RSC Advances

RSC Advances

www.rsc.org/advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

RSC Advances

RSCPublishing

ARTICLE

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

Zhenghe Zhang, Lizhi Hong, Jinxia Li, Feng Liu, Haibo Cai, Yun Gao, Weian Zhang*

The poly(maleimide isobutyl polyhedral oligomeric silsesquioxane-*alt*-vinylbenzyl polyethylene glycol) (P(MIPOSS-*alt*-VBPEG)) amphiphilic copolymer brushes with a sequence of alternating MIPOSS and polyethylene glycol (PEG) side chains were synthesized *via* ordinary radical polymerization and reversible addition-fragmentation transfer (RAFT) polymerization, respectively. A series of alternating copolymer brushes prepared by RAFT polymerization had the low polydispersity index (PDI) less than 1.25. The thermal properties of these copolymers were evaluated by differential scanning calorimetry (DSC) and thermo gravimetric analyzer (TGA). The results displayed that MIPOSS units could enhance the thermal properties of the hybrid copolymers effectively. The self-assembly behavior of the P(MIPOSS-*alt*-VBPEG) amphiphilic copolymer brushes in aqueous media was also studied by fluorescence spectrophotometry (FS), transmission electron microscopy (TEM) and dynamic light scattering (DLS). The results showed these alternating copolymer brushes could form spherical aggregates in water.

Introduction

Polymer brushes are unique graft copolymers possessing linear backbones that are covalently attached a high density of side chains, which have been architecturally investigated by material researchers [1, 2]. Comparing with the random coil conformation formed by the conventional polymers, the backbone of polymer brushes is extended greatly to display a wormlike morphology due to the strong steric repulsion between crowded side chains [3]. In general, comb-shaped polymer brushes can be divided into homopolymer brushes and multipolymer brushes. For multipolymer brushes, there are three types including double-cylinder type [4-6], alternation-type [7-12] and block-type [13, 14]. Compared to homopolymer brushes, the alternating polymer brushes, which are incorporated by another type of polymer graft, could afford polymer brushes with extra structural diversity and unusual aggregation properties.

According to the previous reports, the polymer brushes could be synthesized mainly by "grafting from" [9, 11, 15, 16] and "grafting to"[11, 12, 17, 18] approaches. The "grafting through" method, which refers to the direct polymerization of macromonomers, is also regarded as one of the synthetic strategies for polymer brushes in recent years, especially for alternating copolymer brushes. For example, Chen *et al.* successfully synthesized a novel amphiphilic polymer brush with a sequence of alternating poly(ε-caprolactone) (PCL) and poly(ethylene oxide) (PEO) side chains through "grafting through" approach [10]. Ishizu *et al.* obtained alternating hetero-arm copolymer brushes which were synthesized by free-radical copolymerization of methacryloyl-terminated poly(ethylene oxide)(PEO-MA) with vinylbenzyl-terminated polystyrene (PS-VB) or methacryloyl-terminated poly(propylene oxide)(PPO-MA) with vinyl benzyl-terminated poly(ethylene oxide) (PEO-VB), and further investigated their self-assembly behaviors in water [7, 8]. Hillmyer *et al.* synthesized well-defined '*mikto*-brush' terpolymers using alternating radical copolymerization of maleimide (MI) end functionalized poly(methyl-caprolactone) (MI-PMCL) and styrene end functionalized poly(perfluoro propylene oxide) (PFPO) [19]. However, to the best of our knowledge, the alternating copolymer brushes based on inorganic components have not been reported.

Polyhedral oligomeric silsesquioxanes (POSS), with a size in nanoscale, has attracted a great deal of attention in materials fields, since it can be incorporated into polymer matrices to obtain many novel hybrid polymers with extraordinary properties [20-30]. Over the past few decades, self-assembly based on POSS has also attracted great interests in polymer science, since it could form a wide range of assembled morphologies in nanoscale [30]. A wide variety of POSS-containing hybrid polymers with topological structures have been synthesized, such as hemi-telechelic (tadpole-shaped) [31-36], di-telechelic (dumbbell-shaped) [37-40], multi-telechelic [36], star-shaped polymers [41-43], alternating copolymers [44] and block copolymers [45-51], and some interesting self-assembled morphologies based on these hybrid polymers have also been achieved. Recently, we constructed POSS-containing poly(styrene-*alt*-maleimide isobutyl POSS) alternating copolymer by alternating copolymerization of maleimide isobutyl POSS with styrene, and the molecular weight of the alternating copolymer can be well controlled by the amount of RAFT agent. Poly(styrene-*alt*-

maleimide isobutyl POSS)-*block*-polystyrene (PSMIPOSS-*b*-PS) block copolymers were also prepared by one-pot RAFT polymerization, and their self-assembly behavior in bulk exhibited a series of short-range order phase transitions from the POSS sphere, POSS cylinder to lamella structures with varying the weight fraction of MIPOSS from 13% to 64% [44].
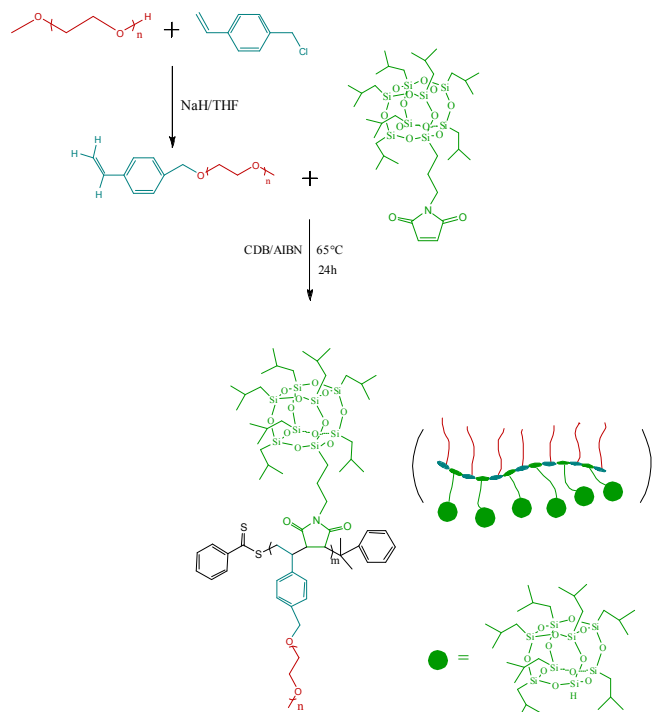
Scheme 1 Synthesis of amphiphilic alternating polymer brushes P(MIPOSS-*alt*-VBPEG) by RAFT polymerization.

Here，we employed the "grafting through" method to synthesize amphiphilic POSS-containing organic-inorganic hybrid alternating copolymer brushes using maleimide isobutyl POSS (MIPOSS) and 4-vinylbenzyl-terminated polyethylene glycol(VBPEG) *via* ordinary radical polymerization and RAFT polymerization (**Scheme 1**), respectively. The well-defined alternating structure of copolymer brushes was characterized by GPC and NMR. Their thermal properties were evaluated by differential scanning calorimetry (DSC) and thermo gravimetric analyzer (TGA). The self-assembly behavior of alternating copolymers P(MIPOSS-*alt*-VBPEG) in aqueous solution was further studied by transmission electron microscopy (TEM) and dynamic light scattering (DLS).

Experimental Section

Materials

Maleimide isobutyl polyhedral oligomeric silsesquioxane (MIPOSS) was purchased from Hybrid Plastics Company without further purification. Tetrahydrofuran (THF, Shanghai LingFeng Chemical Reagent Co.) was distilled over sodium prior before use. Methoxypolyethylene glycol (PEG, M_n = 550/1000/2000, Aladdin) and diethylene glycol monomethyl ether (DEG, M_n = 120, Aladdin) was azeotropically dried by toluene. 2, 2'-Azobisisobutyronitrile (AIBN) was recrystallized twice from ethanol. Benzoyl peroxide (BPO) was dissolved in chloroform to filter off the insoluble impurity, then the filtrate

was dropwise added into cold methanol and white crystals were collected. 4-Vinylbenzyl chloride (VBC, TCI), Sodium hydride (NaH, Shanghai LingFeng Chemical Reagent Co.) and other reagents were used directly as received.

Characterization

The ^{1}H NMR and ^{13}C NMR measurements were carried out on a BRUKER AV400 spectrophotometer. The samples were dissolved with CDCl$_3$ with tetramethylsilane (TMS) as an internal reference. The number average weight (M_n) and polydispersity index (PDI) were determined using a Waters 1515 gel permeation chromatograph (GPC) equipped with refractive index detector and ultrastyragel columns of 100-10 000 Å porosities. The GPC system was calibrated using polystyrene as the standards and tetrahydrofuran (THF) was used as the eluent at a flow rate of 1 mL/min. Transmission electron microscopy (TEM) analysis was carried out on a JEOL JEM1400 electron microscope operated at 100 kV. The self-assembly aggregate solution was directly dropped onto a carbon-coated copper grid, and then dried in ambient atmosphere. The hydrodynamic diameter (D_h) was characterized by dynamic light scattering (DLS) performed on a BECKMAN COULTER Delasa Nano C particle analyzer with wavelength of 532 nm at 25 °C and scattering angle was 165°. The critical micelle concentration (CMC) of P(MIPOSS-*alt*-VBPEG) alternating copolymer in aqueous solution was measured by fluorescence spectrophotometry (FS) using pyrene as the hydrophobic fluorescent probe. Differential scanning calorimetry (DSC) was performed using a Perkin Elmer Diamond DSC instrument under a N$_2$ atmosphere. The samples were first heated up to 160 °C at the heating rate of 50 °C/min and hold at this temperature for 5 min, then followed by quenching to -80 °C. The second heating scans were carried out from -80 °C to 160 °C at the heating rate of 10 °C/min and the thermograms were recorded. The thermal stability of the samples was characterized using a Perkin Elmer Pyris 1 thermo gravimetric analyzer (TGA) under a N$_2$ atmosphere. The cured samples under a N$_2$ (flow rate: 60 mL/min) were heated up from 30 to 800 °C at the heating rate of 20 °C/min. The crystallization was observed using a Leitz Laborlux 12PolS polarized optical microscopy (POM) equipped with a Mettler FP 802 hot-stage. The sample was sandwiched between two thin glass slides. It 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.

Synthesis of alternating copolymer brushes P(MIPOSS-*alt*-VBPEG) 1 by ordinary radical polymerization

The P(MIPOSS-*alt*-VBPEG) amphiphilic copolymer brushes were first synthesized *via* ordinary radical polymerization. The ordinary radical polymerization procedure for the synthesis of alternating copolymer brush P(MIPOSS-*alt*-VBPEG550) **1b** as following: A 10 mL flask containing a stirring bar was charged with MIPOSS (0.477 g, 0.5 mmol), VBPEG550 (0.33 g, 0.5 mmol), BPO (4.84 mg, 0.02 mmol) and 2.0 mL of 1, 4-dioxane. The solution in the flask was degassed by three freeze-evacuate-thaw cycles, and then the glass tube was sealed under vacuum. The polymerization was carried out in an oil bath at 65 °C for 48 h. The polymerization was stopped immediately by plunging the tube into liquid nitrogen. The polymerization tube was opened. Then the solution was diluted into 10 mL and dialyzed in THF using a dialysis membrane (MWCO = 12 000). After one week, the nonreactive MIPOSS and VBPEG were

completely removed. The product was dried at room temperature in a vacuum oven for 24 h. M_n = 28 500, PDI = 1.25.

Synthesis of alternating copolymer brushes P(MIPOSS-*alt*-VBPEG) 2 by RAFT polymerization

A typical RAFT polymerization procedure for the synthesis of alternating copolymer brush P(MIPOSS-*alt*-VBPEG550)$_{18}$ **2b** as following: A 10 mL flask containing a stirring bar was charged with MIPOSS (0.477 g, 0.5 mmol), VBPEG550 (0.33 g, 0.5 mmol), AIBN (0.33 mg, 0.002 mmol)，CDB (5.43 mg, 0.02 mmol) and 2.0 mL of 1, 4-dioxane. The solution in the flask was degassed by three freeze-evacuate-thaw cycles, and then the glass tube was sealed under vacuum. The polymerization was carried out in an oil bath at 65 °C for 24 h. The product purification was similar to above produce. M_n = 16 100, PDI = 1.23. ^{1}H NMR (CDCl$_3$, ppm): 6.30-7.26(m, Ar*H*); 3.51-3.67(m, -C*H$_2$*C*H$_2$*O-); 3.35(m, -OC*H$_3$*); 3.00-3.70, 1.00-1.55 (m, main chain -C*H$_2$*-); 1.88 (m, -CH$_2$C*H* (CH$_3$)$_2$); 0.94 (m, -CH$_2$CH (C*H$_3$*)$_2$); 0.63 (m, -C*H$_2$*CH (CH$_3$)$_2$).

Self-assembly of P(MIPOSS-*alt*-VBPEG) in aqueous solution

The typical self-assembly procedure for alternating copolymer P(MIPOSS-*alt*-VBPEG) is described below: P(MIPOSS-*alt*-VBPEG) (1 mg) was first dissolved in THF (1 mL) to get the solution with the concentration of 1 mg/mL. Then 5 mL of deionized water was slowly added with a syringe pump at the rate of 2.5 mL/h. After the addition was completed, the solution was stirred overnight and gradually dialyzed against deionized water for 3 days. The self-assembly solution was dialyzed at least three times using deionized water to make sure to remove THF completely. Finally, the deionized water was added to the self-assembly solution until the volume of the solution increased to 10 mL, and the concentration of the self-assembly aggregate solution was 0.1 mg/mL.

Results and discussion

Synthesis of P(MIPOSS-*alt*-VBPEG) alternating copolymer brushes

The P(MIPOSS-*alt*-VBPEG) alternating copolymer brushes were synthesized *via* ordinary radical polymerization and RAFT polymerization, and the polymerization results are listed in **Table 1** and **Table 2,** respectively. Firstly，the ordinary radical polymerization was carried out in 1, 4-dioxane at 65 °C for 48 h using BPO as initiator. **Fig. 1** shows the GPC traces of P(MIPOSS-*alt*-VBPEG) alternating copolymer brushes synthesized by ordinary radical polymerization. It is seen that all the GPC curves of P(MIPOSS-*alt*-VBPEG) are unsymmetrical. The curves of samples **1a** and **1b** show some shoulders towards higher elution volume, while the curve of sample **1c** shows a shoulder towards lower elution volume. Additionally, there are clear trailing phenomenon in the curves of samples **1b** and **1d**. Thus, it was hard to obtain well-defined P(MIPOSS-*alt*-VBPEG) alternating copolymer brushes by ordinary radical polymerization.

The RAFT polymerization was carried out in 1, 4-dioxane at 65 °C for 24 h using AIBN as initiator, cumyl dithiobenzoate (CDB) as a chain transfer agent. **Fig. 2** shows the GPC traces of P(MIPOSS-*alt*-VBPEG) alternating copolymer brushes

synthesized by RAFT polymerization. In contrast to the GPC curves of P(MIPOSS-*alt*-VBPEG) synthesized *via* ordinary radical polymerization, all the GPC traces of P(MIPOSS-*alt*-VBPEG) synthesized *via* RAFT polymerization are well symmetric and no shoulder appeared. Moreover, the molecular weight distribution is quite narrow (less than 1.25) which indicated that the alternating copolymerization of MIPOSS and VBPEG was living/well-controlled *via* RAFT polymerization.

Additionally, from **Fig.1** and **Fig. 2**, the molecular weight of alternating copolymers measured by GPC does not increase with the molecular weight of VBPEG monomers increasing, but the NMR results show they increase with the molecular weight of VBPEG monomers **(Table 2)**. This is resulted from the GPC measurement based on linear polystyrene standards. Comparing to the linear polymers, the molecular weight of non-linear polymers such as branched and star-shaped polymers measured by GPC is much smaller than their absolute molecular weight because of their rather small hydrodynamic volume in the eluent[41, 52, 53]. In this work, P(MIPOSS-*alt*-VBPEG) alternating copolymers are not linear polymers, but brush-shaped polymers. With increasing the chain length of VBPEG monomer, these polymer brushes which are similar to conventional star-shaped polymers should also have a smaller hydrodynamic volume in GPC measurement. Thus, the molecular weight of P(MIPOSS-*alt*-VBPEG) measured by GPC ($M_{n,GPC}$) is smaller than that measured by ^{1}H NMR ($M_{n,NMR}$).
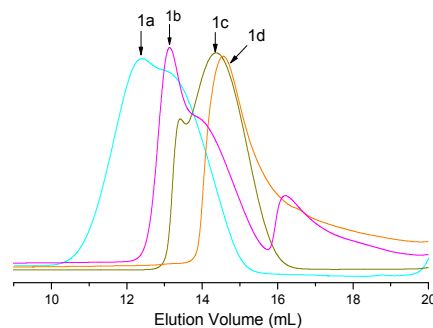

Fig. 1 GPC chromatograms of alternating copolymer brushes P(MIPOSS-*alt*-VBPEG) **1** synthesized by ordinary radical polymerization.
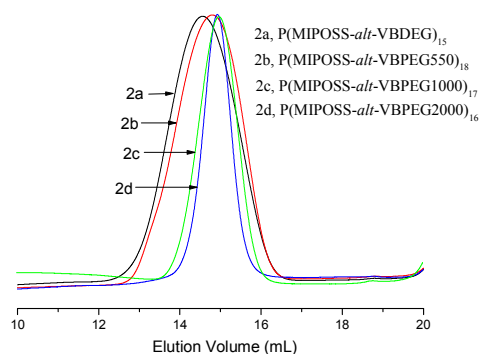

Fig. 2 GPC chromatograms of alternating copolymer brushes P(MIPOSS-*alt*-VBPEG) **2** synthesized by RAFT polymerization.

Table 1 Results of alternating copolymer brushes, P(MIPOSS-*alt*-VBPEG) **1** prepared *via* ordinary radical polymerization

No.	Samples[a]	M_n (g/mol)[b]	M_w/M_n[b]
1a	P(MIPOSS-*alt*-VBDEG)	49 700	1.59
1b	P(MIPOSS-*alt*-VBPEG550)	28 500	1.25
1c	P(MIPOSS-*alt*-VBPEG1000)	19 600	1.21
1d	P(MIPOSS-*alt*-VBPEG2000)	9 100	1.55

[a] the polymerization reaction proceeded in 1, 4-dioxane at 65 °C for 48 h; [MIPOSS]$_o$/[VBPEG]$_o$/[BPO]$_o$ = 25:25:1
[b] determined by GPC with polystyrene standards.

Table 2 Results of alternating copolymer brushes, P(MIPOSS-*alt*-VBPEG) **2** prepared *via* RAFT polymerization

No.	Samples[a,c]	$M_{n,GPC}$[b]	χ[d]	$M_{n,NMR}$[d]	M_w/M_n[b]	Wt % (MIPOSS)
2a	P(MIPOSS-*alt*-VBDEG)$_{15}$	17 200	0.62	18 700	1.25	88.8
2b	P(MIPOSS-*alt*-VBPEG550)$_{18}$	16 100	0.71	29 000	1.23	63.4
2c	P(MIPOSS-*alt*-VBPEG1000)$_{17}$	14 500	0.67	34 900	1.08	48.8
2d	P(MIPOSS-*alt*-VBPEG2000)$_{16}$	14 900	0.65	50 100	1.05	32.3

[a] the polymerization reaction proceeded in 1, 4-dioxane at 65 °C for 24 h; [MIPOSS]$_o$/[VBPEG]$_o$/[CDB]$_o$/[AIBN]$_o$ = 25:25:1:0.1
[b] determined by GPC with polystyrene standards.
[c] the numbers correspond to the degree of polymerization, as determined by ^{1}H NMR.
[d] $M_{n,NMR}$ = [M]$_o$ / [CTA]$_o$ × (M_{MIPOSS} + M_{VBPEG}) × χ + M_{CDB} , where M_{MIPOSS}, M_{VBPEG} and M_{CDB} are the molecular weights of MIPOSS, VBPEG and CDB, respectively; χ is the conversion determined by ^{1}H NMR.

It was well known that the copolymerization of styrene derivative with maleic anhydride or maleimide could produce well-defined alternating structure through a charge-transfer complex (CTC) [10, 11, 17, 19, 54-57]. The ^{1}H NMR spectrum of alternating copolymer brush P(MIPOSS-*alt*-VBPEG550)$_{18}$ **2b** is shown in **Fig. 3**. Besides the signals from the methine and methylene protons of the main chain in alternating copolymer appear at 1.00-1.55 ppm, the characteristic signals at 3.35 (f) and 3.59 (e) ppm are respectively ascribed to the methyl and methylene protons derived from PEG. The aromatic protons in styrene unit are detected at 6.30-7.26 (h) ppm, then the methylene protons derived from benzyl group (ArC*H*$_2$O-) and MIPOSS monomer (=N-C*H*$_2$CH$_2$-) are detected at 4.20-4.75 (d, g) ppm. The signals of resonance at 0.63 (a, a'), 0.94 (c) and 1.88 (b, b') ppm are assignable to the protons from the *iso*-butyl group of POSS units. By comparing the integration area of the signal at 0.63 ppm to that of methyl protons at 3.35 ppm in PEG, the ratio of MIPOSS and VBPEG repeating units was determined to be 1:1, which suggested the alternating sequence structure of the copolymer.
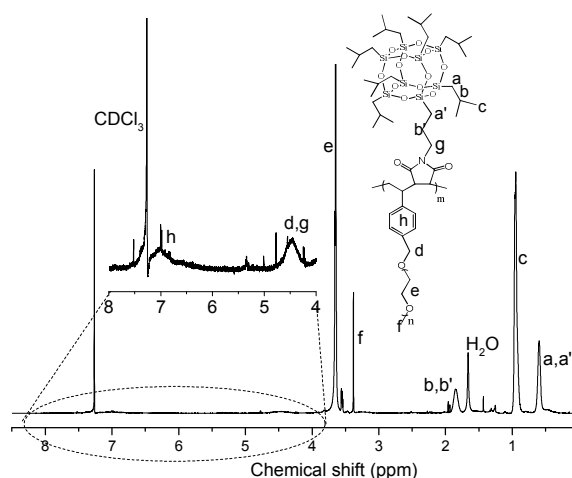
Previously, Fu *et al.* synthesized poly(*N*-phenyl maleimide-*alt*-*p*-chloromethyl styrene) (P(NPMI-*alt*-CMS)) by RAFT polymerization. To demonstrate that the copolymers possess an alternating structure, the copolymerization of NPMI and CMS in equimolar comonomer feed was carried out. They found that the compositions of the alternating copolymers were always close to 1:1 at different conversions determined from ^{1}H NMR [55]. Additionally, Li *et al.* prepared poly(maleic anhydride-*alt*-styrene) (P(MAn-*alt*-St)) copolymer using RAFT polymerization, and they used GC to determine the conversions of both MAn and St to reveal the alternating nature of the P(MAn-*alt*-St) [54]. So, to further prove the alternating nature of the P(PMIPOSS-*alt*-VBPEG) copolymers, we also chose the MIPOSS and VBDEG with a molar feed of 1:1 to demonstrate the RAFT alternating polymerization process. The conversion of both MIPOSS and VBDEG was determined by ^{1}H NMR. As shown in **Fig. 4**, with the polymerization time increasing from 0 to 24 h, the conversion of MIPOSS almost equally increases with that of VBDEG, indicating P(PMIPOSS-*alt*-VBPEG) copolymers prepared by RAFT polymerization owned a predominantly alternating character at any monomer conversion.
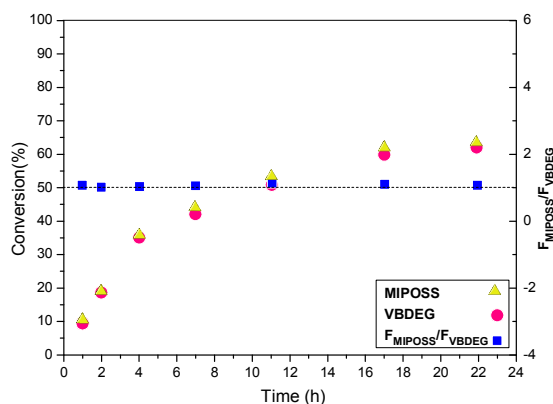

Fig. 3 The ^{1}H NMR spectrum of P (MIPOSS-*alt*-VBPEG550)$_{18}$ **2b** in CDCl$_3$.

Fig. 4 Evolution of monomer conversion for MIPOSS and VBDEG and their molar ratio (F_{MIPOSS}/F_{VBDEG}) in copolymer with the polymerization time *via* RAFT polymerization.

Thermal properties

The thermal stability of the alternating copolymer brushes P(MIPOSS-*alt*-VBPEG) **2** synthesized by RAFT polymerization was investigated by differential scanning calorimetry (DSC) analysis. **Fig. 5** is the second heating traces of these POSS-containing copolymers. From the DSC thermograms, we can see two characteristic melting peaks, where the lower melting point (T_m) is due to PEG, while the higher one is ascribed to the MIPOSS moieties [58]. In the case of sample 2d, the narrow peak based on T_m of PEG segments is clearly observed at 34 °C. It can be also found a small shoulder in the peak, which may be due to phase separated PEG crystallites of different sizes and thicknesses. With decreasing the molecular weight of PEG, corresponding to the increase of the content of MIPOSS moieties, the PEG-based T_m of sample **2c** is shifted to 2 °C, while the peak is broadened. The decrease of T_m about PEG implied that MIPOSS moieties could hinder the crystallization of PEG chains [59, 60]. However, in the case of samples **2b** and **2a**, we can not find any sharp endothermic peaks corresponding to the PEG-based T_m. The absence of such melting endotherms was probably due to the following two reasons: first, the molecular weight of PEG in samples **2a** and **2b** is too low to form the PEG crystals; second, the bulky MIPOSS moieties may be complete disruption of the orderly pattern of the PEG crystals [60]. Comparing to the PEG-based T_m, the T_m of MIPOSS in samples **2b, 2c** and **2d** is almost invariable, which ranged between 119 °C and 126 °C. In order to confirm the MIPOSS crystal morphology, POM was employed. **Fig. S4** shows the POM images of sample **2d.** The POM image shows the spherulite clearly when the sample **2d** is prepared by thermal annealing at 160 °C for 30 min, then cools from 120 °C to 100 °C at the rate of 2 °C /min. Additionally, the MIPOSS-based T_m in sample **2a** can not be observed as well, which was perhaps because while MIPOSS units destroyed the orderly PEG crystals, the PEG with the low molecular weight suppresses the crystallization of MIPOSS moieties as well.
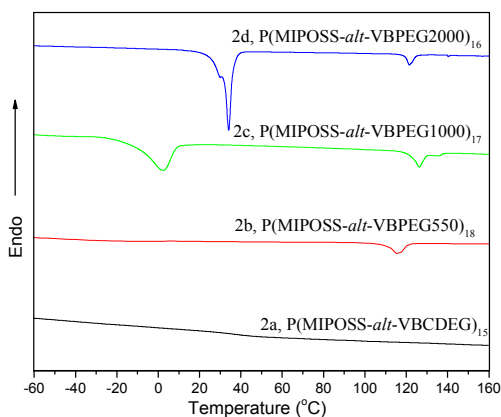

Fig. 5 DSC thermograms of alternating copolymer brushes P(MIPOSS-*alt*-PEG) **2** synthesized by RAFT polymerization.
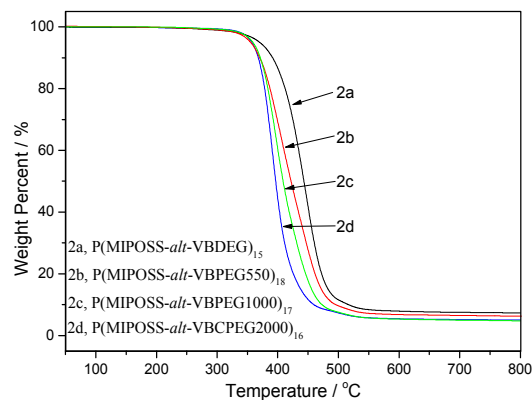

Fig. 6 TGA analyses of alternating copolymer brushes P(MIPOSS-*alt*-VBPEG) **2** synthesized by RAFT polymerization.

The alternating copolymer brushes P(MIPOSS-*alt*-VBPEG) **2** synthesized by RAFT were also investigated by the thermo gravimetric analysis (TGA) in nitrogen atmosphere. **Fig. 6** shows the TGA curves of these POSS-containing copolymers. The initial decomposition temperature of the alternating copolymers is quite close, so we chose the 20 wt % weight loss temperature to judge the thermal stability of all samples. It can be seen that the degradation temperature (T_d) of P(MIPOSS-*alt*-VBPEG) alternating copolymer brushes at 20 wt % weight loss decreased with increasing the molecular weight of PEG in copolymers, corresponding to the decrease of the content of MIPOSS moieties in polymeric matrixes. Additionally, the yield of degradation residues increases with increasing the mass fraction of MIPOSS in copolymers [61]. Thus, it indicated the MIPOSS units obviously enhanced the thermal stability of the P(MIPOSS-*alt*-VBPEG) alternating copolymer brushes.

Self-assembly of P(MIPOSS-*alt*-VBPEG) in aqueous solution

With both a hydrophilic segment and a hydrophobic segment, amphiphilic alternating polymer brushes often show an amphiphilic character that they could self-assemble into interesting nanostructures in aqueous solution. Previously, Liu *et al.* synthesized P(MMA-*alt*-NIPAM) amphiphilic alternating copolymer brushes. They could self-assemble into spherical aggregates in water [11]. Zheng *et al.* synthesized P(MAPOSS-*r*-MAPEO) random copolymers with the different molar ratios of MAPOSS to MAPEO. As a result, the micelle-like aggregates were obtained [59]. In this case, the brush-shaped P(MIPOSS-*alt*-VBPEG) alternating copolymers with hydrophobic POSS segment and hydrophilic PEG segment provided an opportunity to investigate their self-assembly behavior in aqueous solution.
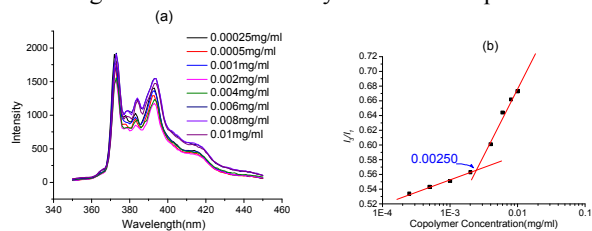

Fig. 7 (1) Fluorescence spectra of pyrene with different concentration of P(MIPOSS-*alt*-VBPEG550)$_{18}$ **2b** in aqueous

solution. (2) Plots of the fluorescence intensity ratio I_3/I_1 from pyrene with different concentration of the sample **2b** in aqueous solution.

The critical micelle concentration (CMC) of the P(MIPOSS-*alt*-VBPEG) **2** in aqueous solution was measured by using pyrene as the fluorescent probe. Pyrene would preferentially partition into hydrophobic microdomain showing strong fluorescence intensity while weak fluorescence intensity in water [62]. **Fig. 7** is the fluorescence spectra of pyrene with different concentration of P(MIPOSS-*alt*-VBPEG550)$_{18}$ **2b** in aqueous solution and plots of the fluorescence intensity ratio of I_3/I_1 from pyrene with different concentration of sample **2b** in aqueous solution. It was found that I_3/I_1 increased sharply when the concentration exceeded a certain value, which means the incorporation of the pyrene into the hydrophobic core of micelles. The CMC of the sample **2b** was then determined to be the intersection of two straight lines with a value of 0.00250 mg/mL. Additionally, **Fig. S5** shows the intensity ratio of I_3/I_1 as a function of P(MIPOSS-*alt*-VBPEG) **2a**, **2c** and **2d** with different concentration in aqueous solution. The CMC of these samples was calculated 0.00183, 0.00194 and 0.00614 mg/mL, respectively.
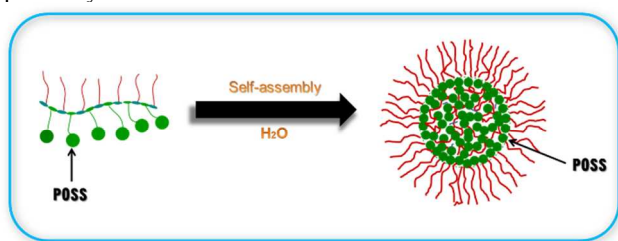
Scheme 2 Self-assembly of amphiphilic alternating polymer brushes P(MIPOSS-*alt*-VBPEG) **2**.
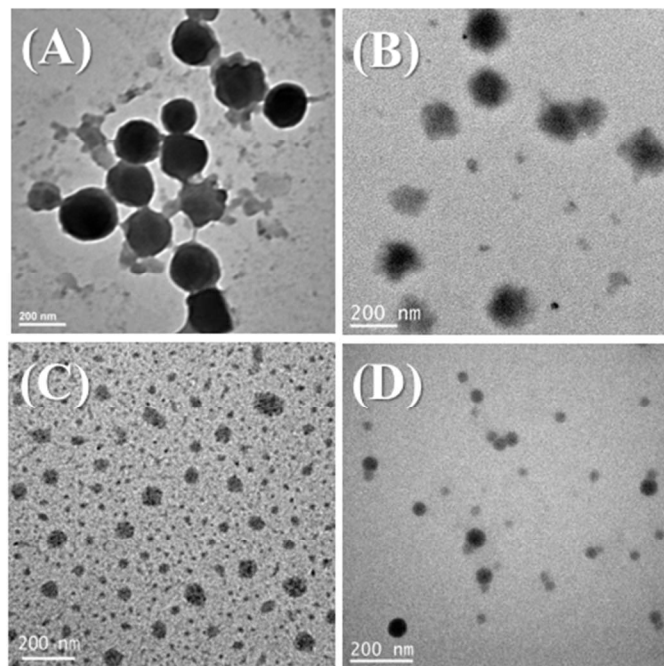

Fig. 8 TEM images obtained by of self-assembled aggregates solution of P(MIPOSS-*alt*-VBPEG) at a concentration of 0.1 mg/mL, (A) P(MIPOSS-*alt*-VBDEG)$_{15}$ **2a**, (B) P(MIPOSS-*alt*-VBPEG550)$_{18}$ **2b,** (C) P(MIPOSS-*alt*-VBPEG1000)$_{17}$ **2c,** and (D) P(MIPOSS-*alt*-VBPEG2000)$_{16}$ **2d**.

Transmission electron microscopy (TEM) is used to characterize the morphology of the self-assembled aggregates from alternating copolymer brushes P(MIPOSS-*alt*-VBPEG) **2** (Fig. 8). From the images, we observe that all the alternating copolymer brushes can form spherical aggregates with the size range from 70 to 200 nm. Moreover, the average size of the spherical aggregates decreases with the increase of the chain length of hydrophilic PEG monomer. The similar result was also observed by He *et al*. They found the size of assembled aggregates decreased with decreasing hydrophobic PMAPOSS content of PEG-*b*-P(MA-POSS) diblock copolymers in aqueous solution [48]. Additionally, for a single aggregate, it can be seen that its density is not uniform, especially for the aggregate from P(MIPOSS-*alt*-VBPEG1000)$_{17}$ copolymer **(Fig. 8c)**, which means it is not a typical core-shell micelle with hydrophobic POSS moieties as the core and hydrophilic PEG chains as the shell. Here, the core of these spherical aggregates may contain some PEG chains except for POSS moieties, which is resulted from the alternating structure of P(MIPOSS-*alt*-VBPEG) copolymers **(Scheme 2)**.
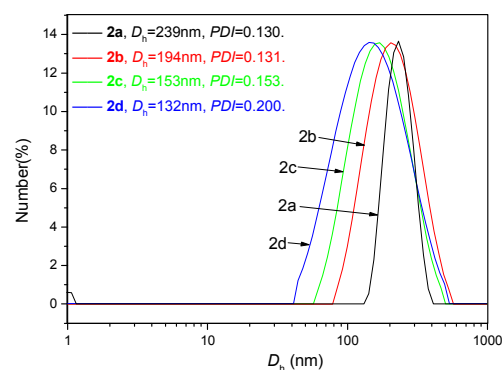

Fig. 9 Z-average hydrodynamic Diameter (D_h) of P(MIPOSS-*alt*-VBPEG) **2** self-assembled aggregates and polydispersity index (P.D.I.) with a concentration of 0.1mg/mL in aqueous solution.

The self-assembly aggregate solution was also evaluated by DLS. **Fig. 9** is the DLS curves of P(MIPOSS-*alt*-VBPEG) **2** self-assembly aggregates with a concentration of 0.1 mg/mL in aqueous solution. DLS measurement shows the size of these aggregates varies at 132-239 nm. Here, the size of the aggregates measured with DLS was slightly higher than that by TEM, since PEG as the corona of spherical aggregates could not be observed in TEM images. Additionally, DLS results also showed the size of the aggregates of these alternating copolymer brushes increases with the decrease of the chain length of PEG monomer, which was agreeable to that measured by TEM.

Conclusions

The P(MIPOSS-*alt*-VBPEG) amphiphilic alternating copolymer brushes were prepared *via* ordinary radical polymerization and RAFT polymerization, respectively. In contrast to P(MIPOSS-*alt*-VBPEG) copolymers synthesized *via* ordinary radical polymerization, all the P(MIPOSS-*alt*-VBPEG) copolymers prepared by RAFT polymerization had a well-defined alternating structure. The DSC results showed the crystallization behavior of PEG segments was greatly

suppressed by the POSS moieties in copolymers. TGA results indicated that the thermal stability of the P(MIPOSS-*alt*-VBPEG) could be effectively enhanced by the incorporation of MIPOSS. For the self-assembly behavior of the P(MIPOSS-*alt*-VBPEG) amphiphilic copolymer brushes in aqueous media, TEM and DLS results showed that P(MIPOSS-*alt*-VBPEG) could form spherical aggregates. Moreover, the size of the assembled aggregates of these alternating copolymer brushes increased with the decrease of the chain length of PEG monomer.

Acknowledgements

Notes and references

Shanghai Key Laboratory of Advanced Polymeric Materials, State Key Laboratory of Bioreactor Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, P. R. China

*Correspondence to: Weian Zhang (E-mail: wazhang@ecust.edu.cn)

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

1.   S. S. Sheiko, B. S. Sumerlin and K. Matyjaszewski, *Progress in Polymer Science*, 2008, **33**, 759-785.
2.   H. I. Lee, J. Pietrasik, S. S. Sheiko and K. Matyjaszewski, *Progress in Polymer Science*, 2010, **35**, 24-44.
3.   M. F. Zhang and A. H. E. Muller, *Journal of Polymer Science Part a-Polymer Chemistry*, 2005, **43**, 3461-3481.
4.   H. G. Börner, K. Beers, K. Matyjaszewski, S. S. Sheiko and M. Möller, *Macromolecules*, 2001, **34**, 4375-4383.
5.   G. Cheng, A. Böker, M. Zhang, G. Krausch and A. H. E. Müller, *Macromolecules*, 2001, **34**, 6883-6888.
6.   R. Djalali, S.-Y. Li and M. Schmidt, *Macromolecules*, 2002, **35**, 4282-4288.
7.   K. Tsubaki, H. Kobayashi, J. Sato and K. Ishizu, *Journal of Colloid and Interface Science*, 2001, **241**, 275-279.
8.   K. Ishizu, N. Sawada, J. Satoh and A. Sogabe, *Journal of Materials Science Letters*, 2003, **22**, 1219-1222.
9.   K. Ishizu and H. Yamada, *Macromolecules*, 2007, **40**, 3056-3061.
10.   H. Zhu, G. Deng and Y. Chen, *Polymer*, 2008, **49**, 405-411.
11.   J. Yin, Z. Ge, H. Liu and S. Liu, *Journal of Polymer Science Part a-Polymer Chemistry*, 2009, **47**, 2608-2619.
12.   W. Hadasha, M. Mothunya, N. Akeroyd and B. Klumperman, *Australian Journal of Chemistry*, 2011, **64**, 1100-1105.
13.   Y. Xia, B. D. Olsen, J. A. Kornfield and R. H. Grubbs, *Journal of the American Chemical Society*, 2009, **131**, 18525-18532.
14.   W. Gu, J. Huh, S. W. Hong, B. R. Sveinbjornsson, C. Park, R. H. Grubbs and T. P. Russell, *ACS Nano*, 2013, **7**, 2551-2558.
15.   Y. Zhang, X. Li, G. Deng and Y. Chen, *Macromolecular Chemistry and Physics*, 2006, **207**, 1394-1403.
16.   Y. Zhang, Z. Xu, X. Li and Y. Chen, *Journal of Polymer Science Part a-Polymer Chemistry*, 2007, **45**, 3994-4001.
17.   Y. H. Zhang, J. Huang and Y. M. Chen, *Macromolecules*, 2005, **38**, 5069-5077.
18.   Y. Zhang, Z. Xu, X. Li and Y. Chen, *Journal of Polymer Science Part a-Polymer Chemistry*, 2007, **45**, 3303-3310.
19.   A. O. Moughton, T. Sagawa, W. M. Gramlich, M. Seo, T. P. Lodge and M. A. Hillmyer, *Polymer Chemistry*, 2013, **4**, 166-173.
20.   D. B. Cordes, P. D. Lickiss and F. Rataboul, *Chemical Reviews*, 2010, **110**, 2081-2173.
21.   A. Fina, O. Monticelli and G. Camino, *Journal of Materials Chemistry*, 2010, **20**, 9297-9305.
22.   H. Ghanbari, B. G. Cousins and A. M. Seifalian, *Macromolecular Rapid Communications*, 2011, **32**, 1032-1046.
23.   R. Y. Kannan, H. J. Salacinski, P. E. Butler and A. M. Seifalian, *Accounts of Chemical Research*, 2005, **38**, 879-884.
24.   S.-W. Kuo and F.-C. Chang, *Progress in Polymer Science*, 2011, **36**, 1649-1696.
25.   S. A. Madbouly and J. U. Otaigbe, *Progress in Polymer Science*, 2009, **34**, 1283-1332.
26.   K. Pielichowski, J. Njuguna, B. Janowski and J. Pielichowski, in *Supramolecular Polymers Polymeric Betains Oligomers*, eds. B. Donnio, D. Guillon, A. Harada, A. Hashidzume, W. Jaeger, B. Janowski, S. Kudaibergenov, A. Laschewsky, J. Njuguna, J. Pielichowski, K. Pielichowski and Y. Takashima, 2006, vol. 201, pp. 225-296.
27.   K. Tanaka and Y. Chujo, *Journal of Materials Chemistry*, 2012, **22**, 1733-1746.
28.   F. Wang, X. Lu and C. He, *Journal of Materials Chemistry*, 2011, **21**, 2775-2782.
29.   J. Wu and P. T. Mather, *Polymer Reviews*, 2009, **49**, 25-63.
30.   W. Zhang and A. H. E. Müller, *Progress in Polymer Science*, 2013, **38**, 1121-1162.
31.   F. Du, J. Tian, H. Wang, B. Liu, B. Jin and R. Bai, *Macromolecules*, 2012, **45**, 3086-3093.
32.   C. F. Huang, S. W. Kuo, F. J. Lin, W. J. Huang, C. F. Wang, W. Y. Chen and F. C. Chang, *Macromolecules*, 2006, **39**, 300-308.
33.   L. Ma, H. Geng, J. Song, J. Li, G. Chen and Q. Li, *Journal of Physical Chemistry B*, 2011, **115**, 10586-10591.
34.   X. Yu, S. Zhong, X. Li, Y. Tu, S. Yang, R. M. Van Horn, C. Ni, D. J. Pochan, R. P. Quirk, C. Wesdemiotis, W.-B. Zhang and S. Z. D. Cheng, *Journal of the American Chemical Society*, 2010, **132**, 16741-16744.
35.   W. A. Zhang, B. Fang, A. Walther and A. H. E. Muller, *Macromolecules*, 2009, **42**, 2563-2569.

36. W. A. Zhang and A. H. E. Muller, *Macromolecules*, 2010, **43**, 3148-3152.
37. W. Lee, S. Ni, J. Deng, B.-S. Kim, S. K. Satija, P. T. Mather and A. R. Esker, *Macromolecules*, 2007, **40**, 682-688.
38. L. Wang, K. Zeng and S. Zheng, *Acs Applied Materials & Interfaces*, 2011, **3**, 898-909.
39. J. Wei, B. H. Tan, Y. Bai, J. Ma and X. Lu, *Journal of Physical Chemistry B*, 2011, **115**, 1929-1935.
40. W. A. Zhang, J. Y. Yuan, S. Weiss, X. D. Ye, C. L. Li and A. H. E. Muller, *Macromolecules*, 2011, **44**, 6891-6898.
41. K. Y. Mya, X. Li, L. Chen, X. P. Ni, J. Li and C. B. He, *Journal of Physical Chemistry B*, 2005, **109**, 9455-9462.
42. J. Pyun and K. Matyjaszewski, *Macromolecules*, 2000, **33**, 217-220.
43. Y.-S. Ye, W.-C. Shen, C.-Y. Tseng, J. Rick, Y.-J. Huang, F.-C. Chang and B.-J. Hwang, *Chemical Communications*, 2011, **47**, 10656-10658.
44. Z. Zhang, L. Hong, Y. Gao and W. Zhang, *Polymer Chemistry*, 2014, **5**, 4534-4541.
45. J. Pyun, K. Matyjaszewski, J. Wu, G. M. Kim, S. B. Chun and P. T. Mather, *Polymer*, 2003, **44**, 2739-2750.
46. T. Hirai, M. Leolukman, T. Hayakawa, M. Kakimoto and P. Gopalan, *Macromolecules*, 2008, **41**, 4558-4560.
47. Y. Kim, F. Zhao, M. Mitsuishi, A. Watanabe and T. Miyashita, *Journal of the American Chemical Society*, 2008, **130**, 11848-11849.
48. H. Hussain, B. H. Tan, G. L. Seah, Y. Liu, C. B. He and T. P. Davis, *Langmuir*, 2010, **26**, 11763-11773.
49. B. H. Tan, H. Hussain and C. B. He, *Macromolecules*, 2011, **44**, 622-631.
50. C. Yang, Y. Deng, B. Zeng, C. Yuan, M. Chen, W. Luo, J. Liu, Y. Xu and L. Dai, *Journal of Polymer Science Part a-Polymer Chemistry*, 2012, **50**, 4300-4310.
51. Y. Zheng, L. Wang, R. Yu and S. Zheng, *Macromolecular Chemistry and Physics*, 2012, **213**, 458-469.
52. P. Maitra and S. L. Wunder, *Chemistry of Materials*, 2002, **14**, 4494-4497.
53. K. Kanki and T. Masuda, *Macromolecules*, 2003, **36**, 1500-1504.
54. M. Q. Zhu, L. H. Wei, M. Li, L. Jiang, F. S. Du, Z. C. Li and F. M. Li, *Chemical Communications*, 2001, 365-366.
55. Y. Shi, Z. F. Fu and W. T. Yang, *Journal of Polymer Science Part a-Polymer Chemistry*, 2006, **44**, 2069-2075.
56. S. Harrisson and K. L. Wooley, *Chemical Communications*, 2005, 3259-3261.
57. J. Weiss, A. Li, E. Wischerhoff and A. Laschewsky, *Polymer Chemistry*, 2012, **3**, 352-361.
58. J. A. Wu, Q. Ge and P. T. Mather, *Macromolecules*, 2010, **43**, 7637-7649.
59. K. Wei, L. Li, S. X. Zheng, G. Wang and Q. Liang, *Soft Matter*, 2014, **10**, 383-394.
60. B. S. Kim and P. T. Mather, *Macromolecules*, 2002, **35**, 8378-8384.
61. K. Y. Mya, E. M. J. Lin, C. S. Gudipati, L. Shen and C. He, *Journal of Physical Chemistry B*, 2010, **114**, 9119-9127.
62. S. Wang, Q. Shen, M. H. Nawaz and W. Zhang, *Polymer Chemistry*, 2013, **4**, 2151-2157.

For Table of Contents Graphical Abstract Use Only

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

Zhenghe Zhang, Lizhi Hong, Jinxia Li, Feng Liu, Haibo Cai, Yun Gao, Weian Zhang *

The amphiphilic alternating copolymer brushes P(MIPOSS-*alt*-VBPEG) with a sequence of alternating MIPOSS and polyethylene glycol (PEG) side chains were synthesized *via* RAFT polymerization, and they could form spherical aggregates.