

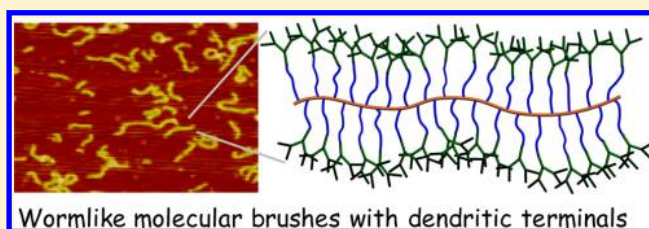
# Synthesis of Cylindrical Polymer Brushes with Umbrella-Like Side Chains via a Combination of Grafting-from and Grafting-onto Methods

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**S** Supporting Information

**ABSTRACT:** Cylindrical polymer brushes with umbrella-like side chains have been synthesized by a combination of grafting-from and grafting-onto methods. First, the polymer brushes with azido end-functionalized poly(*tert*-butyl acrylate) (PtBA- $N_3$ ) side chains, PBIEM-*g*-(PtBA- $N_3$ ), were prepared by atom transfer radical polymerization (ATRP) of *t*BA monomers using polyinitiator PBIEM followed by a substitution of bromo-side terminals with sodium azide. Subsequently, polyamidoamino dendrons of three generations with a propargyl focal point ( $G_n$ ) were introduced onto the brush-shaped PtBA- $N_3$  by copper-catalyzed azide–alkyne cycloaddition (CuAAC) coupling reaction. The efficiency of CuAAC between PtBA- $N_3$  side chains and  $G_n$  has showed a dependence on generation number  $n$  of the dendrons. At the feed ratio of  $[G_n]:[N_3] = 1:1$ , the grafting efficiency of the first generation dendron ( $G_1$ ) reached above 95%, whereas that of  $G_2$  and  $G_3$  was at least 84% and 73%, respectively. AFM images indicated that diameter of the brushes hybridized with  $G_3$  increased obviously than that of the brushes without dendrons.



## INTRODUCTION

In recent years, with rapid development of synthetic chemistry, many kinds of new polymers with various topological structures, such as star polymers, cyclic polymers, hyper-branched polymers, dendrimers, polymer brushes, and dendronized polymers have been synthesized.<sup>1–19</sup> Among these topological structures, polymer brushes<sup>14,20–23</sup> and dendronized polymers<sup>17,24–28</sup> have attracted much attention because of their wormlike single chain morphology. The polymer brushes and dendronized polymers have a similar molecular structure; i.e., they have densely grafted with bulky branches along a backbone. The difference is the structures of their grafted side chains. The side chains of polymer brushes are linear polymer segments while that of dendronized polymers bears dendritic wedges of different generation. The molecular structures of two molecular objects are illustrated by cartoon presentation in Scheme 1, parts A and B. Because these side chains are densely grafted, the linear polymer backbone is stretched, and the whole polymer demonstrates a worm-like cylindrical conformation for the backbones with large enough degree of polymerization. Compared with the polymer brushes with linear side chains, the dendronized polymers may have a better controlled morphology because of the well-defined dendritic wedges.

There are three strategies, namely grafting-through,<sup>29–31</sup> grafting-from,<sup>15,32</sup> and grafting-onto approaches,<sup>33–35</sup> for synthesis of polymer brushes and dendronized polymers. The grafting-through approach refers to polymerization of the dendritic or linear macromonomers. So far it is still difficult to control the length of polymer brushes and dendronized

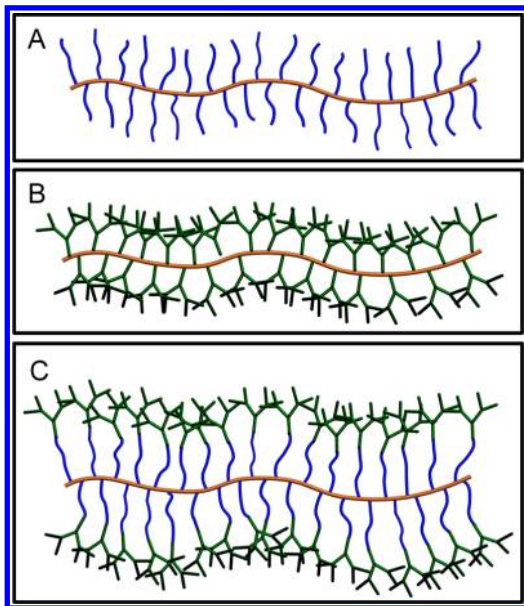
polymers by radical polymerization of macromonomers. Recently it has been shown that ring-opening metathesis polymerization of macromonomers may produce brushes with a controlled length.<sup>22,36</sup> The grafting-from method refers to the strategy that side chains formed by grafting polymerization from the preformed backbones bearing densely modified initiating groups. Using grafting-from method, the backbones and side chains may be formed by controlled polymerization or stepwise synthesis and thus the polymers may have a well-defined structure. It needs to mention that the grafting efficiency using controlled radical polymerization for synthesis of polymer brushes is not very high and it suffers low monomer conversion due to serious radical–radical coupling reaction. The grafting-onto approach utilizing coupling reaction, namely the dendritic or linear side chains with end functionality are directly attached to a polymer backbone containing anchor groups. To ensure a high grafting density, a highly efficient coupling reaction and optimization of reaction condition are rather important. As a highly efficient coupling reaction, copper-catalyzed azide–alkyne cycloaddition (CuAAC) reaction<sup>37,38</sup> has been applied to prepare well-defined polymer brushes and dendronized polymers. Helms et al. reported the synthesis of dendronized polymers through grafting-onto approach by using CuAAC coupling reaction. For the first to the third generation dendrons, almost quantitative coverage of the polymer backbone with dendrons has been fulfilled.<sup>34</sup> Very

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**Scheme 1. Schematic Illustration of (A) Polymer Brush with Linear Polymer Side Chains, (B) Dendronized Polymer with Dendritic Side Chains, and (C) Hybrid Polymer Brush with Umbrella-Like Side Chains of This Work**



recently, our group reported an efficient synthesis of molecular brushes grafted with PEO ( $M_n = 5000$  Da) by using CuAAC click chemistry. Using  $\text{CuSO}_4$ /ascorbic acid as the catalyst system, the efficiency of coupling reaction reached 98% in a few hours under an equivalent feed of the functionalities.<sup>39</sup>

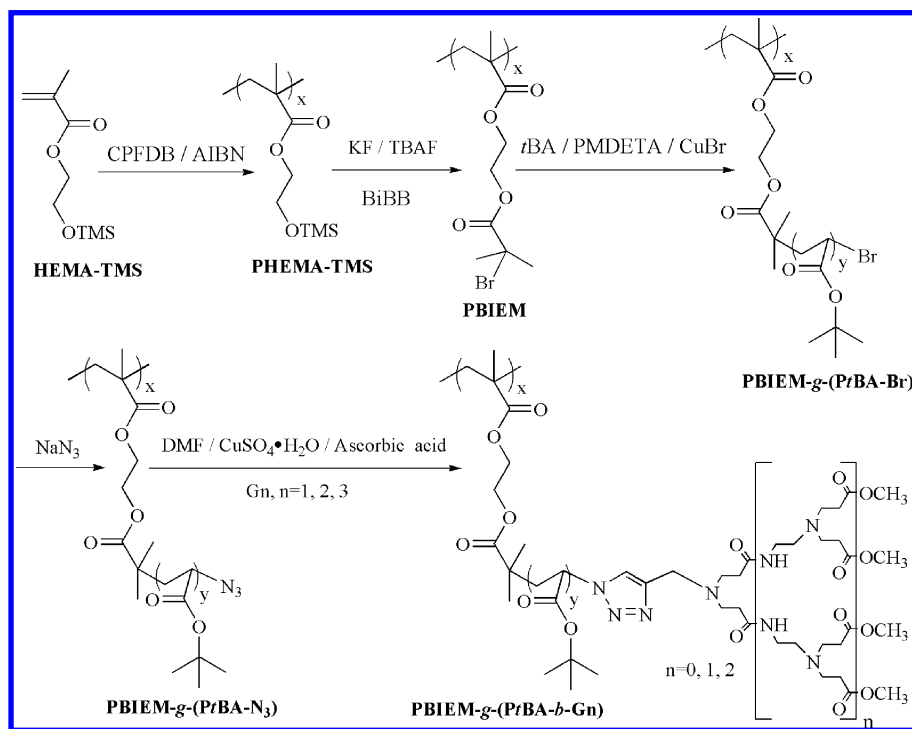
Generally, functions of polymer brushes, such as solubility, pH- and thermo-responses, are mainly dependent on the property of side chains.<sup>40–42</sup> Polymer brushes can be considered as periphery functionalized wormlike molecular

objects. Thus, functions of brushes should be mainly depended by periphery groups of the side chains. However, there is only one terminal group for each linear side chain for polymer brushes. In contrast, the dendritic wedges of dendronized polymers bear a defined number of periphery groups. However, it is very difficult to get dendronized polymers with thicker diameter due to the tedious chemistry to form high generation dendron units. Also the dendronized polymers have a compact internal structure and thus they may have no enough intramolecular space to be used as molecular capsules. Therefore, we proposed to prepare hybridized polymer brushes with umbrella-like side chains, i.e., linear polymer-*block*-dendron as side chains. As shown by Scheme 1C, the dendrons are located at the periphery of polymer brushes and each side chain bears multiple terminals defined by dendron generation. Since the dendrons may be pushed outward, novel brushes may have a high intramolecular space surrounded by dendron shells. Thus, they may be considered as pseudomolecular tubes, which could be very interesting for application development.

Combination of linear and dendritic polymer side chains has been reported scarcely. Our group reported the synthesis of hybrid polymer brushes with alternating dendritic wedges and linear chains as side chains.<sup>43</sup> Zhang et al. reported synthesis of the hybrid dendronized polymers in which each dendritic wedge bears four linear polymethacrylate branches.<sup>44</sup> As far as we know, there is no report on synthesis of polymer brushes with umbrella-like side chains.

Herein, we present the synthesis of such hybrid polymer brushes with umbrella-like side chain, PBIEM-*g*-(PtBA-*b*-Gn), synthesized by the combination of grafting-from and grafting-onto methods as shown in Scheme 2. The polymer brush with linear PtBA side chains was synthesized by ATRP of *t*BA with PBIEM as polyinitiator. Then the terminal groups -Br of side chain PtBA were substituted with azido groups by a nucleophilic substitution using  $\text{NaN}_3$ . Finally, alkynyl poly-

**Scheme 2. Schematic Illustration of the Synthesis of Polymer Brushes with Umbrella-Like Side Chains**



amidoamine dendrons of different generation ( $G_n$ ) were anchored onto the polymer brush PBIEM- $g$ -(PtBA- $N_3$ ) by CuAAC.

## EXPERIMENTAL SECTION

**Materials.** 2-(Trimethylsilyloxy)ethyl methacrylate (HEMA-TMS) and 2-cyanoprop-2-yl(4-fluoro)dithiobenzoate (CPFDB) were synthesized according to literature procedure.<sup>45,46</sup> *tert*-Butyl acrylate (*t*BA) (99%, Alfa Aesar) was purified by vacuum distillation prior to use. 2,2'-Azobis(isobutyronitrile) (AIBN) was purified by recrystallization from ethanol. Potassium fluoride (KF) (99%, Acros) was dried at 200 °C for 12 h prior to use. *N,N*-Dimethylformamide (DMF) was dried over calcium hydride and then distilled under reduced pressure prior to use. Triethylamine was dried over KOH. CuBr was purified by washing with acetic acid and acetone. Tetrahydrofuran (THF) was distilled over Na prior to use. Tetrabutylammonium fluoride (TBAF) (98%, Acros), propargylamine (99%, Acros), methyl acrylate (99%, Alfa Aesar), ethyl 2-bromoisobutyrate (EBiB) (98%, Aldrich), 2-bromoisobutryl bromide (BiBB) (98%, Aldrich) and *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA) (98%, Aldrich) were used as received.

**Characterization Methods.** Polymer characterization and development of brush formation were analyzed by different SEC systems. System 1: A combination of Waters 515 HPLC pump and Waters 2414 refractive index detector equipped with three Waters styragel columns HT2, HT4 and HT5, the effective molecular weight range being 100–10 k, 5 k–600 k, and 50 k–4000 k. Analysis was carried out in DMF with LiBr (1.0 g/L) running at a flow rate of 1.0 mL/min and 50 °C. Polystyrene standards were used for the calibration. System 2: A combination of a Series III pump (Lab Alliance) and Wyatt Optilab DSP differential refractometer detectors. Separations were achieved using 10<sup>5</sup>, 10<sup>4</sup>, and 10<sup>3</sup> Å Phenomenex Phenogel 5  $\mu$ m columns with 0.02 M LiBr in DMF as eluent.

Nuclear magnetic resonance spectroscopy (NMR) spectra were recorded on a Bruker DMX 400 spectrometer operated in the Fourier transform mode. CDCl<sub>3</sub> was used as the solvents. Fourier transform infrared spectroscopy (FT-IR) was conducted using a Thermo Nicolet Avatar 330 FT-IR spectrometer equipped with a deuterated triglycine sulfate detector and KBr optics and controlled by OMNIC software. The spectra were collected at 32 scans with a resolution of 4 cm<sup>-1</sup>. Atomic force microscopy (AFM) images were recorded under ambient conditions using a Digital Instrument Multimode Nanoscope IIIA operating in the tapping mode at 0.5–1.5 Hz with a coefficient of elasticity of 40 N/m. Samples were prepared by spin-coating 10  $\mu$ L of ethanol solution at a concentration of 0.01 mg/mL onto mica.

**Synthesis of Linear PtBA- $N_3$ .**<sup>47</sup> Bromo-terminated PtBA chain (PtBA-Br) was prepared by ATRP using CuBr/PMDETA as catalyst and EBiB as initiator. EBiB (195.0 mg, 1.0 mmol), PMDETA (86.5 mg, 0.5 mmol), *t*BA (6.4 g, 50.0 mmol) and acetone (2.75 g) were added into a 20 mL of flask. The mixture was degassed by three freeze–evacuate–thaw cycles, and then the CuBr (72.0 mg, 0.5 mmol) was added into the flask. The flask was sealed under vacuum and the polymerization was carried out in an oil bath at 60 °C for 3 h. The resulted crude product was passed through a column filled with neutral alumina and purified by precipitating into a large amount of methanol and water mixture (1:1 in volume ratio) three times. After purification, the resulting polymer was dissolved in DMF, NaN<sub>3</sub> (5 times excess to the mole of bromo group) was added, and the resulting solution was allowed to stir for 48 h at 30 °C. After precipitation into methanol/water mixture (1:1 in volume ratio), linear PtBA- $N_3$  was obtained. <sup>1</sup>H NMR analysis (in CDCl<sub>3</sub>,  $\delta$ ): 4.10 (2H, CH<sub>3</sub>CH<sub>2</sub>O in EBiB), 3.71 (1H, CH<sub>2</sub>CHN<sub>3</sub> in PtBA), 2.26 (1H, CH<sub>2</sub>CH in PtBA), 1.47 (9H, COO(CH<sub>3</sub>)<sub>3</sub> in PtBA). SEC analysis (System 1):  $M_{n,SEC}$  = 9.8 kg/mol;  $M_w/M_n$  = 1.12. Theoretical molecular weight:  $M_{n,theor}$  = 5.7 kg/mol, given by monomer conversion by <sup>1</sup>H NMR analysis. FT-IR analysis: 2111 cm<sup>-1</sup> ( $\nu$ , -N<sub>3</sub>).

**Synthesis of PHEMA-TMS.** Bulk RAFT mediated radical polymerization of HEMA-TMS was performed in a sealed ampule equipped with a stir bar under vacuum. A typical procedure was as

follows: CPFDB (13.8 mg,  $5.8 \times 10^{-2}$  mmol), AIBN (1.9 mg,  $1.2 \times 10^{-2}$  mmol) and HEMA-TMS (14.0 g, 69.3 mmol) were added into a 20 mL glass ampule. The mixture was degassed through four freeze–evacuate–thaw cycles, and then the ampule was sealed under vacuum. The polymerization was carried out in an oil bath at 90 °C for 1 h, and was terminated by cooling the mixture with an ice bath. The resulted crude product was purified by precipitating into a large amount of methanol and water mixture (7:3 in volume ratio) three times. The final product was then dried under vacuum to a constant mass. Yields: 50%. <sup>1</sup>H NMR analysis (in CDCl<sub>3</sub>,  $\delta$ ): 4.03 (2H, COOCH<sub>2</sub>CH<sub>2</sub>Si), 3.78 (2H, COOCH<sub>2</sub>CH<sub>2</sub>Si), 0.16 (9H, CH<sub>2</sub>Si(CH<sub>3</sub>)<sub>3</sub>). SEC analysis (system 1):  $M_{n,SEC}$  = 120.5 kg/mol ( $M_w/M_n$  = 1.22).  $M_{n,theor}$  = 122.5 kg/mol (based on HEMA-TMS conversion determined by <sup>1</sup>H NMR).

**Synthesis of Polyinitiator PBIEM.**<sup>32,48</sup> P(HEMA-TMS) (3.17 g, 15.7 mmol) was dissolved in dry THF (30 mL) under nitrogen. Potassium fluoride (2.18 g, 37.5 mmol) was added followed by slow addition of tetrabutylammonium fluoride (82 mg, 0.31 mmol) in THF. 2-Bromoisobutryl bromide (4.74 mL, 37.6 mmol) was added dropwise over a course of 20 min. The reaction mixture was stirred at room temperature for 36 h and afterward precipitated from THF into methanol/ice (1:1 in volume ratio). The isolated polymer was precipitated three times in hexane and dried under vacuum at 30 °C for 24 h. The final product was then dried under vacuum to a constant mass. Yields: 90%. <sup>1</sup>H NMR analysis (in CDCl<sub>3</sub>,  $\delta$ ): 4.41 (2H, COOCH<sub>2</sub>CH<sub>2</sub>O), 4.22 (2H, COOCH<sub>2</sub>CH<sub>2</sub>O), 1.98 [6H, CH<sub>2</sub>COO(CH<sub>3</sub>)<sub>2</sub>Br]. SEC analysis (system 1):  $M_{n,SEC}$  = 142.1 kg/mol ( $M_w/M_n$  = 1.26).

**Synthesis of PBIEM- $g$ -PtBA-Br.** A typical procedure to prepare bromine end-functionalized PBIEM- $g$ -PtBA is as follows. PBIEM (0.56 g, 2.0 mmol), PMDETA (70 mg, 0.4 mmol), *t*BA (20.48 g, 0.16 mmol), and acetone (11.5 g) were added into a 50 mL of flask. The mixture was degassed by three freeze–evacuate–thaw cycles, and then CuBr (57.6 mg, 0.4 mmol) was added into the flask. The flask was sealed under vacuum. The polymerization was carried out in an oil bath at 60 °C for 1 h. The resulted crude product was passed through a column filled with neutral alumina and purified by precipitating into large amount of methanol and water mixture (1:1 volume ratio) three times. The final product was then dried under vacuum to a constant mass. Yields: 12.5%. <sup>1</sup>H NMR (in CDCl<sub>3</sub>,  $\delta$ ): 4.15 (5H, COOCH<sub>2</sub>CH<sub>2</sub>O in backbone and CH<sub>2</sub>CHBr in PtBA), 2.26 (1H, CH<sub>2</sub>CH in PtBA), 1.47 [9H, COO(CH<sub>3</sub>)<sub>3</sub> in PtBA]. SEC analysis (system 1):  $M_{n,SEC}$  = 318.8 kg/mol ( $M_w/M_n$  = 1.25).

**End group modification of PBIEM- $g$ -PtBA-Br.** PBIEM- $g$ -PtBA-Br (1.0 g, 0.65 mmol Br groups) was dissolved in 100 mL DMF in a dry flask, sodium azide (0.42 g, 6.5 mmol, 10 equiv. to Br) was added to this solution. The reaction was stirred for 2 days at 40 °C. After reaction, the polymer was precipitated into a large amount of water three times and was dried under vacuum to a constant mass. <sup>1</sup>H NMR analysis (in CDCl<sub>3</sub>,  $\delta$ ): 4.15 (4H, COOCH<sub>2</sub>CH<sub>2</sub>O in backbone) 3.71 (1H, CH<sub>2</sub>CHN<sub>3</sub> in PtBA), 2.26 (1H, CH<sub>2</sub>CH in PtBA), 1.47 (9H, COO(CH<sub>3</sub>)<sub>3</sub> in PtBA). SEC analysis (system 1):  $M_{n,SEC}$  = 318.8 kg/mol ( $M_w/M_n$  = 1.25). The SEC trace was similar to PBIEM- $g$ -PtBA. FT-IR analysis: 2111 cm<sup>-1</sup> is the characteristic absorption bands of the azido.

**Synthesis of PAMAM Dendron  $G_n$  with Propargyl Focal Point.** The propargyl focal point PAMAM dendrons of one, two and three generations ( $G_n$ ,  $n$  = 1, 2, 3) were synthesized according to a protocol similar to that described by Lee et al.<sup>49,50</sup> In brief, a solution of propargylamine (1.5 g, 27.3 mmol) in methanol (5 mL) was added dropwise to the solution of methyl acrylate (MA, 9.4 g, 109.2 mmol) in methanol (10 mL). The reaction mixture was stirred vigorously for 24 h at room temperature under nitrogen atmosphere. The reaction solution was evaporated, and then the residue was dried in vacuum at 35 °C to give the methyl ester-terminated dendron (G1). The solution of PAMAM dendron (G1, 5.36 g, 23.6 mmol) in methanol (20 mL) was added dropwise to the solution of ethylenediamine (21.2 g, 0.35 mol) in methanol (30 mL). The reaction mixture was stirred vigorously for 48 h at room temperature. After the reaction, the solution was evaporated, and the residue was dried in vacuum at 35 °C to give the amino terminated PAMAM dendron (G1.5). The amino-



terminated PAMAM dendron was reacted with MA in methanol to afford the methyl ester-terminated dendron (G2). The methyl ester-terminated dendron (G3) was synthesized from the dendron (G2) using the same process of successive amidation and addition.  $^1\text{H}$  NMR (in  $\text{CDCl}_3$ ,  $\delta$ ): G1: 2.18 (1H,  $\text{HC}\equiv\text{C}$ ), 2.43 (4H,  $\text{CH}_2\text{CH}_2\text{COOCH}_3$ ), 2.81 (4H,  $\text{CH}_2\text{CH}_2\text{COOCH}_3$ ), 3.41 (2H,  $\text{HC}\equiv\text{CH}_2$ ), 3.67 (6H,  $\text{COOCH}_3$ ); G2: 2.18 (1H,  $\text{HC}\equiv\text{C}$ ), 2.38 (4H,  $\text{CH}_2\text{CONH}$ ), 2.43 (8H,  $\text{CH}_2\text{COOCH}_3$ ), 2.54 (4H,  $\text{CH}_2\text{CH}_2\text{N}$ ), 2.75 (8H,  $\text{CH}_2\text{CH}_2\text{CO}$ ), 2.84 (4H,  $\text{CH}_2\text{CH}_2\text{CONH}$ ), 3.29 (4H,  $\text{CONHCH}_2$ ), 3.46 (2H,  $\text{HC}\equiv\text{CCH}_2$ ), 3.67 (12H,  $\text{COOCH}_3$ ), 7.08 (2H,  $\text{CONHCH}_2$ ); G3: 2.2 (1H,  $\text{HC}\equiv\text{CCH}_2\text{N}$ ), 2.36–2.45 (28H,  $\text{CH}_2\text{CONH}$  and  $\text{CH}_2\text{COOCH}_3$ ), 2.52–2.57 (12H,  $\text{CONHCH}_2$ ), 2.72–2.82 (28H,  $\text{NCH}_2$ ), 3.27–3.29 (12H,  $\text{CH}_2\text{N}$ ), 3.46 (2H,  $\text{HC}\equiv\text{CCH}_2\text{N}$ ), 3.67 (24H,  $\text{COOCH}_3$ ), 7.07 and 7.7 (6H,  $\text{CONH}$ ).

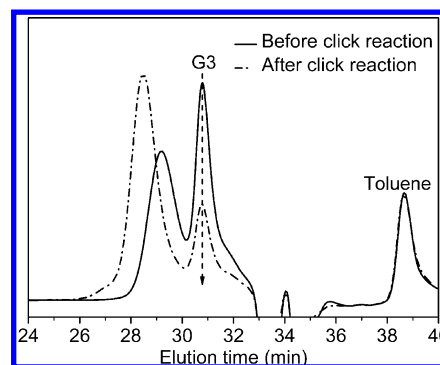
**Synthesis of Polymer Brushes with Umbrella Side Chain by Click Reactions.** A typical procedure to prepare polymer brushes with umbrella side chain PBIEM-*g*-(PtBA-*b*-G3) is as follows. PBIEM-*g*-PtBA- $\text{N}_3$  (156.0 mg, 0.1 mmol), ascorbic acid (17.6 mg, 0.1 mmol), G3 (142.8 mg, 0.1 mmol) and DMF (2.5 mL) were added into a 10 mL of flask. The mixture was degassed by three freeze–evacuate–thaw cycles, and then the  $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$  (2.5 mg, 0.01 mmol) was added into the flask. Toluene (0.05 mL) was added initially into the reaction system as internal standard for calculation of the percentage of reacted G3 via SEC measurement. The flask was sealed under vacuum and the click reaction was carried out in an oil bath at 45 °C for 5 h. The polymer solution was exposed to air to terminate reaction. One portion was diluted by DMF with LiBr for SEC measurement. Another portion was diluted with DMF and precipitated into large amount of water two times.  $^1\text{H}$  NMR analysis (in  $\text{CDCl}_3$ ,  $\delta$ ):  $\delta$  = 3.67, 3.29, 2.75, 2.56, and 2.45 were assigned to the proton of G3. SEC analysis (system 1):  $M_{n,\text{SEC}}$  = 534.1 kg/mol ( $M_w/M_n$  = 1.24). FT-IR analysis: The characteristic absorption band of the azido ( $2111\text{ cm}^{-1}$ ) was disappeared, and the main characteristic absorption bands of the G3 Dendron (1548 and  $1650\text{ cm}^{-1}$ ) were emerged.

The procedure for preparing polymer brushes with umbrella side chain PBIEM-*g*-(PtBA-*b*-Gn ( $n = 1, 2$ )) was similar to that described above except for using Gn ( $n = 1, 2$ ) dendrons. The click coupling reaction between linear PtBA- $\text{N}_3$  and G3 was investigated according to the same procedure as that described above except for using linear PtBA- $\text{N}_3$  and the molar ratio of G3 to azido groups.

## RESULTS AND DISCUSSION

The PAMAM dendrons of different generation with a propargyl focal point, defined as Gn ( $n = 1, 2$ , and 3), were synthesized from propargylamine using repetitive Michael addition and amidation reaction. To prepare the polymer brushes which possess umbrella-like side chains, a combination of controlled radical polymerization and click chemistry was applied as indicated in Scheme 2.

**Model coupling reaction.** The efficiency of chain-end modification of bromine-terminated polymer PtBA was evaluated by performing the model coupling reaction between linear PtBA- $\text{N}_3$  and G3 dendron. To allow all of the azide functional groups of PtBA involved in the reaction, G3 dendron was reacted with linear PtBA- $\text{N}_3$  using the molar ratio of G3 to azido group equal to 1.8:1. By using  $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ /ascorbic acid as catalyst and DMF as solvent, the coupling reaction between G3 dendron and linear PtBA- $\text{N}_3$  was completed within 4.5 h. The SEC traces of before and after the click coupling reaction are shown in Figure 1. It was clearly demonstrated that the SEC trace of coupling product exhibited a clear shift to higher molecular weight region. The efficiency was quantified by comparing the peak areas of the G3 before and after coupling reaction with toluene as internal calibration.<sup>33</sup> At the feed ratio of  $[\text{G3}]:[\text{N}_3] = 1.8:1$ , percentage of the reacted dendron G3 was ca. 56% and the coupling efficiency of the click reaction was ca.100%. The result confirmed that the click



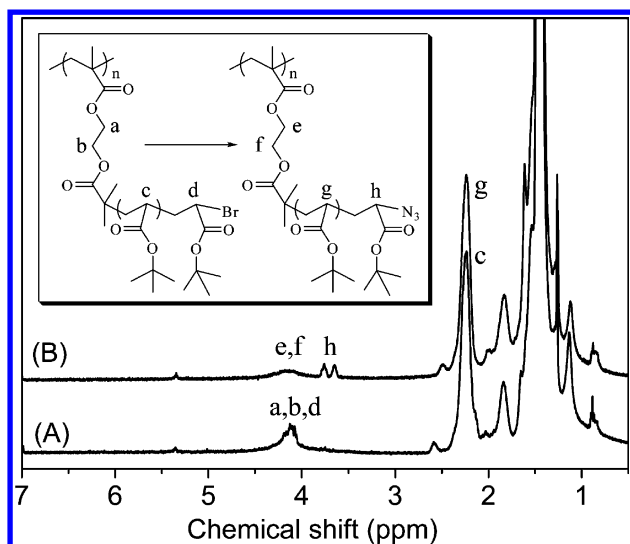
**Figure 1.** SEC traces in DMF (system 2) for the mixtures before and after click reaction between PtBA<sub>43</sub>-N<sub>3</sub> and G3 at a feed ratio of  $[\text{G3}]:[\text{N}_3] = 1.8:1$ .

reaction between linear PtBA- $\text{N}_3$  and G3 dendron was fast and highly efficient. It also revealed that the terminal -Br of PtBA was fully substituted with the -N<sub>3</sub> group.

**Synthesis of Polymer Brush PBIEM-*g*-PtBA.** In order to obtain a PtBA brush with controlled molecular weight, a two-step controlled radical polymerization procedure was introduced.<sup>16,51</sup> The main chain polymer PHEMA-TMS was synthesized by RAFT polymerization of HEMA-TMS in bulk using CPFDB as RAFT agent and AIBN as initiator, and subsequently the PHEMA-TMS was esterified with 2-bromoisobutyryl bromide in the presence of a catalytic amount of TBAF to yield a well-defined backbone polyinitiator PBIEM. Then tBA was polymerized by ATRP using the polyinitiator to prepare the bromine-end polymer brush PBIEM-*g*-PtBA-Br as shown in Scheme 2.

The degree of polymerization (DP) of PHEMA-TMS estimated by monomer conversion according to  $^1\text{H}$  NMR spectra was 600. Figure S1A, Supporting Information, gives the SEC curve of PHEMA-TMS homopolymer, indicating a monomodal peak and a low polydispersity index ( $M_w/M_n$ ). The  $^1\text{H}$  NMR spectrum of PHEMA-TMS was shown in Figure S2A, Supporting Information, there are three typical resonance peaks at 4.03, 3.78, and 0.15 ppm (a, b and c), which represent two methylenes protons adjacent to ester group and three methyl groups of TMS, respectively. As shown in Figure S1B, Supporting Information, after the esterification reaction, the SEC trace of the resulting backbone polyinitiator PBIEM is monomodal and the  $M_w/M_n$  is low. Figure 2B gives the  $^1\text{H}$  NMR spectrum of polyinitiator PBIEM, there are three typical peaks at 4.41, 4.22, and 1.98 ppm (d, e, and f), which are assigned to methylene protons between two ester groups and methyl groups near the bromide group, respectively. There are no peaks at 4.03, 3.78, and 0.15 ppm of PHEMA-TMS, indicating a complete esterification of PHEMA-TMS with 2-bromoisobutyryl bromide.

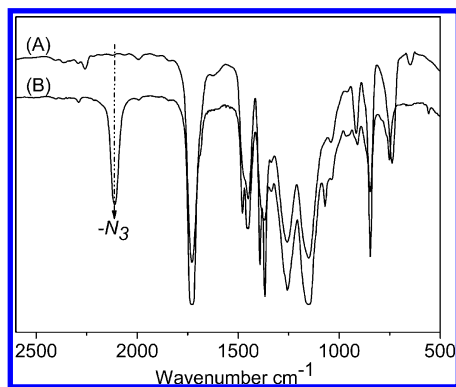
Because of the high initiation efficiency for ATRP of acrylate monomer from a polyinitiator,<sup>52,53</sup> we chose tBA as monomer for preparing the brush polymer. After formation of the brushes with PtBA side chains, SEC curve of the brush polymer PBIEM-*g*-PtBA was shifted toward higher molecular weight by comparison with the backbone polyinitiator, and the  $M_w/M_n$  remained low (1.27), as shown in Figure S1C, Supporting Information. The  $^1\text{H}$  NMR spectrum of PBIEM-*g*-PtBA was showed in Figure S2C, Supporting Information, a characteristic strong peak at 1.44 ppm (peak j) corresponding to methyl protons in the *tert*-butyl group and peak at 2.25 ppm (peak i)



**Figure 2.**  $^1\text{H}$  NMR spectra of (A)  $\text{PBIEM}_{600}\text{-g-PtBA}_{10}\text{-Br}$  and (B)  $\text{PBIEM}_{600}\text{-g-PtBA}_{10}\text{-N}_3$ .

is assigned to the main chain of PtBA side chains. The polymerization degree (DP) of side chains estimated by monomer conversion according to  $^1\text{H}$  NMR was 10. This indicates a well-defined brush polymer  $\text{PBIEM}_{600}\text{-g-PtBA}_{10}\text{-Br}$  was obtained.

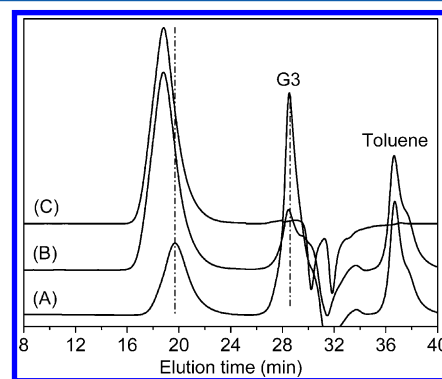
**End Group Modification of  $\text{PBIEM-g-PtBA-Br}$  with  $\text{NaN}_3$ .** In this step, the end groups  $-\text{Br}$  of PtBA side chains were converted into azido functionalized by a nucleophilic substitution using  $\text{NaN}_3$ . After optimization of the reaction conditions, i.e., ten folds of  $\text{NaN}_3$ , a nearly quantitative end group conversion was obtained as determined by  $^1\text{H}$  NMR spectroscopy and FT-IR spectrum. Figure 2A depicts the starting brush polymer, there are typical peaks at 3.95–4.40 ppm (a, b and d), which are assigned to methylene protons between two ester groups of the polyinitiator and the proton adjacent to the terminal bromine groups. After modification of  $\text{PBIEM-g-PtBA-Br}$  with  $\text{NaN}_3$ , new peaks at 3.58–3.84 ppm, which are assigned to the proton adjacent to the terminal  $\text{N}_3$  group, as shown in Figure 2B. The efficiency of end group  $-\text{Br}$  converted to  $-\text{N}_3$  was derived to be quantitatively based on  $^1\text{H}$  NMR spectra. The reaction was also confirmed by FT-IR spectroscopy. As shown in Figure 3, the FT-IR spectra of  $\text{PBIBM-g-PtBA-Br}$  (Figure 3A) and  $\text{PBIBM-g-PtBA-N}_3$  (Figure 3B), where the characteristic  $-\text{N}_3$  stretch of the azido peak is



**Figure 3.** FT-IR spectra of (A)  $\text{PBIEM}_{600}\text{-g-PtBA}_{10}\text{-Br}$  and (B)  $\text{PBIEM}_{600}\text{-g-PtBA}_{10}\text{-N}_3$ .

clearly visible at  $2100\text{ cm}^{-1}$ , indicated that the end group  $-\text{Br}$  turned into  $-\text{N}_3$  successfully.

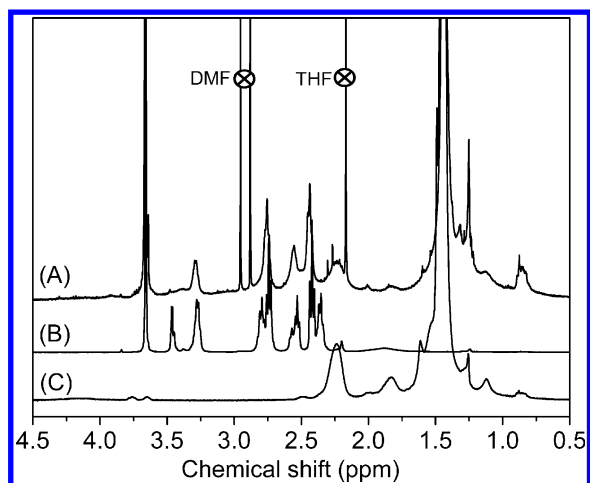
**Synthesis of  $\text{PBIEM-g-(PtBA-b-G3)}$ .** The PtBA brush-shaped polymers with azido ends were applied for grafting alkyne-containing PAMAM dendrons ( $G_n$ ) by the CuAAC reaction with formation of a stable 1,2,3-triazole ring. The efficiency of CuAAC between the polymer brush with PtBA- $\text{N}_3$  side chains and  $G_n$  was evaluated by SEC traces of the reaction mixture before and after reaction. The G3 dendron was first reacted with  $\text{PBIEM-g-PtBA-N}_3$  with molar feed ratio of  $[\text{G3}]:[-\text{N}_3] = 1:1$ . By using  $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ /ascorbic acid as catalyst and DMF as solvent, the coupling reaction between G3 dendron and  $\text{PBIEM-g-PtBA-N}_3$  was completed within 4.5 h. Figure 4A and 4B give the SEC traces of the mixtures of



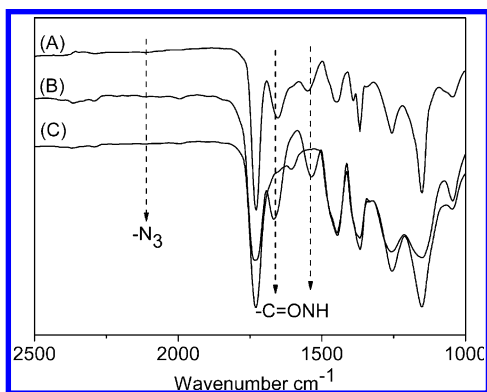
**Figure 4.** SEC traces (system 1) in DMF of reaction mixture of  $\text{PBIEM}_{600}\text{-g-PtBA}_{10}\text{-N}_3$  and G3 (A) before and (B) after click reaction, and (C) of the purified product.

$\text{PBIEM-g-PtBA-N}_3$  and G3 before and after click reaction. After click reaction, increase of the molecular weight of the coupling product is shown by shifting the SEC trace to shorter retention time (Figure 4B), indicating formation of  $\text{PBIEM-g-(PtBA-b-G3)}$ .

During the coupling reaction, the conversion of G3 dendron was determined by SEC using toluene as internal calibration, which was preadded into the reaction system. When the initial molar ratio of G3 dendron to azido was 1:1, the percentage of reacted G3 dendron was ca. 73% and thus the grafting density of the hybridized molecular brushes was ca. 73%. We had increased the feed ratio of G3 dendron to azido to 2:1 and the grafting density (75%) increased slightly. The resulting polymer brushes with umbrella-like side chains were isolated by removing the unreacted G3 dendron by precipitating into a large amount of water two times. Figure 4C shows the SEC trace of the purified  $\text{PBIEM-g-(PtBA-b-G3)}$ . The  $^1\text{H}$  NMR spectrum of the obtained products is given in Figure 5A and new peaks at 3.67, 3.29, 2.75, 2.56, and 2.45 ppm were assigned to the protons of G3 (Figure 5B). Moreover, no characteristic absorption of azido at  $2111\text{ cm}^{-1}$  could be found in IR spectrum of the  $\text{PBIEM-g-(PtBA-b-G3)}$  (Figure 6A), indicating a very high conversion of coupling reaction. The actual grafting density could be higher than the results evaluated by SEC. It is believed that the dendron conversion by SEC could have been underestimated because the SEC of G3 was overlapped partially with the solvent. Moreover, the characteristic bands of carbonyl of amide units in G3 dendron at  $1548$  and  $1650\text{ cm}^{-1}$  were observed obviously. These results indicated that the successful click coupling between the G3 dendron and  $\text{PBIEM-g-PtBA-N}_3$ .

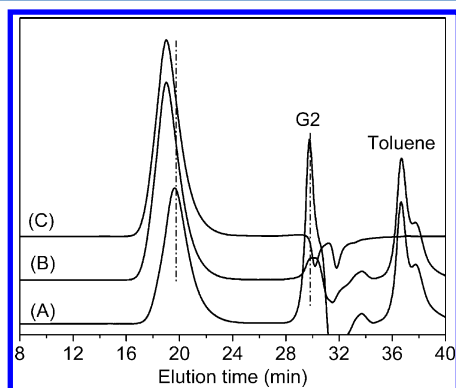


**Figure 5.**  $^1\text{H}$  NMR spectra of (A)  $\text{PBIEM}_{600}\text{-g-(PtBA}_{10}\text{-b-G3)}$ , (B) dendron G3, and (C)  $\text{PBIEM}_{600}\text{-g-PtBA}_{10}\text{-N}_3$ .

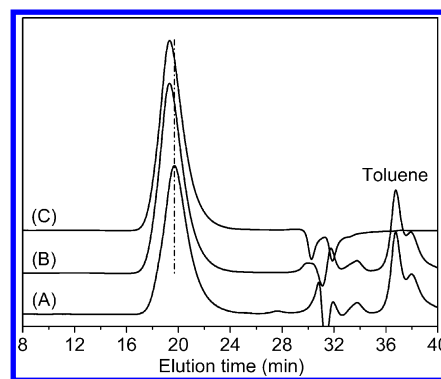


**Figure 6.** FT-IR spectra recorded for (A)  $\text{PBIEM}_{600}\text{-g-(PtBA}_{10}\text{-b-G3)}$ , (B)  $\text{PBIEM}_{600}\text{-g-(PtBA}_{10}\text{-b-G2)}$ , and (C)  $\text{PBIEM}_{600}\text{-g-(PtBA}_{10}\text{-b-G1)}$ .

**Synthesis of  $\text{PBIEM-g-(PtBA-b-Gn)}$  ( $n = 1, 2$ ).** To study the effect of generation number of dendron to the reaction,  $\text{Gn}$  ( $n = 1, 2$ ) of low generation was also used for synthesis of  $\text{PBIEM-g-(PtBA-b-Gn)}$  ( $n = 1, 2$ ) polymer brushes. The click coupling reactions between  $\text{PBIEM-g-PtBA-N}_3$  and  $\text{Gn}$  ( $n = 1, 2$ ) were investigated according to the same procedure as that described above. As shown in Figure 7 and Figure 8, the SEC traces of the resulting polymer brushes shifted toward higher molecular weight by comparison with the  $\text{PBIEM-g-PtBA-N}_3$



**Figure 7.** SEC traces (system 1) recorded for (A) before click reaction and (B) after click reaction between  $\text{PBIEM}_{600}\text{-g-PtBA}_{10}\text{-N}_3$  and G2 and for (C) the coupling product after purification.



**Figure 8.** SEC traces (system 1) recorded for (A) before click reaction and (B) after click reaction between  $\text{PBIEM}_{600}\text{-g-PtBA}_{10}\text{-N}_3$  and G1 and for (C) the coupling product after purification.

precursors, indicating the formation of  $\text{PBIEM-g-(PtBA-b-Gn)}$  ( $n = 1, 2$ ).

From parts A and B of Figure 7, the percentage of reacted G2 dendron at the feed ratio of 1:1 was ca. 84% and thus the grafting density of the obtained molecular brushes was ca. 84%. Figure 7C gives the SEC trace of purified  $\text{PBIEM-g-(PtBA-b-G2)}$ . The  $^1\text{H}$  NMR spectrum of  $\text{PBIEM-g-(PtBA-b-G2)}$  was shown in Figure S3A, Supporting Information, and the new peaks at 3.67, 3.32, 2.79, 2.59, and 2.47 ppm were attributed to the protons of G2. The FT-IR spectrum (Figure 6B) demonstrated that the characteristic absorption band of the azido ( $2111\text{ cm}^{-1}$ ) was disappeared completely, and the characteristic bands of the G2 dendron were exhibited ( $1539$  and  $1666\text{ cm}^{-1}$ ). These results indicated that the click coupling reaction between the G2 dendron and  $\text{PBIEM-g-PtBA-N}_3$  was also very high.

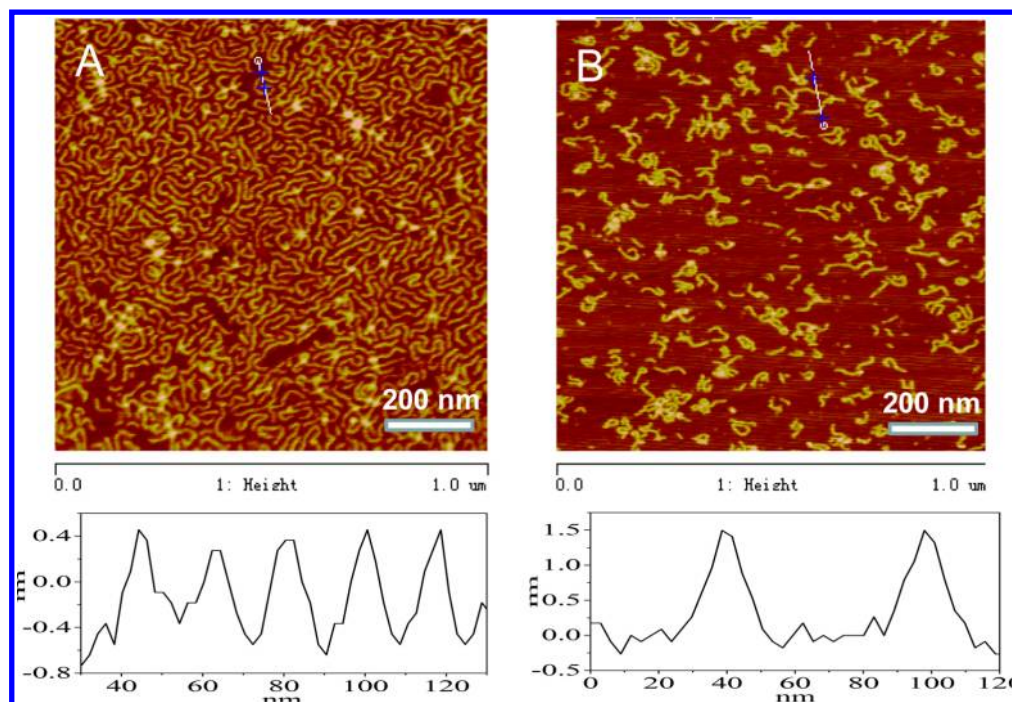
Since the SEC of G1 dendron was overlapped with the solvent, it is impossible to evaluate the dendron conversion during reaction. Thus, the grafting efficiency of G1 dendron was estimated by  $^1\text{H}$  NMR spectrum that was higher than 95%. As shown in Figure S4A, Supporting Information, the new peaks at 7.55, 3.67, 2.85, and 2.51 ppm appeared and the peak at 7.55 ppm presented the proton of the 1,2,3-triazole rings and others were assigned to the protons of G1. The IR spectrum of  $\text{PBIEM-g-(PtBA-b-G1)}$  is given in Figure 6C, the characteristic absorption band of the azido ( $2111\text{ cm}^{-1}$ ) was completely disappeared, further confirmed the coupling reaction between  $\text{PBIEM-g-PtBA-N}_3$  and G1 dendron was highly efficient. The molecular weight and polydispersity indices ( $M_w/M_n$ ) of polymer brushes with umbrella-like side chains  $\text{PBIEM-g-(PtBA-b-Gn)}$  ( $n = 1, 2$  and 3)) were summarized in Table 1. It may learn that three brushes with hybridized side chains had relative low polydispersity indices, demonstrating a controlled synthetic strategy. It is noteworthy that the  $M_{n,\text{SEC}}$  data is much

**Table 1.** Summary of Click Reactions between  $\text{PBIEM-g-PtBA-N}_3$  and  $\text{Gn}^a$

Gn	% eff <sup>b</sup>	$M_{n,\text{SEC}}$ (kg/mol) <sup>c</sup>	$M_w/M_n^c$	$M_{n,\text{theor}}$ (kg/mol) <sup>d</sup>
G3	73	510	1.25	1555
G2	84	465	1.26	1240
G1	95	413	1.24	1042

<sup>a</sup>Experimental conditions:  $[-\text{N}_3]:[\text{Gn}]:[\text{CuSO}_4\cdot 5\text{H}_2\text{O}]:[\text{Ascorbic acid}] = 1:1:0.1:1$ , DMF,  $45^\circ\text{C}$ . <sup>b</sup>Grafting efficiency was calculated by SEC except for G1, which was estimated by  $^1\text{H}$  NMR. <sup>c</sup>Obtained from the final product of  $[\text{Gn}]:[-\text{N}_3] = 1:1$ . <sup>d</sup>Estimated by grafting efficiency.





**Figure 9.** AFM images of (A) PBIEM<sub>600</sub>-g-PtBA<sub>10</sub> and (B) PBIEM<sub>600</sub>-g-(PtBA-*b*-G3) on mica.

lower than the  $M_{n,theor}$ , implying that the brushes had a rather compact molecular structure.

**AFM Analysis of PBIEM-g-(PtBA-*b*-G3).** AFM was performed to visualize single chains of the polymer brushes with umbrella-like side chains G3. The samples of PBIEM-g-PtBA and PBIEM-g-(PtBA-*b*-G3) were prepared by spin-casting the dilute ethanol solutions of polymer brushes onto freshly cleaved mica surface. Both samples were analyzed by using the same test condition. Figure 9A shows the AFM image of PBIEM<sub>600</sub>-g-PtBA<sub>10</sub> and uniform wormlike morphology was observed in large area, indicating uniformity of the precursor molecular brushes. The height and the width of PBIEM<sub>600</sub>-g-PtBA<sub>10</sub> brushes were ca. 0.9 and 17 nm. The AFM image of PBIEM-g-(PtBA-*b*-G3) is shown in Figure 9B, the height and the width of novel polymer brushes with umbrella-like side were ca. 1.6 and 35 nm. Although the height and width value are apparent data, the comparison of the dimensions of two samples is still meaningful under the same test condition. Thus, the novel molecular brushes became thicker obviously, which were contributed to the incorporation of dendritic periphery.

## CONCLUSIONS

Combining grafting-from and grafting-onto approaches, a new type of hybrid polymer brushes with umbrella-like side chain was synthesized. As a result, core-shell hybrid polymer brushes with defined multiple terminals were prepared, and the number of functional terminal could be precisely tuned by using dendrons with different generation. This polymer brushes with novel hybrid side chains could demonstrate unique properties and may stimulate further research interest to explore their potential application.

## ASSOCIATED CONTENT

### Supporting Information

SEC traces (Figure S1) and <sup>1</sup>H NMR spectra (Figure S2) of PBIEM<sub>600</sub>-g-PtBA<sub>10</sub> brush formation and <sup>1</sup>H NMR spectra of

PBIEM<sub>600</sub>-g-(PtBA<sub>10</sub>-*b*-G2) (Figure S3) and PBIEM<sub>600</sub>-g-(PtBA<sub>10</sub>-*b*-G1) (Figure S4). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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