Supporting information for

POSS Solid Solutions Exhibiting Orientationally Disordered Phase Transition

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Materials

Heptaisobutyl-hydride-T_8 cage (H-POSS),[1] heptaisobutyl-vinyl-T_8 cage (V-POSS),[2] heptaisobutyl-allyl-T_8 cage (A-POSS),[3] and hexaisobutyl-T_8 cage (iBu-POSS)[4] were prepared according to the previous reports.

Other mono-functionalized-heptaisobutyl-T_8-silsesquioxanes (Me-POSS, SH-POSS) were prepared referring to the reported general corner capping reaction.[5, 6]

Synthesis of heptaisobutyl-methyl-T_8 cage (Me-POSS)

Me-POSS was prepared by corner-capping reaction of heptaisobutyl incompletely condensed POSS (5.01 g, 6.33 mmol) with trichloromethylsilane (0.89 ml, 7.58 mmol). Yield: 66%

^{1}H-NMR ($CDCl_3$, δ in ppm): δ 1.81-1.91 (m, $CH_2CH(CH_3)_2$, 7H), 0.95 (d, J = 6.6 Hz, CH_3, 42H), 0.59-0.61 (m, CH_2-Si, 14H), 0.12 (s, Si-CH_3, 3H).

^{29}Si-NMR ($CDCl_3$, δ in ppm): δ -66.1, -67.9 (T_8 cage).

^{13}C-NMR ($CDCl_3$, δ in ppm): δ 25.6 ($CH_2CH(CH_3)_2$), 23.8 ($CH_2CH(CH_3)_2$), 22.4

(CH$_2$CH(CH$_3$)$_2$), 4.60 (Si-CH$_3$).

Synthesis of heptaisobutyl-mercaptopropyl-T$_8$ cage (SH-POSS)

SH-POSS was prepared by corner-capping reaction of heptaisobutyl incompletely condensed POSS (5.07 g, 6.32 mmol) with trimethoxy-3-mercaptopropylsilane (1.40 ml, 7.58 mmol)). Yield: 27%

^{1}H-NMR (CDCl$_3$, δ in ppm): δ 2.51-2.57 (m, CH$_2$CH$_2$CH_2SH, 2H), 1.79-1.92 (m, CH$_2$CH(CH$_3$)$_2$, 7H), 1.67-1.75 (m, CH$_2$CH_2CH$_2$SH, 2H), 1.29-1.33 (m, CH$_2$CH$_2$CH$_2$SH, 1H), 0.95 (d, J = 6.8 Hz, -CH_3, 42H), 0.71-0.75 (m, CH_2CH$_2$CH$_2$SH, 2H), 0.59-0.62 (m, Si-CH_2, 14H),.

^{29}Si-NMR (CDCl$_3$, δ in ppm): δ -67.6, -67.9 (T$_8$ cage).

^{13}C-NMR (CDCl$_3$, δ in ppm): δ 41.6 (CH$_2$CH$_2$$CH_2$SH), 27.5 (CH$_2$$CH_2CH_2$SH), 25.6 (CH$_2$CH($CH_3$)$_2$), 23.8 (CH$_2$$C$H(CH$_3$)$_2$), 22.4 ($CH_2$CH(CH$_3$)$_2$), 11.2 ($CH_2CH_2CH_2$SH).

Measurements

Differential scanning calorimetry (DSC) was measured on a DSC-60 Plus, Shimadzu Thermogravimetric Analyzer (Shimadzu, Kyoto, Japan). Powder X-ray diffractometry (XRD) studies were performed on a Rigaku Smartlab X-ray diffractometer with Cu Kα radiation (λ = 1.5406 Å) in the 2θ/θ mode at room temperature. The 2θ scan data were collected at 0.01° intervals and the scan speed was 5° (2θ) / min. Thermal conductivity was measured on a Rigaku C-Therm TCi

Max-k. A pellet sample with a diameter of 20 mm and 3 mm thickness was prepared by pressing at 300 kg/cm^2 for 1 min at room temperature.

[1] (a) C.-H. Lu, C.-H. Tsai, F.-C. Chang, K.-U. Jeong, S.-W. Kuo, J. Colloid Interface Sci. 2011, 358, 93. (b) M. Takeda, K. Kuroiwa, M. Mitsuishi, J. Matsui, Chem. Lett. 2015, 44, 1560-1562. (c) H. Imoto, Polym. J. 47, 609-615.

[2] P. Zak, C. Pietraszuk, B. Marciniec, G. Spólnik, W. Danikiewicz, *Adv. Synth. Catal*. **2009**, *351*, 2675-2682.

[3] Y. Yasumuto, Polym. J., 2016, 48, 281-287.

[4] C. Jost, A. Kuehnle, H. C. L. Abbenhuis, PCT Int. Appl., 2003042223, 22 May 2003

[5] I. Blanco, L. Abate, A. Bottino, P. Bottino, *J. Therm. Anal. Calorim.,* **2012**, *108*, 807.

[6] W. Zhang, A. H. E. Muller, *Polymer,* **2010**, *51*, 2133.

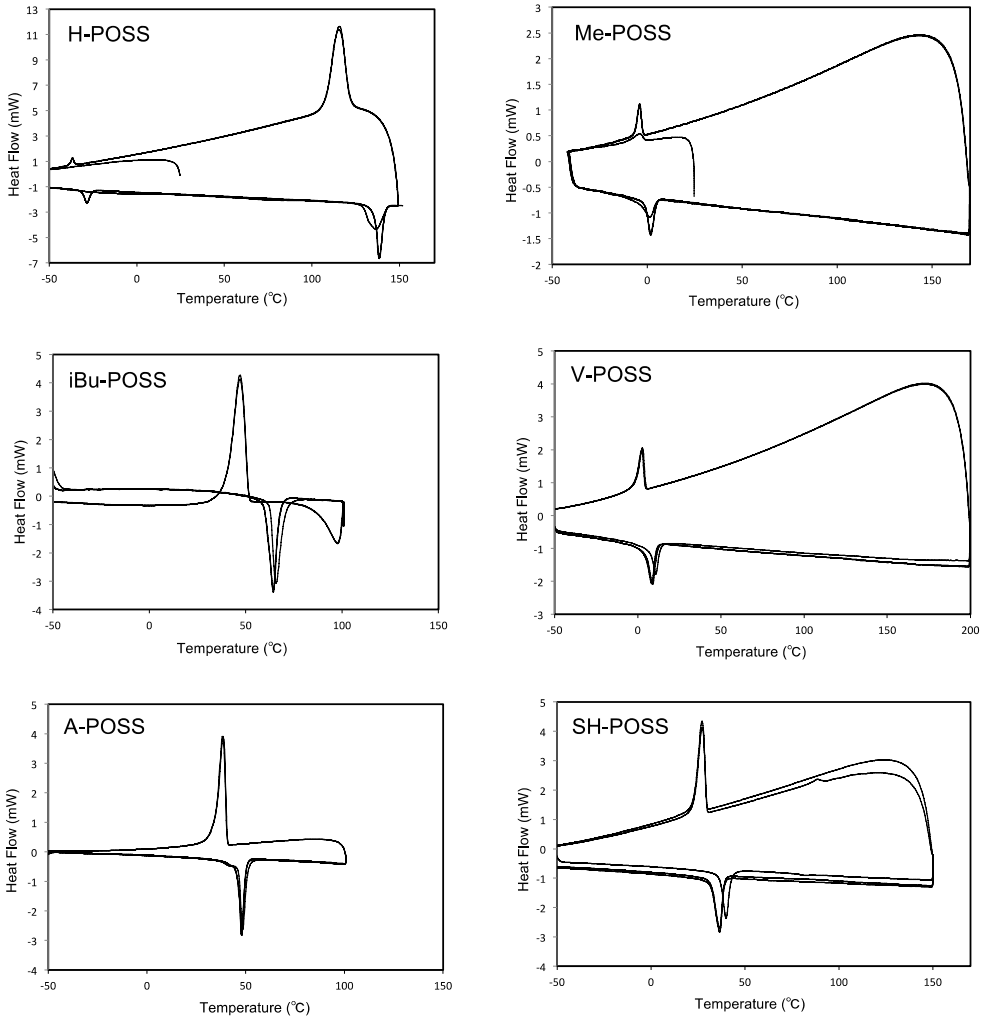

Figure S1 DSC traces of the mono-functionalized POSS (R-POSS).

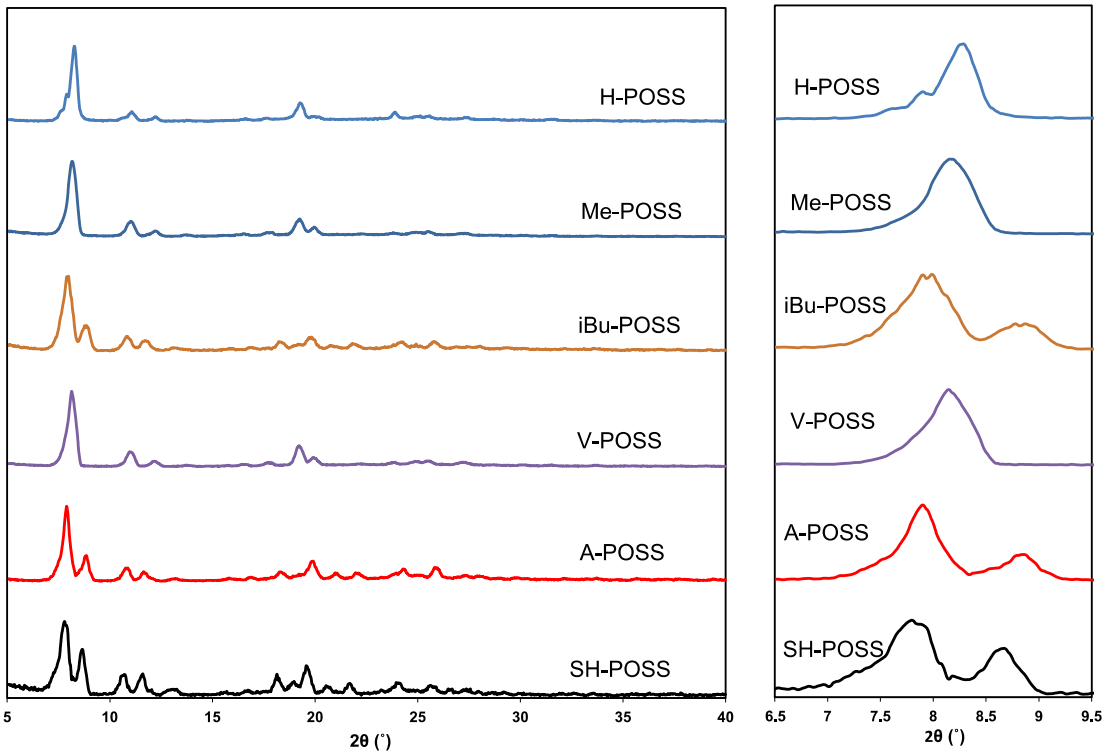

Figure S2 XRD traces of the mono-functionalized POSS (R-POSS).

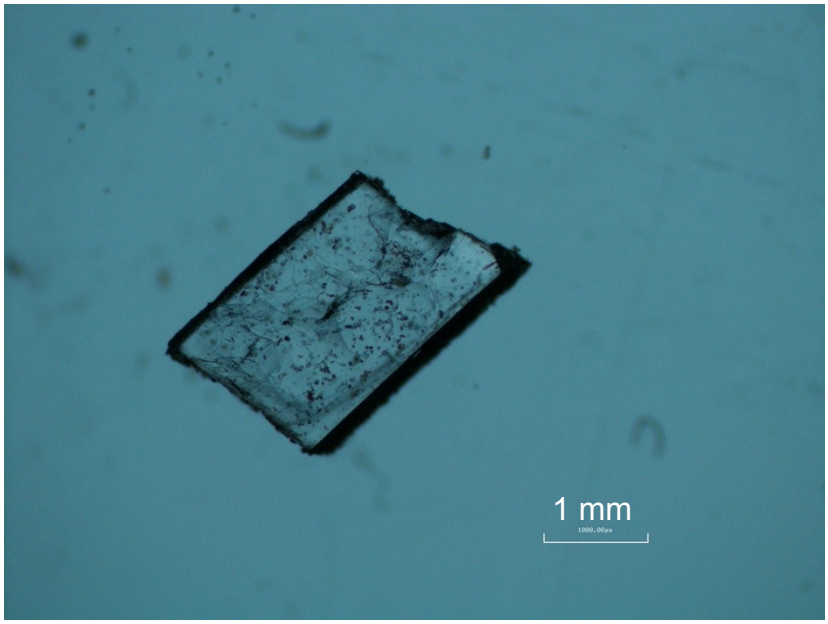

Figure S3 Optical microscopic image of a co-crystal of A-POSS and SH-POSS (1:1).

POSS solid solutions were also obtained in the different combinations of monofunctionalized heptaiosbutyl-substituted octasilsesquoxanes (R-POSS). Same amounts of A-POSS and V-POSS were dissolved in THF and reprecipitated by adding methanol to obtain a mixing sample. The molar ratio was estimated as 0.55/0.45 by 1H NMR analysis. A DSC analysis of the co-precipitates of A-POSS and V-POSS showed a sharp endothermic peak at 29 ˚C which was different from the physical mixture of A-POSS and V-POSS showed two endothermic peaks at 11˚C and 48 ˚C, corresponding of the endothermic peaks of A-POSS and V-POSS, respectively (Figure S4). The simple physical mixture of A-POSS and SH-POSS showed two endothermic peaks at 48 ˚C and 38 ˚C, corresponding of the endothermic peaks of A-POSS and SH-POSS, respectively, even after the first heating to 150 ˚C, suggesting no melting after the phase transition to 150 ˚C.

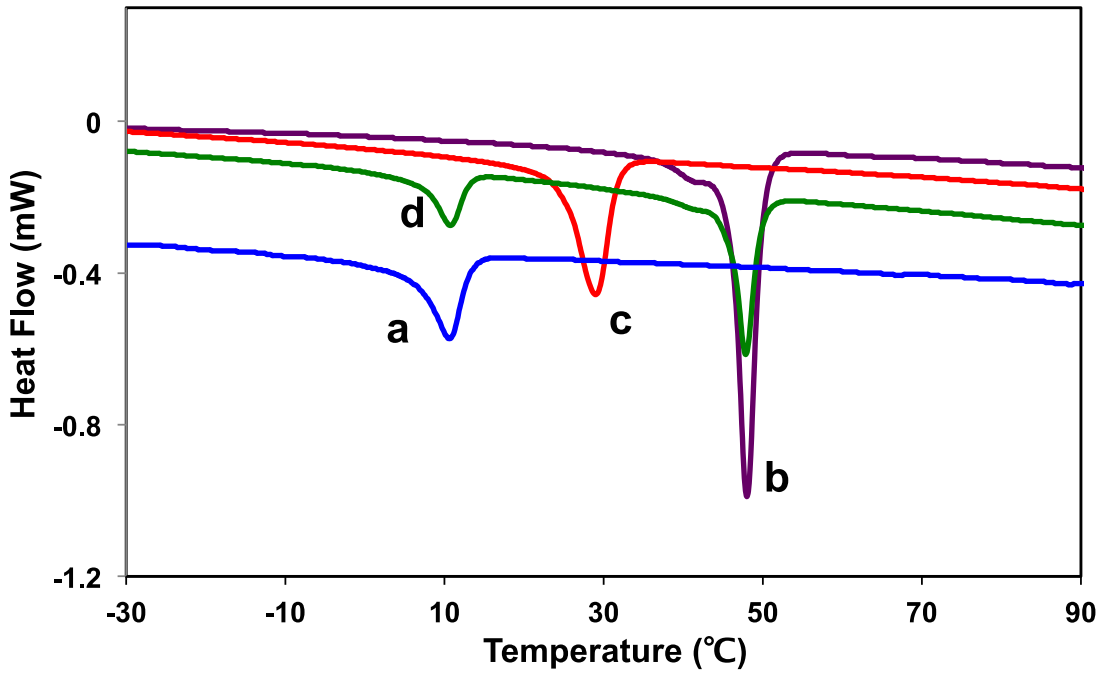

Figure S4. DSC data for (a) V-POSS, (b) A-POSS, (c) co-precipitates of V-POSS and A-POSS (1:1), and (d) physical mixture of V-POSS and A-POSS (1:1).