

An insight into the amphiphobicity and thermal degradation behavior of PDMS-based block copolymers bearing POSS and fluorinated units

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Supporting Information

1. Synthesis

1.1 Preparation of PDMS-Br macroinitiator

PDMS-Br using as a macroinitiator in atom transfer radical polymerization (ATRP) reaction was first prepared by esterification of the BiBB with PDMS-OH (~1000 Da), PDMS-OH (~5000 Da) and PDMS-OH (~10000 Da), respectively. In a typical preparation, a solution of THF (50.0 mL), PDMS-OH (0.002 mol), TEA (0.003 mol) and DMAP (0.0045 mol) was added into a 100 mL Schlenk flask degassed by flushing with nitrogen. When the flask was transferred into an ice-bath, BiBB (0.30 mL, 0.0024 mol) was added dropwise into the flask using a syringe under vigorous magnetic stirring. After 24 h, the yielded yellow-white suspension was settled *via* centrifugation and the supernatant was concentrated *via* rotary evaporation. Subsequently, the resultant viscous

liquid was re-dissolved in CH_2Cl_2 , followed by washing with 8 %wt NaHCO_3 aqueous solution, drying over anhydrous MgSO_4 , filtering and removing solvent under vacuum in sequence. This process was repeated thrice to obtain final pure PDMS-Br. By using different PDMS-OH in the same manner as that described above, three macroinitiators were yielded and denoted as PDMS (~1000 Da)-Br, PDMS (~5000 Da)-Br and PDMS (~10000 Da)-Br, respectively.

1.2 ATRP synthesis of di-block copolymer PDMS-*b*-PMMA

Three di-block copolymers PDMS-*b*-PMMA were synthesized *via* ATRP of MMA by using PDMS (~1000 Da)-Br, PDMS (~5000 Da)-Br and PDMS (~10000 Da)-Br as a macroinitiator, respectively. In a typical procedure, into a 100 mL Schlenk flask, a mixture consisting of PDMS-Br (1 mmol), MMA (0.2 mol), PMDETA (1 mmol) and cyclohexanone (40.0 mL) was charged. Then, the mixture was degassed *via* three freeze-pump-thaw cycles, followed by adding CuCl (1 mmol) rapidly under a nitrogen atmosphere and sealing the flask tightly with a rubber stopper. The polymerization was initiated when the reaction flask was placed into an oil bath preheated at 80 °C. After being stirred for 24 h, the polymerization was stopped by cooling the flask rapidly to room temperature and opening to air. Subsequently, the solution of crude product was diluted with THF and percolated through an alumina column in sequence. Collected filtrate was rotary-evaporated before it was added into methanol to precipitate the polymer. Finally, the pure di-block copolymer PDMS-*b*-PMMA was yielded by drying precipitate under vacuum at 40 °C. A yield of approximately 70% is calculated by gravimetric analysis. According to the procedure described above, the yielded di-block copolymers PDMS-*b*-PMMA by using PDMS (~1000 Da)-Br, PDMS (~5000 Da)-Br and PDMS (~10000 Da)-Br as a macroinitiator were correspondingly denoted as DP1, DP2 and DP3.

1.3 ATRP synthesis of tri-block copolymer PDMS-*b*-PMMA-*b*-P(MAPOSS) and PDMS-*b*-

PMMA-*b*-PDFHM

Three PDMS-*b*-PMMA (DP1, DP2 and DP3) were further used as macroinitiators to polymerize either MAPOSS or DFHM *via* ATRP. Correspondingly, the obtained PDMS-*b*-PMMA-*b*-P(MAPOSS) were denoted as TPS1, TPS2 and TPS3. The obtained tri-block copolymer PDMS-*b*-PMMA-*b*-PDFHM were denoted as TPF1, TPF2 and TPF3. A typical ATRP synthesis of tri-block copolymer was described in the following. First, PDMS-*b*-PMMA (containing 0.1 mmol of Br) was dissolved in cyclohexanone (4.2 mL) in a 100 mL Schlenk flask. Then, either DFHM or MAPOSS (1 mmol) and PMDETA (0.1 mmol) were transferred into the polymer solution. After the mixture was degassed *via* three freeze-pump-thaw cycles, CuCl (0.1 mmol) was added rapidly under a nitrogen atmosphere, followed by degassing again and then sealing the flask tightly in the case of the flask refilled with nitrogen. The reaction mixture was stirred for 24 h at 120 °C. Subsequently, it was cooled rapidly to room temperature and exposed to air. The final products of PDMS-*b*-PMMA-*b*-PDFHM and PDMS-*b*-PMMA-*b*-P(MAPOSS) were obtained in a yield of approximately 70% according to the same purification procedure used for PDMS-*b*-PMMA except that hexane was selected as the precipitant.