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Sliding Supramolecular Polymer Brushes with Tunable Amphiphilicity: One-Step Parallel Click Synthesis and Self-Assembly

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ABSTRACT: A one-step parallel grafting strategy is presented to readily prepare multifunctional complex macromolecules and miktoarm polymer brushes. Typically, a series of amphiphilic "sliding supramolecular polymer brushes" (SSPBs) were synthesized with cyclodextrin-based polyrotaxanes (PRs) as backbones. The amphiphilicity of SSPBs could be facilely tuned by the feed ratio of hydrophilic poly(ethylene glycol) (PEG) and hydrophobic palmitoyl (C16) side chains. Click chemistry of Cu(I)-catalyzed azide−alkyne cycloaddition was employed as the parallel coupling reaction, and high grafting density (ca. 18 side chains immobilized on each α-cyclodextrin ring) and click conversion (∼100%) was achieved in a short reaction time (several minutes to 3 h). The SSPB with close proportion of PEG to C16 miktoarms showed balanced amphiphilicity and could aggregate into a Janus film at the interface of hexane and water, which was confirmed with a dye-labeling method and fluorescence measurements. The amphiphilic SSPBs could also assemble into microporous films on mica surfaces via spin-coating. The formation of the superstructured films was proved to be affected by the relative humidity, rotational speed of spin-coating, and composition of SSPBs.

Introduction

Molecular brushes are a special class of graft copolymers, in which side chains (SCs) are distributed densely along the backbones. These macromolecules have attracted continuing interest over the past decades due to their unusual architectures, fascinating properties, and potential applications in many fields involving biomimetic materials such as proteoglycan.[1,2]

A large number of molecular brushes with various molecular architectures have been synthesized.[3] However, almost all of the corresponding backbones are the conventional covalent polymers, and accordingly, the SCs cannot move along the backbones. This strongly limits the applications of molecular brushes in some fields such as biomimetics and self-assembly. Then, is it possible to utilize a supramolecular polymer as the backbone to access a supramolecular brush with sliding side arms that would be a very interesting object?

To answer this question, we consider that polyrotaxane (PR), a supramolecular polymer constructed from a polymeric axis, threaded cyclic molecules and bulky stoppers,[4] should be a promising candidate for the construction of sliding supramolecular brushes. In this regard, the PRs made from inclusion complexes between α-cyclodextrins (α-CDs) and poly(ethylene glycol) (PEG) axes are of particular importance due to (1) the sliding nature of α-CDs along the PEG axis that would result in sliding brushes with linear chains immobilized on the CDs,[5] (2) plenty of hydroxyl groups on the CDs that ground the further modification for the fabrication of brushes, and (3) biocompatibility of the products[6] that promises bioapplications of the brushes. To date, even though numerous papers about CD-based PRs have been published,[7] including their uses as precursors for gene carriers,[8] molecular tubes,[9] and slide-ring materials,[10] the applications of the PRs as backbones of sliding brushes were rarely addressed after the pioneer report by Araki et al.,[11] mainly due to the difficulties of (1) facile large-scale availability of the PRs, (2) reasonable methodology for grafting side arms on the PRs, and (3) complete separation of free chains from the brush products.

Most recently, we have developed a facile method to prepare *β*-CD-capped PRs based on α-CDs and PEG axes ("full-CD" PRs) via one-pot Cu(I)-catalyzed "click" reaction of azides and alkynes[12] in water with high efficiency,[13] paving the way for large-scale production of PRs. Herein, we employ these full-CD PRs to synthesize "sliding supramolecular polymer brushes" (SSPBs) with amphiphilic miktoarms composed of hydrophilic PEG and hydrophobic palmitoyl (C16) SCs via a one-step click "grafting onto" approach. Previously, "grafting from", "grafting onto", and "grafting through" strategies have been developed to construct molecular brushes with homogeneous arms.[14] However, multistep/pot reactions and tedious separations are generally needed for grafting heteroarms, which hinder the advancement in this field and limit the study of the properties and applications of molecular brushes. Hence, the one-step approach for miktoarm brushes would be solicitously expected.

Our one-step strategy is schematically depicted in Scheme 1. Different molecules or chains with the same terminal functional groups (A) are added into the reaction system simultaneously to react with another kind of functional groups (B) on the backbone, giving rise to a multifunctional polymer or miktoarm molecular brush. Particularly, if A and B are alkynyl and azido groups, respectively, the reaction could be the well-known Cu(I)-catalyzed "click" chemistry[12] which has been widely used to synthesize functional molecules, molecular brushes, and organic−inorganic conjugates with the merits of fast reaction, high efficiency, and tolerance of protonic solvents. Moreover, if the backbone is a PR, multifunctional PR or miktoarm SSPB would be

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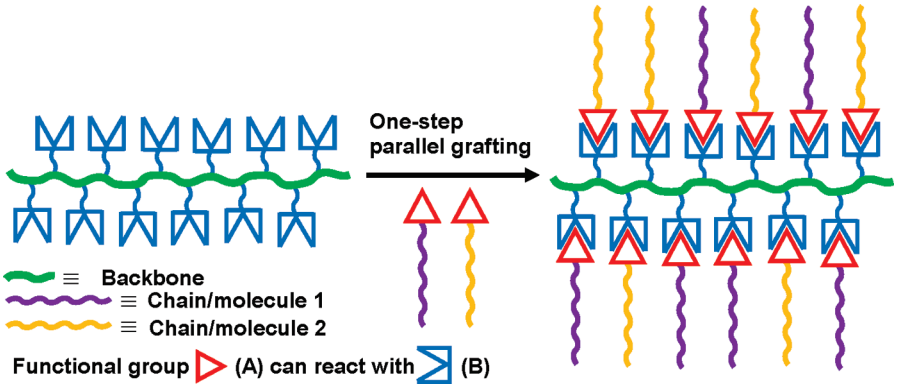
Scheme 1. Schematic Illustration of the One-Step Parallel "Grafting Onto" Strategy for Preparation of Miktoarm Molecular Brushes[a]



[a] This strategy can also be extended to synthesize multifunctional macromolecules and surface brushes readily.

accessed readily. Since different chains are attached to the backbone via the same reaction according to the one-step approach, we coin it as "parallel" grafting strategy in order to distinguish it from the published "orthogonal" grafting strategy,[15] in which different chains react with different functional groups on the backbone independently. The advantages of such a parallel methodology are that (1) only two kinds of functional groups are required for the grafting reaction, simplifying the preparation procedures of building blocks; (2) the functions and properties of the product could be tuned by the feed ratio of different molecules/chains to some extent, making molecular brushes with tunable amphiphilicity or other properties realizable; (3) the purification process would be relatively convenient since the excess material molecules with the same kind of functional groups could be removed from the product via one-step treatment (an example is shown in the article below); and (4) this principle could be extended to fabricate multifunctional conjugates such as surface brushes and bio-nanohybrids. (Note: it would be more controlled for the parallel strategy if the reactivities of the two kinds of side arms/compounds are the same or close.)

Besides the parallel preparation, we also undertook a study on the properties of the corresponding SSPBs. A fluorescent Janus film assembled from the rhodamine B (RhB)-labeled amphiphilic SSPBs was observed at the interface of hexane and water. More significantly, we found that the as-prepared SSPBs showed very interesting spin-coating-induced self-assembly behavior on mica substrates, demonstrating the versatility and great potential of the novel materials with miktoarm sliding brushes.

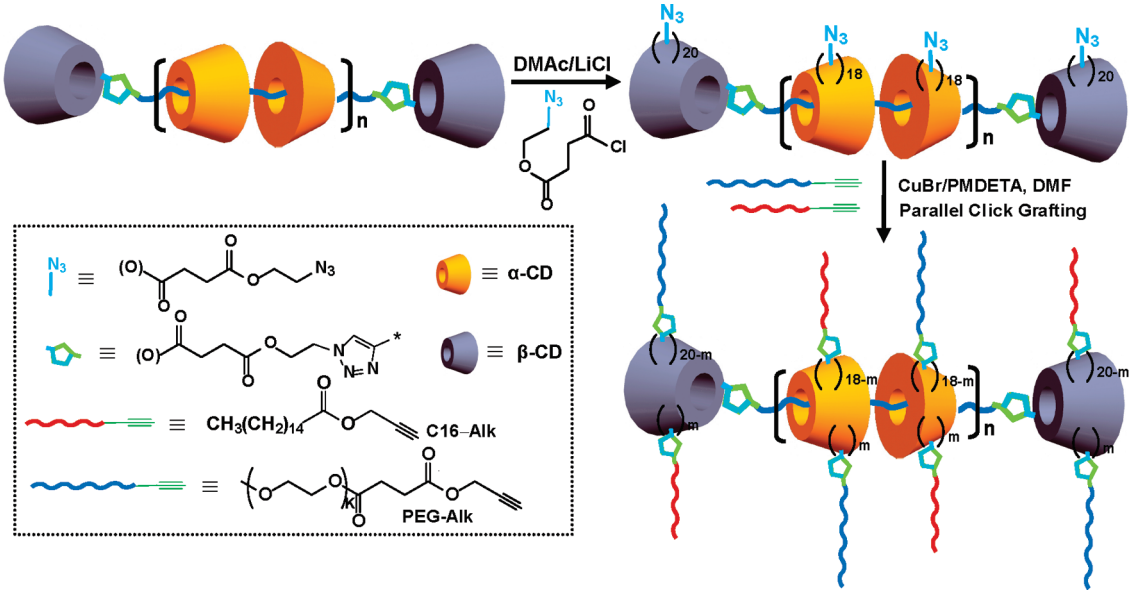
Experimental Section

Materials. 4-(Dimethylamino)pyridine (DMAP, 99%), 1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA, 98%), sodium azide (99%), succinic anhydride (98%), propargyl alcohol (99%), poly(ethylene glycol) monomethyl ether (PEG_{350}-OH, M_n = 350 Da), PEG_{750}-OH (M_n = 750 Da), and PEG_{1900}-OH (M_n = 1.9 kDa) were all purchased from Alfa Aesar. Merrifield resin and *N*,*N*′-dicyclohexylcarbodiimide (DCC, 98%) were obtained from GL Biochem Shanghai Ltd. CuBr (purified according to ref 16 before use, 98%) and RhB (95%) were purchased from Sigma-Aldrich. Palmitic acid (97%), oxalyl chloride (98%), dimethyl sulfoxide (DMSO), and all the other materials were purchased from Sinopharm Chemical Reagent Co., Ltd. Triethylamine (TEA) and dichloromethane (CH_2Cl_2) were dried with CaH_2 and distilled under reduced pressure before use. *N*,*N*-Dimethylacetamide (DMAc) and dimethylformamide (DMF) were dried with $MgSO_4$ overnight prior to use. 4-(2-Azidoethoxy)-4-oxobutanoic acid (carboxylic azide) was synthesized in our lab according to the reported procedures.[17] Monoalkyne-terminated PEG (PEG_{350}-Alk, PEG_{750}-Alk, and PEG_{1900}-Alk) and propargyl alcohol-esterified palmitic acid (C16-Alk) were prepared via DCC/DMAP condensation reactions according to ref 18 (^{1}H NMR spectra of PEG_{350}-Alk and C16-Alk are shown in the Supporting Information, Figure S1). Azido-functionalized Merrifield resin was prepared according to ref 19, and the corresponding FTIR spectrum is shown in Supporting Information, Figure S2. The brush backbone of full-CD PR was made from α-CDs, PEG axis (M_n = 4.6 kDa), and β-CD stoppers via one-pot click end-capping reaction in water according to the reported procedures,[13] and the average number of the threaded α-CDs per PR molecule is 32.9.

Instrument. Gel permeation chromatography (GPC) was recorded on a Perkin-Elmer HP 1100 (LiBr/DMF 0.01 mol/L as the eluent, RI-WAT 150CV+ as a detector, and polystyrene standards at 70 °C). ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) measurements were carried out on a Varian Mercury plus 400 NMR spectrometer using $CDCl_3$ or DMSO-d_6 as solvent. Fourier transform infrared (FTIR) spectra were recorded on a PE Paragon 1000 spectrometer (film or KBr disk). Atomic force microscopy (AFM) was performed under tapping mode on a NanoScope IIIa SPM from Digital Instruments Inc. Scanning electron microscopy (SEM) images were recorded using a Hitachi S-4800 field-emission microscope. Dynamic light scattering (DLS) measurements were conducted using a Brookhaven 90 Plus particle size analyzer. Fluorescence spectra were measured with a RF-5301PC fluorophotometer (Shimadzu Corp.). Confocal fluorescence imaging was performed with a Zeiss LSM-510 confocal laser scanning microscope with excitation wavelength (λ_{ex}) of 543 nm.

Synthesis of Azido-Functionalized Polyrotaxane (PR-N_3). To 25 mL of dry CH_2Cl_2 solution containing 10.38 g of carboxylic azide (55.51 mmol), oxalyl chloride (14.38 g, 111.02 mmol) dissolved in 25 mL of dry CH_2Cl_2 was added dropwise at 0 °C under a nitrogen atmosphere within 2 h. A gas treatment unit containing high concentration NaOH solution was necessary to adsorb the released toxic gas. The reaction mixture was allowed to stir at room temperature for 5 h and then gently heated to 50 °C. The excess oxalyl chloride and the solvent were removed under reduced pressure, and then the residue was coevaporated several times with dry CH_2Cl_2 (5 × 20 mL). The resulting azido acyl chloride was used in the next step directly without further purification. PR (1.00 g, ca. 18.50 mmol −OH) and 10 mL of TEA were dissolved in 20 mL of dry DMAc containing 8% w/w lithium chloride. To this solution, the as-prepared azido acyl chloride (ca. 3.0 equiv to the hydroxyl groups of PR) dissolved in dry DMAc (5 mL) was added slowly under a nitrogen atmosphere at 0 °C. After stirring at room temperature overnight, the reaction mixture was poured into ethanol, and the precipitate was collected by centrifugation. The solid was dissolved in DMF and precipitated from ethanol and ethyl ether several times to get a pale-brown powder. Yield: 2.24 g, 54%. ^{1}H NMR (DMSO-d_6, δ, ppm): 2.57 (br, $OCOCH_2CH_2COO$), 3.50 (br overlapped,

Scheme 2. Preparation of Sliding Supramolecular Polymer Brushes (SSPBs) via Parallel Click Grafting Methodology



H of PR and N_3CH_2), 3.88−5.04 (br overlapped, H of PR and $N_3CH_2CH_2$).

Synthesis of Sliding Supramolecular Polymer Brushes (SSPBs) via One-Step Parallel Click Coupling (see Scheme 2). A typical SSPB, PR-PEG_{750}25%, which meant the feed molar ratio of PEG_{750}-Alk to C16-Alk reagents was 1/3 (25%/75%), was prepared according to the following procedures. To a DMF solution (2 mL) containing 20.0 mg of PR-N_3 (ca. 0.09 mmol of $-N_3$), a mixture of PEG_{750}-Alk (35.8 mg, 0.04 mmol) and C16-Alk (35.6 mg, 0.12 mmol) dissolved in 1 mL of DMF, PMDETA (6.4 μL, 0.03 mmol) and CuBr (4.3 mg, 0.03 mmol) were added under a nitrogen atmosphere. The reaction mixture was allowed to stir at room temperature for 3 h, and then azido-functionalized Merrifield resin (1.0 g) was added to react with the excess alkynyl groups. The resin was removed by centrifugation, and the collected solution was poured into ethyl ether. The obtained solid was redissolved in $CHCl_3$ and passed through a neutral alumina column to remove the copper catalyst. The collected eluent was concentrated and precipitated in ethyl ether to afford the product. Yield: 33.5 mg. ^{1}H NMR ($CDCl_3$, δ, ppm): 0.87 (s, CH_3 of C16), 1.24 (s, CH_2 of C16), 1.59 (s, CH_2CH_2COO of C16), 2.31 (s, CH_2CH_2COO of C16), 3.38 (s, CH_3O of PEG), 3.64 (s, CH_2 of PEG), 4.00−5.46 (br overlapped, H-1,2,3,5,6 of CD, $COOCH_2CH_2O$ of PEG, CH_2CH_2-triazole−CH_2OCO), 7.85 (s, H of triazole ring). According to the ^{1}H NMR spectrum, the molar ratio of PEG_{750} to C16 SCs in the product was 1/3.22, which was close to the feed ratio. Likewise, other SSPBs with various ratios of PEG to C16 SCs were prepared by changing corresponding PEG-Alk/C16-Alk feed ratios or molecular weights of PEG-Alk.

Results and Discussion

Synthesis and Characterization of Clickable PR Backbone (PR-N_3). As illustrated in Scheme 2, the PR was first treated with an azido acyl chloride to prepare the clickable backbone of PR-N_3, which then could click with the monoalkyne-terminated SC precursors, PEG-Alk and C16-Alk, to prepare the SSPBs with tunable amphiphilicity. An excess of azido acyl chloride (ca. 3.0 equiv to the hydroxyl groups of PR) was used to increase the conversion of hydroxyl groups, and accordingly, this acylation reaction was quite efficient and no peaks assigned to hydroxyl groups of PR were observed in the ^{1}H NMR spectrum of PR-N_3 (Figure 1A).

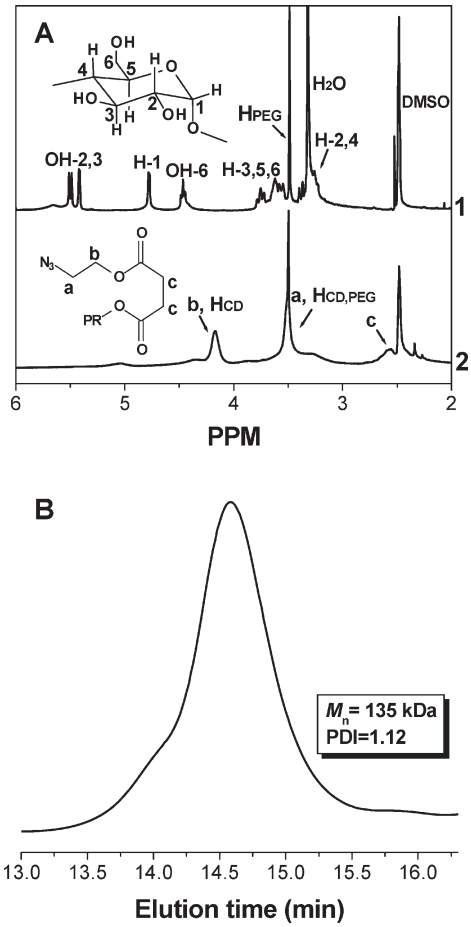


Figure 1. (A) ^{1}H NMR spectra of (1) PR and (2) PR-N_3. (B) GPC trace of PR-N_3.

Besides, PR-N_3 was characterized by FTIR and GPC measurements. As shown in Figure 2a, the characteristic peaks of azido group (asymmetric stretching), carbonyl, and CH bonds are clearly observed at 2104, 1739, and 2877 cm^{-1}, respectively. The number-average molecular weight (M_n) of PR-N_3 determined by GPC (Figure 1B) was ca. 135 kDa

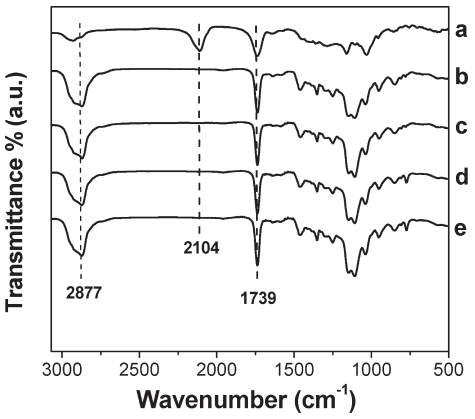


Figure 2. FTIR spectra of (a) PR-N_3 and the samples taken from the click coupling reaction of PR-N_3 with PEG_{750}-Alk at given times: (b) 1 min, (c) 3 min, (d) 10 min, and (e) 3 h after the addition of PEG_{750}-Alk.

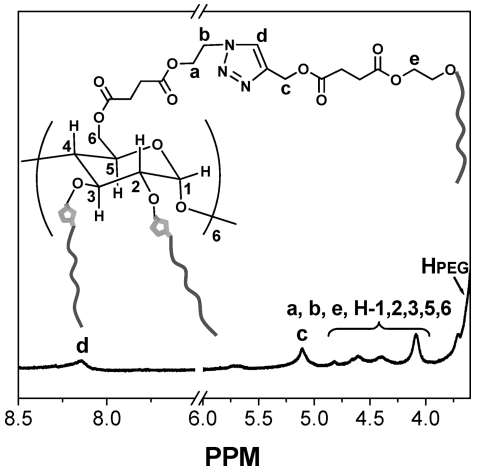


Figure 3. ^{1}H NMR spectrum of PR-PEG_{750}100% in DMSO-d_6 in the region of 3.6−8.5 ppm.

(M_w/M_n = 1.12), which is in accordance with the calculated value, ca. 145 kDa.

Sliding Supramolecular Brushes with Tunable Amphiphilicity. Generally, the SCs can be attached to PR backbone via either "grafting from"[20] or "grafting onto"[21]strategies. Araki et al.[11] first prepared this kind of brush with linear SCs of poly(ε-caprolactone) (PCL) via a "grafting from" method. Unfortunately, the ring-opening polymerization of the ε-caprolactone monomer initiated by the trace amount of residual water in PRs could hardly be avoided, leading to a mixture of brushes and free PCL molecules that were hard to be separated from the desired product. In addition, it was quite difficult to know the initiating efficiency of the hydroxyl groups of the PR and the molecular parameters of the SCs such as molecular weight and polydispersity index (PDI). On the contrary, according to the "grafting onto" approach, both the backbones and the SCs can be prepared independently and characterized accurately, so this strategy is superior to prepare the aforementioned SSPBs with well-defined architectures.

In order to overcome the limitation of "grafting onto" strategy, i.e., low grafting efficiency resulting from steric hindrance, a highly efficient coupling reaction and relatively small and flexible SCs should be taken into consideration in the molecular design.[3] Thereby, we selected C16 and PEG with relatively low molecular weights as the SCs and highly efficient click chemistry as the coupling reaction. Furthermore, an excess of SC precursors is necessary for high grafting density according to the principle of "grafting onto" strategy. In our experiments, the molar ratio of alkynyl to azido groups was optimized as 1.80/1.[3] The removal of excess alkyne reagents was facilely achieved by clicking onto azido-functionalized Merrifield resin and the subsequent centrifugation step.[19]

The SSPBs with sole PEG_{750} or C16 arms were first prepared to understand the reactivity of the SC precursors with the PR backbone. In the case of PEG_{750}-grafted PR (PR-PEG_{750}100%), surprisingly, FTIR spectra showed that the characteristic peak of azido group at 2104 cm^{-1} disappeared immediately within 1 min after the addition of PEG_{750}-Alk, accompanying increasing intensities of the absorption bands corresponding to carbonyl at 1739 cm^{-1} and CH bonds at 2877 cm^{-1} (Figure 2). On the basis of extremely sensitive azido absorption in the FTIR spectrum, the conversion of azido groups (i.e., grafting density, n) approached 100%. This conclusion was further demonstrated by the ^{1}H NMR spectrum of the product. According to Figure 3, the calculation formula for n is shown as follows:

$$\frac{I_1}{I_2} = \frac{2}{n} + 8 \qquad (1)$$

In this equation, I_1 is the integration value of the peaks in the region of 4.00−5.30 ppm (H-1,2,3,5,6 of CD, COOCH_2-CH_2O of PEG, CH_2CH_2−triazole−CH_2OCO) and I_2 is that of signal d at 8.15 ppm (H of triazole rings formed via the click coupling reaction).

The ratio of I_1/I_2 equals 10.08 (Supporting Information, Figure S3), and thus n is ca. 96%, much higher than the reported one (ca. 62.5%) for the brush prepared under similar condition with a covalent polymeric backbone.[3] A similar result was obtained when C16 was chosen as the sole SC. The absorption peak of azido group at 2104 cm^{-1} disappeared within 1 min in the FTIR spectrum (Supporting Information, Figure S4f) of the product (PR-C16100%). According to the corresponding ^{1}H NMR spectrum with integration values (Supporting Information, Figure S5), the conversion of azido groups was proved to reach 100% as well. These experiments demonstrated that both PEG_{750} and C16 arms can be efficiently attached to the PR backbone and have comparable reactivity in the click coupling, which paves the way to miktoarm SSPBs with tunable amphiphilicity via the one-step parallel "grafting onto" approach.

To synthesize the miktoarm SSPBs as efficiently as possible, we present the parallel "grafting onto" strategy to attach two kinds of SCs simultaneously onto the PR backbone. A DMF solution with a given feed molar ratio of PEG_{750}-Alk to C16-Alk (R_f = PEG-Alk/C16-Alk) was added to a DMF solution of as-prepared PR-N_3, followed by the addition of catalyst system of CuBr/PMDETA. The reaction mixture was allowed to stir under a nitrogen atmosphere at room temperature for 3 h to ensure the high conversion of azido groups before the addition of azido-functionalized Merrifield resin for the removal of excess alkyne reagents. The resulting product was then characterized by FTIR and ^{1}H NMR measurements. Typically, in the case of R_f = 50%/50% (PR-PEG_{750}50%), no characteristic peak of the azido group was observed at 2104 cm^{-1} (Supporting Information, Figure S4d), indicating that the conversion of azido groups in the parallel click coupling also approached 100% and both PEG_{750} and C16 chains were immobilized on the PR backbone with an actual molar ratio (R_a = PEG/C16 SCs) since neither PEG_{750}-Alk nor C16-Alk could consume azido groups completely (the feed molar ratio of PEG_{750}-Alk or C16-Alk

Table 1. Selected Reaction Conditions and Results for the Sliding Supramolecular Polymer Brushes (SSPBs)

sample	PR-PEG$_{750}$ 100%	PR-PEG$_{750}$ 75%	PR-PEG$_{750}$ 50%	PR-PEG$_{750}$ 25%	PR-C16 100%	PR-PEG$_{350}$ 50%	PR-PEG$_{1900}$ 50%
R_f[a]	100%/0%	75%/25%	50%/50%	25%/75%	0%/100%	50%/50%	50%/50%
R_a[b]	100%/0%	76%/24%	53%/47%	25%/75%	0%/100%	50%/50%	63%/37%
MW[c] (10^2 kDa)	7.03	6.14	5.27	4.22	3.30	3.90	10.24
M_n (10^2 kDa)	2.37	1.90	1.87	1.56	1.26	1.55	2.78
M_w/M_n[d]	1.66	1.28	1.46	1.32	1.26	1.42	1.39
diameter[e] (nm)	572.2	453.7	456.0	264.9	275.7	299.4	579.9
PDI[f]	0.026	0.005	0.020	0.005	0.005	0.136	0.118

[a] The feed molar ratio of R_f = PEG-Alk/C16-Alk. [b] The actual molar ratio of R_a = PEG/C16 SCs obtained from the ^{1}H NMR spectrum. [c] Molecular weight calculated from the ^{1}H NMR spectrum. [d] Weight-average (M_w) and number-average molecular weight (M_n) obtained via GPC measurements. [e] The particle sizes of the brushes in $CHCl_3$ solution (the details are shown in Supporting Information, Figure S6). [f] DLS polydispersity index.

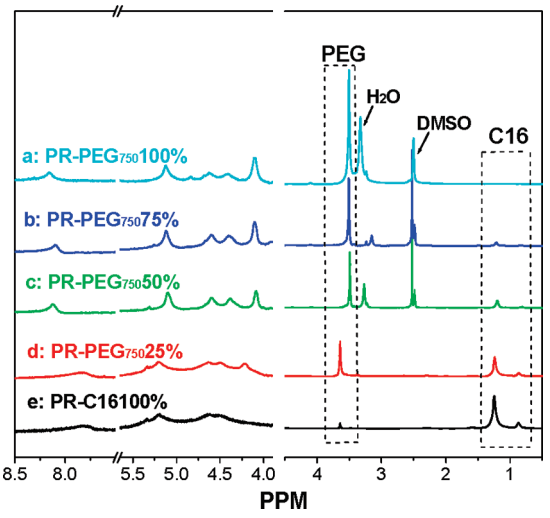


Figure 4. ^{1}H NMR spectra of SSPBs in DMSO-d_6 (cyan, blue, and green) or $CDCl_3$ (red and black): (a) PR-PEG$_{750}$100%, (b) PR-PEG$_{750}$75%, (c) PR-PEG$_{750}$50%, (d) PR-PEG$_{750}$25%, (e) PR-C16100%. The left part is the amplified spectra in the region of 3.9−8.5 ppm.

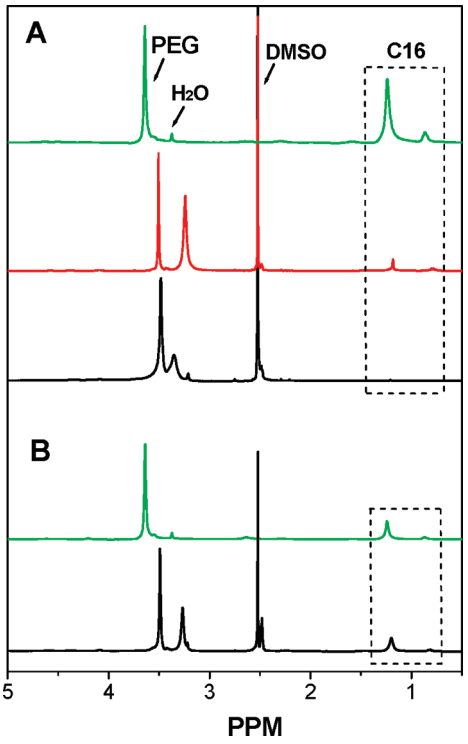


Figure 5. ^{1}H NMR spectra of (A) PR-PEG$_{750}$25% and (B) PR-PEG$_{750}$50%, in $CDCl_3$ (green), the mixed solvents of DMSO-d_6 and $CDCl_3$ (1:1 by volume, red), and DMSO-d_6 (black).

to azido group was only 0.9/1). Significantly, the value of R_a was able to be estimated from the corresponding ^{1}H NMR spectrum (Figure 4c), which was 53%/47% (Table 1), quite close to the value of R_f. This further demonstrated that the click reactivity of both kinds of SCs was comparable, indicating that the SC ratio (R_a) or the ratio of hydrophilicity to hydrophobicity could be tuned readily by the feed ratio of R_f.

In fact, we found that the amphiphilicity of SSPBs could be tuned indeed by the value of R_f. As shown in Figure 4, the intensity of PEG$_{750}$ peak (−CH_2− at 3.50 or 3.64 ppm) increases with the increase of R_f or the relative amount of PEG$_{750}$-Alk, and that of the peak originating from C16 SCs (−CH_2− at 1.24 ppm) decreases simultaneously. The calculated values of R_as of all prepared SSPBs are listed in Table 1 and are close to the corresponding R_fs, indicating that R_a can be controlled simply, to some extent, by adjusting the value of R_f. This result, as well as the high conversion of azido groups, should be ascribed to not only the high efficiency of the click coupling reaction but also the mobility of the adsorbed thin SCs. Moreover, the sliding SCs on PR may result in a lower steric repulsion than those grafted on the conventional polymeric backbone. As such, the parallel strategy developed herein is of particular importance to facilitate the preparation of miktoarm amphiphilic brushes and multifunctional macromolecules with tunable tailor-made properties.

To probe the different characters of hydrophilic and hydrophobic SCs, we examined the solubility/dispersibility of SSPBs with ^{1}H NMR measurements by the addition of DMSO-d_6 that is a good solvent for PEG but poor solvent for C16 moieties. As shown in the ^{1}H NMR spectra of PR-PEG$_{750}$25% (R_a = 25%/75%), the intensity of the proton peak of C16 SCs (at 1.24 ppm) decreases with the increase of DMSO-d_6 proportion in the mixed solvents of $CDCl_3$ and DMSO-d_6, while that of PEG$_{750}$ SCs maintains the same. In the case of PR-PEG$_{750}$50% (R_a = 53%/47%), both signals of C16 and PEG$_{750}$ SCs remain almost unaltered (Figure 5). This phenomenon revealed a significantly limited conformational freedom of C16 SCs of the SSPBs with lower R_a, which probably resulted from the aggregation of C16 SCs with the addition of DMSO. Consequently, the value of R_a greatly influences the solubility/dispersibility of SSPBs.

To reveal the potential versatility of the parallel grafting strategy, we utilized different PEG SCs to show the controllability for the structures of SSPBs through an alternative manner of molecular weight. Significantly, SSPBs with tunable amphiphilicity could also be readily accessed by using PEG$_{350}$ SCs via the one-step parallel strategy, and the resulting R_a was almost equal to the feed ratio of R_f (Table 1, Supporting Information, Figures S4g and S7). In the cases of PEG$_{1900}$-Alk reagent, a highly soluble product, PR-PEG$_{1900}$50%, was also successfully prepared, and no absorption peak was observed at 2104 cm^{-1} in the FTIR spectrum (Supporting

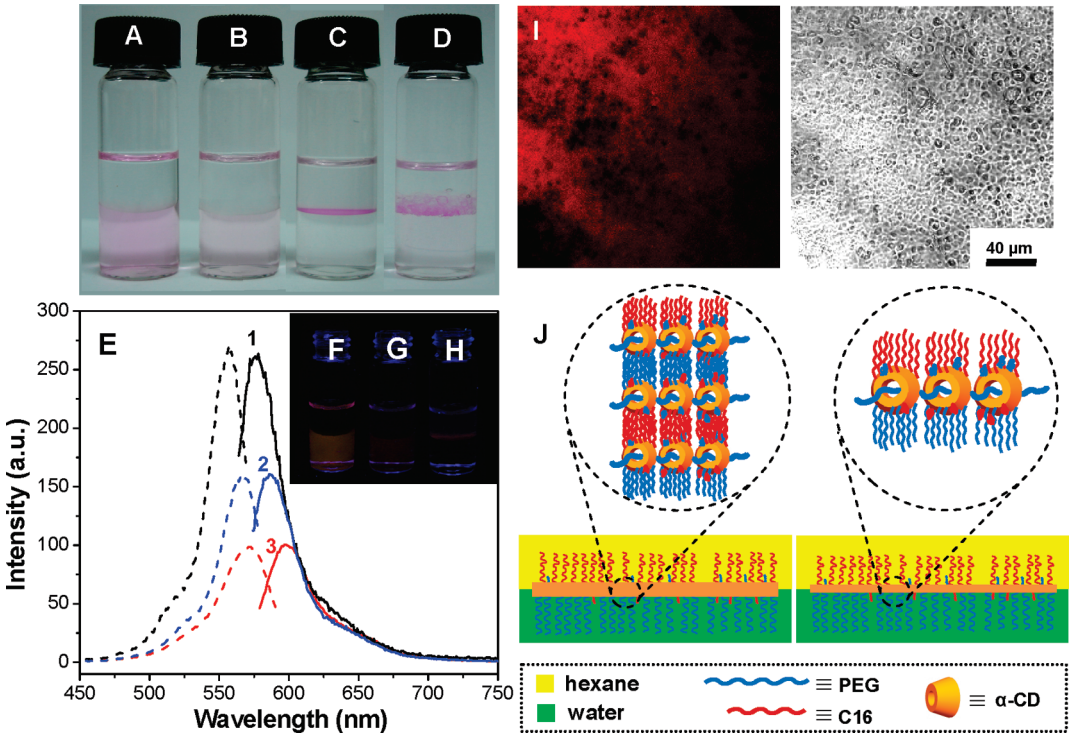


Figure 6. Photographs of (A) RhB, (B) PR-PEG$_{750}$75%, and (C) PR-PEG$_{350}$50% in the mixture of hexane and water under visible light. (D) Photograph of vessel C after being shaken. (E) Emission (solid line) and excitation (dashed line) fluorescence spectra of (1) RhB (ca. 7×10^{-5} mg/mL aqueous solution), (2) PR-PEG$_{750}$75% in water, and (3) the Janus film constructed by PR-PEG$_{350}$50% (the film was supported by a quartz slice). (F−H) Corresponding photographs of vessel A−C irradiated at 365 nm, respectively. (I) Representative confocal microscopy images of the intact Janus film (the left image represents fluorescence image and the right one represents the visible image). (J) Schematic structures of a multilayer (the left image) and a monolayer (the right image) Janus film of PR-PEG$_{350}$50%.

Information, Figures S4h and S7), indicating the high grafting efficiency of parallel click coupling for SCs with relatively high molecular weights. As shown in Table 1, the calculated R_a is 63%/37%, not in accordance with R_f (50%/50%), which is likely caused by the shielding effect of long PEG$_{1900}$ chains on the adjacent short C16 arms and the integration error of ^{1}H NMR signals since the integration value of PEG$_{1900}$ peak is much larger than that of C16 peak. Incidentally, when we tried to synthesize the brush with sole PEG$_{1900}$ SCs, PR-PEG$_{1900}$100%, a macroscopic gel appeared immediately with the addition of PEG$_{1900}$-Alk, which might be attributed to the formation of a stable copper complex between the brushes and copper ions. We did the control experiments of mixing linear PEGs with copper ions and found that an insoluble precipitate also appeared for PEG with high molecular weight (MW > 10 kDa), whereas no gel was observed for low-molecular-weight PEG. Further studies are needed to totally uncover the reason and the actual structures of these complexes.

Furthermore, all of the prepared brushes were characterized by GPC and DLS, and the results are listed in Table 1. The order of M_ns determined by GPC was consistent with that of the theoretical ones (MWs) obtained according to ^{1}H NMR spectra, but unfortunately, M_n was obviously lower than corresponding MW. This error was assumed to result from the compact structures of the grafted copolymers and the different hydrodynamic volumes between the brushes and polystyrene standards in DMF.[22] Because of the complex structures of such kinds of brushes, to exactly determine their M_ns by GPC is a challenge yet. The diameters of the brushes measured by DLS have considerable relationship with MWs, i.e., the higher MW always resulting in larger particle size.

Janus SSPBs at the Interface of Hexane and Water. Similar to the amphiphilic surfactant molecules and block copolymers, our amphiphilic miktoarm SSPBs are expected to show unique molecular arrangement behavior at the interface of oil and water. Herein, we investigated their possible self-assembly behavior by choosing hexane and water as solvents since water is a good solvent for PEG but a poor solvent for C16 SCs, while inversely, hexane is a good solvent for C16 but a poor solvent for PEG arms.

In order to track these tested brushes in solvents, we first labeled them with rhodamine B (RhB) via the addition of a small amount (ca. 5 mol % of the total alkyne reagents) of alkyne-functionalized RhB[23] during the coupling reaction. As a result, both RhB molecules (Figure 6A) and PR-PEG$_{750}$75% with more PEG moiety (Figure 6B) showed hydrophilic behavior as a whole and tended to dissolve in water, while PR-PEG$_{350}$50% with close proportion of PEG to C16 SCs suspended at the hexane−water interface to construct an amphiphilic red Janus[24] film (Figure 6C). When slightly shaken, the thin film exhibited surfactant-like bubbles (Figure 6D) and gradually recovered after a relatively long-standing time (at least 1 week), suggesting the high stability of the bubbles made from the amphiphilic PR-PEG$_{350}$50% brushes.

Furthermore, a highly sensitive fluorescence spectrometer was used to probe the distribution of PR-PEG$_{350}$50% molecules by measuring the fluorescence intensities of the hexane phase, aqueous phase, and the Janus film. According to the fluorescence spectra, the emission peak of the Janus film was strongly observed at 597 nm if excited at its maximum λ_{ex} of 571 nm (Figure 6E, plot 3), while almost no fluorescence was detected for the hexane and water phases (Supporting Information, Figure S8), which further demonstrated that the molecular brushes of PR-PEG$_{350}$50% were only localized at the interface of hexane and water, resulting in the amphiphilic Janus film. Moreover, the Janus film was

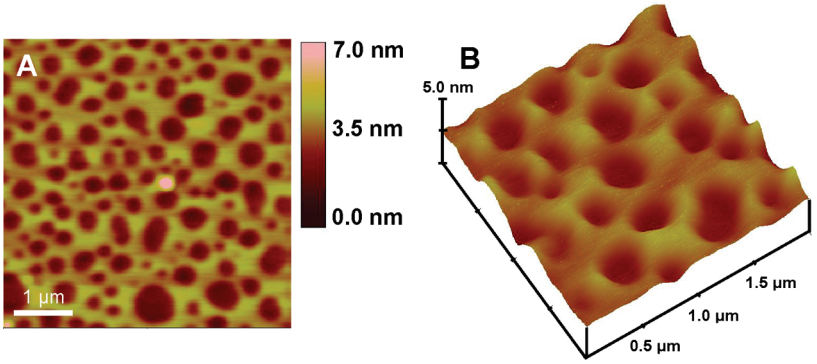


Figure 7. (A) AFM image of self-organized morphology of PR-PEG$_{750}$75% on a mica wafer at 25 °C with rotational speed (RS) = 1500 rpm and relative humidity (RH) = 62%. (B) Amplified 3D image of part A.

carefully transferred onto a quartz slice, and a red fluorescence film with porous spongelike morphology was observed under a confocal laser microscope (Figure 6I) and confirmed by SEM measurements (Supporting Information, Figure S9). Slicing scan confocal measurements showed that the porous film has a micrometer-scale thickness (data not shown).

According to the confocal microscopy images, the Janus film is constructed by multilayer molecules of PR-PEG$_{350}$50% brushes, and the schematic structure is shown in Figure 6J. This film is supposed to show two sides of different polarities, i.e., the hydrophilic side consisting of PEG$_{350}$ SCs contacted with aqueous phase and the hydrophobic side composed of C16 SCs immersed in hexane solution, and the main body of the film is built up by the layer-by-layer aggregation of PEG$_{350}$ and C16 moieties, which is strongly favored by the free rotation and slippage characters of the SCs. Nevertheless, a self-assembled Janus monolayer Langmuir−Blodgett film is supposed to form with a small amount of PR-PEG$_{350}$50% molecules, and the brush can also work as a surfactant at the hexane−water interface.

Primary AFM Observations on Self-Assembly of SSPBs on Solid Substrates. Although numerous reports on supramolecular self-assembly of amphiphilic block copolymers[25] have been published, the intensive studies on the self-assembly of molecular brushes are rarely found due to the difficult availability of amphiphilic miktoarm brushes with well-defined architectures, and normally, only micelles[26] and vesicles[27] were observed for conventional amphiphilic brushes. Considering the facile availability of our SSPBs and their well-defined structures, we investigated the morphology and self-assembly behavior of the SSPBs preliminarily (see Supporting Information, Figures S10−S14) and found that one kind of miktoarm SSPB, PR-PEG$_{750}$75%, was able to organize into microporous films on solid substrates of mica at room temperature via the spin-coating method. As shown in Figure 7A, the film contains some micropores with a nonuniform diameter ranging from 95 to 650 nm, and there are about 100 micropores in an area of 5 × 5 μm^2. According to 3D AFM image (Figure 7B) and the section analysis of the prepared films (Supporting Information, Figures S15 and S16), the depth of the micropores is only ca. 2 nm, indicating that ultrathin porous film can be obtained by self-assembly of SSPB. Furthermore, we found that the morphology of this microporous film was affected by the rotational speed of spin-coating (RS) and relative humidity (RH). At 25 °C, when RH = 50%, the microporous structures could only be detected with RS ranging from 1500 to 2500 rpm (Supporting Information, Figure S10), and when RS = 1500 rpm, the films could be fabricated with RH ranging from 50% to 62% (Figure 7 and Figure S11), indicating that the external force and humidity have great influence on the formation of microporous films. Further studies on the details and mechanism of self-assembly behaviors of SSPBs (supposed mechanism is shown in Supporting Information, Figure S17) are still in process and will be reported later.

Conclusions

In summary, amphiphilic sliding supramolecular polymer brushes (SSPBs) consisting of a PR backbone, hydrophilic PEG SCs, and hydrophobic C16 SCs have been successfully synthesized via a one-step click coupling reaction. This parallel grafting strategy is promising with remarkable merits: (1) the click coupling was extremely efficient, and almost 100% grafting density was achieved in a short reaction time (less than 3 h); (2) different arms were attached onto the PR backbone simultaneously, largely simplifying the preparation procedures for miktoarm brushes; and (3) the ratio of hydrophilicity to hydrophobicity of SSPB was essentially tuned by the feed ratio of corresponding SC precursors. The strategy developed herein opened an avenue for the facile preparation of miktoarm amphiphilic brushes and multifunctional macromolecules such as biomolecules/drugs−polymer conjugates. As a result of their unique structures, the prepared SSPBs showed interesting properties. The brushes with balanced amphiphilicity such as PR-PEG$_{350}$50% self-assemble into a Janus film at the hexane−water interface readily. Besides, spin-coating induced self-assembly to fabricate a microporous film with amphiphilic molecular brushes was observed for the first time, which can be helpful to understand the self-assembly behaviors of complex biomacromolecules. It is also highly expected that by the employment of PR as a supramolecular backbone, a wide variety of novel molecules with fascinating properties can be designed and prepared, introducing a promising perspective toward functional materials.

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Supporting Information Available: Additional ^{1}H NMR spectra, FTIR spectra, fluorescence spectra, AFM images, SEM images, and details of DLS results. This material is available free of charge via the Internet at http://pubs.acs.org.

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