Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

One-pot synthesis of well-defined amphiphilic alternating copolymer brushes based on POSS and their self-assembly behavior in aqueous solution

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Synthesis of cumyl dithiobenzoate (CDB)

CDB was prepared according to the literature [1]. ^{1}H NMR (ppm, $CDCl_3$): 2.00 (s, 6H, C*H*$_3$); 7.21 (t, 1H, Ar*H*); 7.30 (m, 4H, Ar*H*); 7.43 (t, 1H, Ar*H*); 7.54 (d, 2H, Ar*H*); 7.84 (d, 2H, Ar*H*).

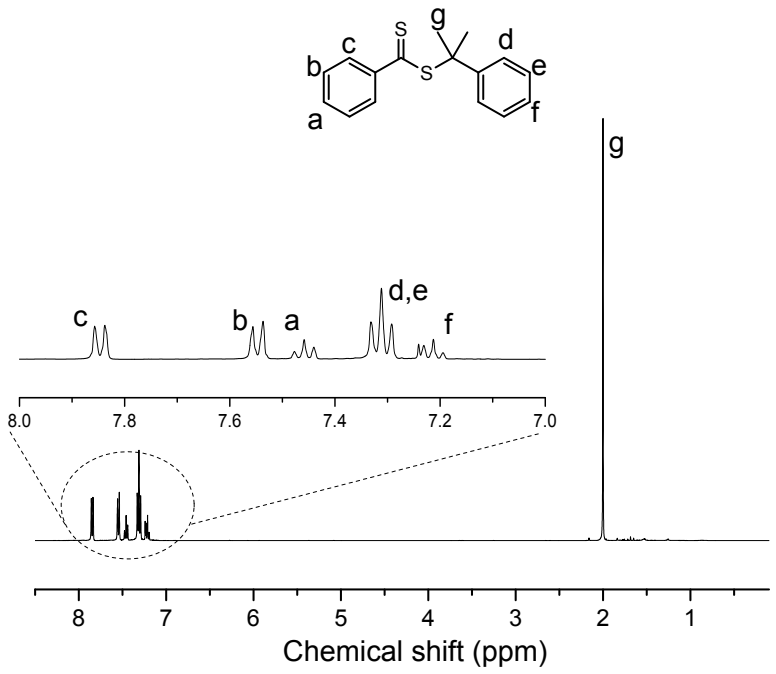

Fig. S1. The ^{1}H NMR spectrum of CDB in $CDCl_3$.

Synthesis of macromonomer (VBPEG)

The macromonomers VBDEG and VBPEG (550/1000/2000) were prepared according to the previous literatures [2, 3]. A typical procedure for the synthesis of VBPEG550 as following: methoxypolyethylene glycol (M_n = 550 g/mol, 4.4 g, 8 mmol) was added into a schlenk flask containing toluene (50 mL), and the mixture was refluxed at 110 ^{o}C overnight. After toluene was removed by evaporation, THF (50 mL) and NaH (0.6 g, 25 mmol) were added under N_2. After the mixture was stirred in an ice bath under N_2 for 1 h, 4-vinylbenzyl chloride (3.05 g, 20 mmol) in THF (20 mL) was added dropwise into above solution. The reaction was carried out at

room temperature for 24 h. Then THF was evaporated and brine (200 mL) was added into the residue. The aqueous phase was extracted with CH_2Cl_2 (50 mL) four times, and the organic phase were dried over anhydrous Na_2SO_4 overnight. The solvent was evaporated under reduced pressure and poured into freezing petroleum ether three times. VBDEG was purified by flash column chromatography on silica gel using ethyl acetate: petroleum ether (1:4 v/v). The product was dried at room temperature in a vacuum oven for 12 h. ^{1}H NMR ($CDCl_3$, ppm): 7.36 (d, 2H, Ar*H*); 7.28 (d, 2H, Ar*H*); 6.69, 5.72, 5.21 (dd, 1H, CH_2=C*H*-); 4.53 (s, 2H, Ar-CH_2-); 3.51-3.67 (m, 88H, -OCH_2CH_2O-), 3.35 (s, 3H, -CH_3).

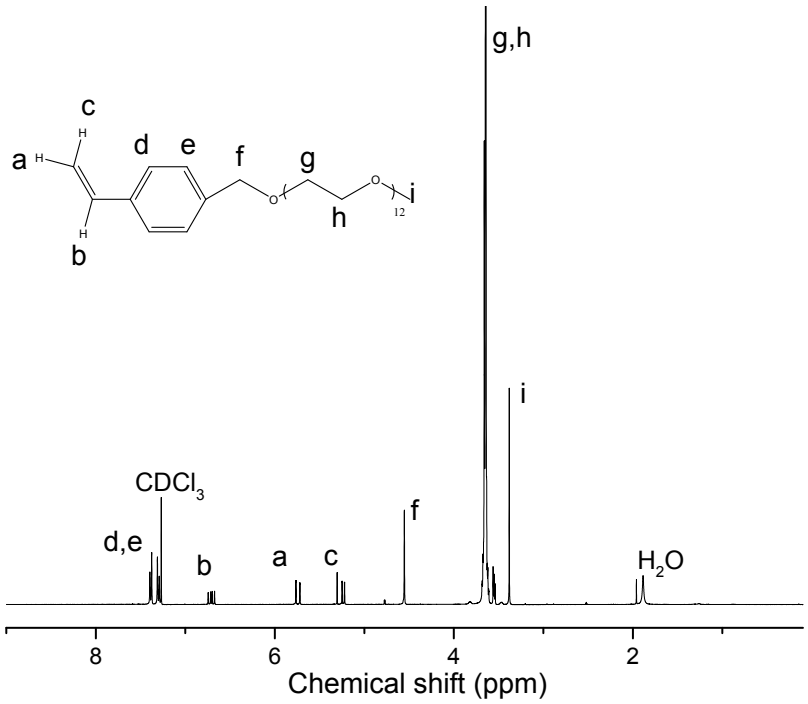

Fig. S2. The ^{1}H NMR spectrum of macromonomer VBPEG550 in $CDCl_3$.

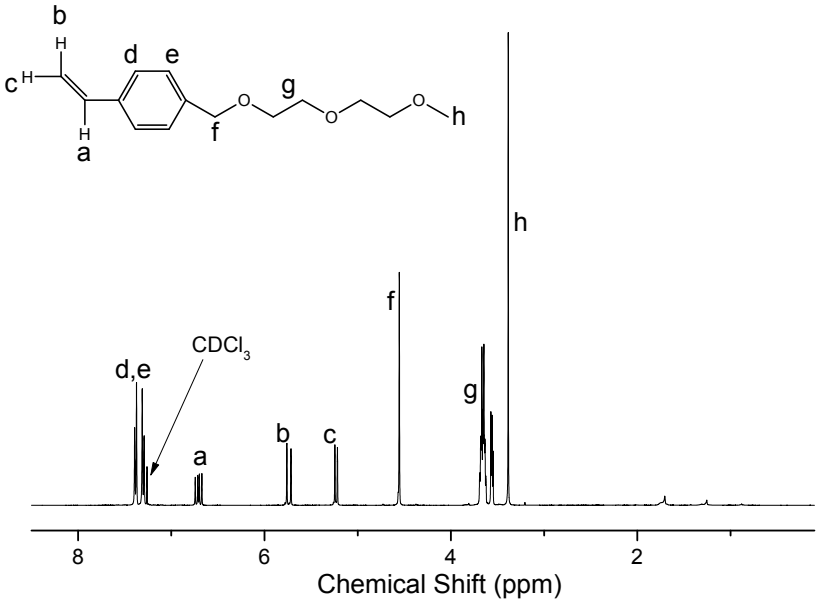

Fig. S3. The ^{1}H NMR spectrum of macromonomer VBDEG in $CDCl_3$.

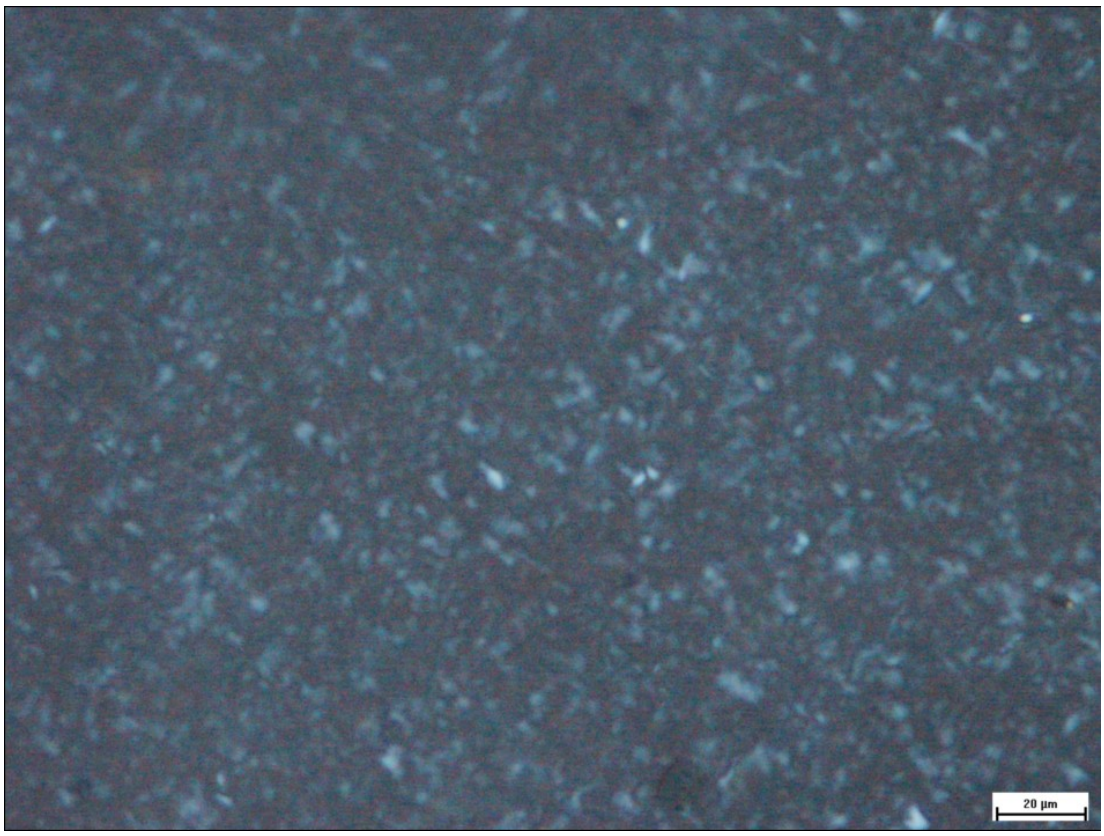

Fig. S4. POM image of P(MIPOSS-*alt*-VBPEG2000)$_{16}$ **2d** crystal. The sample was

prepared by thermal annealing at 160 °C for 30 min, and then cooled from 120 °C to 100 °C at the rate of 2 °C/ min.

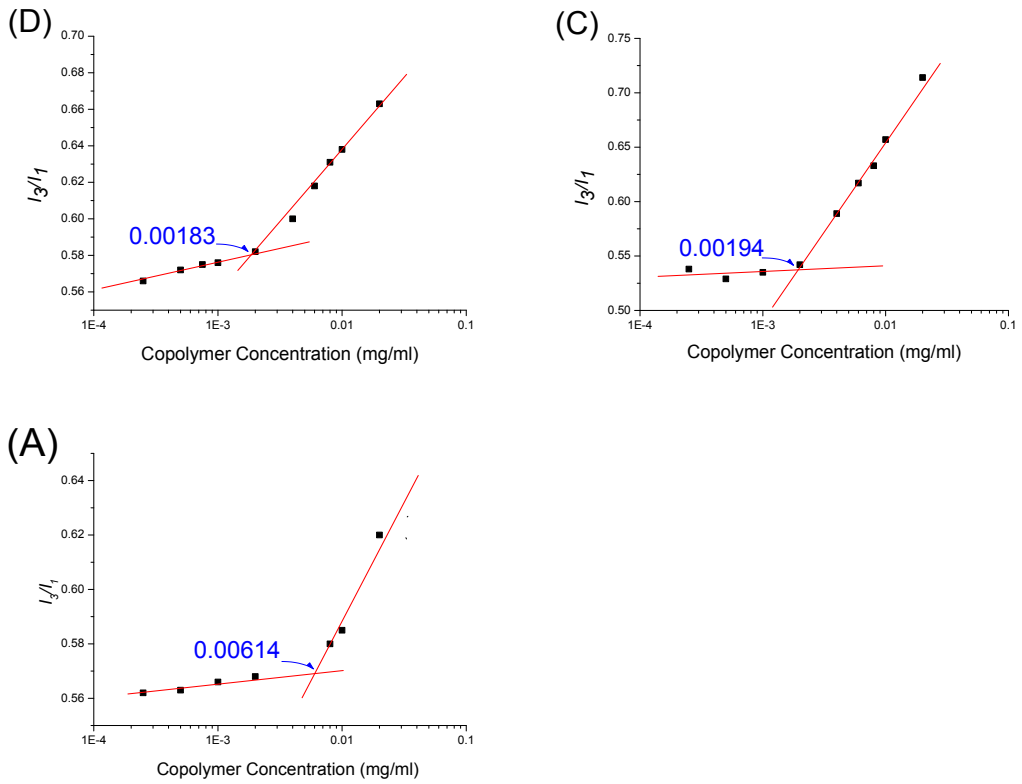

Fig. S5. Plots of the fluorescence intensity ratio I_3/I_1 from pyrene with different concentration of P(MIPOSS-*alt*-VBPEG) in aqueous solution. (A) P(MIPOSS-*alt*-VBDEG)$_{15}$ **2a**, (C) P(MIPOSS-*alt*-VBPEG1000)$_{17}$ **2c**, and (D) P(MIPOSS-*alt*-VBPEG2000)$_{16}$ **2d**.

References

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3. Wilson, M. E.; Paech, K.; Zhou, W. J.; Kurth, M. J. *Journal of Organic Chemistry* **1998,** 63, (15), 5094-5099.