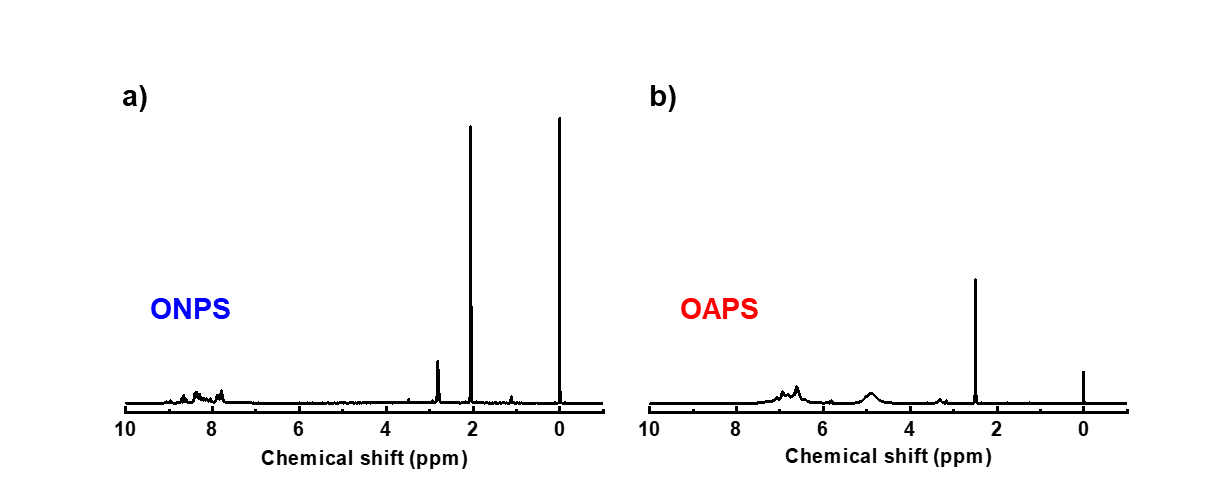


*Figure S1.* Synthesis of OAPS.



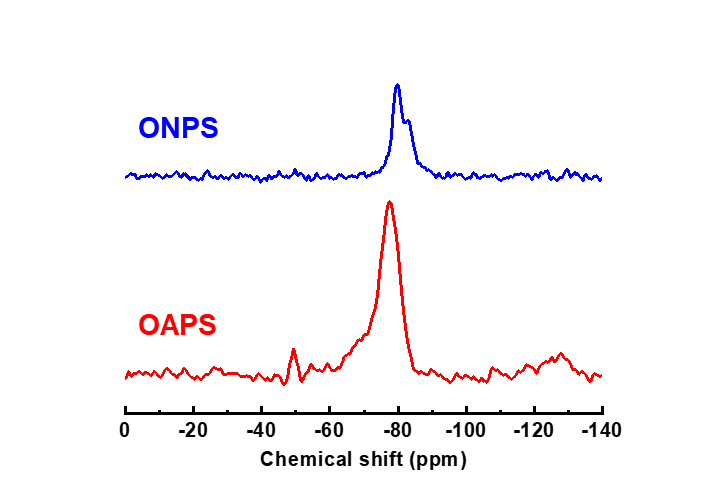
*Figure S2.* FT-IR spectra of ONPS and OAPS.

As shown in Figure S2, the ONPS spectrum shows 1350 cm-1 and 1530 cm-1 assigned to symmetric and asymmetric N=O. 1136 cm-1 represents Si-O-Si stretching vibration. 1136 cm-1 is maintained in the OAPS spectrum. 1350 cm-1 and 1530 cm-1 disappear after reaction and a new broad peak appears at 3367 cm-1 which represents N-H bond.



*Figure S3.* a) 1H NMR (400 MHz, acetone-*d*6, δ): 8.7 (t, 1 H), 8.4-8.0 (m, 2 H), 7.8 (m, 2 H). b) 1H NMR (400 MHz, DMSO-*d*6, δ): 7.3-6.2 (t, 2 H), 5.2-4.5 (s, 1 H).

As shown in Figure S3, new peaks appear in the 1H NMR after the reduction of ONPS, which can be assigned to NH2 groups. The integration ratio of peaks for the amino groups and the aromatic groups ≈ 1:2. The results support the quantitative reduction of the nitro groups to amino groups.



*Figure S4.* 29Si NMR spectra of ONPS and OAPS.

As shown in Figure S4, 29Si NMR spectra of ONPS and OAPS show peaks of -79 ppm for ONPS and -77 ppm for OAPS, indicating that there is only one Si species in each molecule and no destruction of the cubic siloxane cage has occurred in the reduction step.

**2. Mechanical properties**

To evaluate the mechanical properties of PI-POSS hybrid films, we obtained the typical stress-strain curves of 30 mm × 5 mm × 15 µm film via an Instron universal tester. The tensile strength, elongation at break and tensile modulus are listed in Table S1. All of the films exhibit good mechanical stiffness, 121-129 MPa tensile strength, 11-19% elongation at break and 1.4-1.5 GPa tensile modulus, indicating that the films are strong and tough polymeric materials. As OAPS loading reaches 7.6 wt%, the tensile strength increases from 124 MPa to 129 MPa, the modulus increases by 7.9% and the elongation at break is reduced by 45 %. The incorporation of OAPS increases the polymer backbone rigidity and cross-linking density. These results confirm that the incorporation of OAPS enhances the stiffness of the films.

**Table S1** The components and mechanical properties of pure PI and PI-POSS hybrid films.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Sample** | **6FDA (mmol)** | **TFMB (mmol)** | **OAPS (mmol)** | **OAPS (wt%)** | **TS**  **(MPa)a** | **EB**  **(%)b** | **TM**  **(GPa)c** |
| PI-1 | 10 | 10 | 0 | 0 | 124±5 | 20±1 | 1.39±0.12 |
| PI-2 | 10 | 9.5 | 0.125 | 1.9 | 128±8 | 19±1 | 1.41±0.13 |
| PI-3 | 10 | 9 | 0.25 | 3.8 | 125±6 | 14±1 | 1.45±0.12 |
| PI-4 | 10 | 8.5 | 0.375 | 5.7 | 121±4 | 12±1 | 1.48±0.11 |
| PI-5 | 10 | 8 | 0.5 | 7.6 | 129±3 | 11±1 | 1.51±0.14 |

a)Tensile strength. b)Elongation at break. c)Tensile modulus.