

One-Pot Synthesis of Brush Diblock Copolymers through Simultaneous ATRP and Click Coupling

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 Supporting Information

INTRODUCTION

Among polymers with controlled and more complex architectures, brush diblock copolymers (brush-1-*block*-brush-2) have received increasing attention.^{1–9} They are basically two different molecular brushes linked together. There are several demonstrated synthetic strategies for preparing this type of polymer architecture. The most exploited method consists in first preparing a precursor diblock copolymer and then making use of the functional groups on the two blocks to attach two types of arms. The latter step can be achieved by using different approaches: with “grafting from” for the two brushes,^{1–3} with “grafting onto” for the two brushes,⁴ or with combined use of “grafting from” for one brush and “grafting onto” for the other brush.^{5,6} More recently, a “grafting through” approach based on ring-opening metathesis polymerization (ROMP) was shown to be efficient in producing brush diblock copolymers with high molecular weights and low polydispersity index (PDI).^{7,8} It consists in using ROMP to polymerize sequentially two different macromonomers. It is noted that living radical polymerization techniques can also be applied to polymerize macromonomer via “grafting through”. This has been combined with “grafting from” to synthesize brush diblock copolymers.⁹ Each of these strategies has its advantages and disadvantages.^{1–9} While ROMP-based “grafting through” is one-pot synthesis, generally, the utilization of two “grafting from” or two “grafting onto” or one “grafting from” with one “grafting onto” based on a precursor diblock copolymer requires separate steps for the two brushes, often necessitating purification after obtaining the first brush and protection/deprotection steps for functional groups.

To our knowledge, there are few reports on combined use of “grafting from” and “grafting onto” to synthesize brush diblock copolymers. Deffieux and co-workers used a precursor diblock copolymer of poly(chloroethyl vinyl ether) (PCEVE) and poly(hydroxy ethyl vinyl ether) (POHEVE) to attach separately arms of polystyrene (PS) and poly(ethylene oxide) (PEO), obtaining the (PCEVE-*g*-PS)-*b*-(POHEVE-*g*-PEO) brush diblock copolymer.⁵ They first grafted polystyryllithium onto the reactive chloro functions of the PCEVE block (“grafting onto”) and then polymerized ethylene oxide by means of anionic polymerization from the hydroxyl functions of the POHEVE block (“grafting from”). In another study, starting with a different precursor diblock copolymer of PCEVE and poly(2-(1,3-dioxane) ethyl vinyl ether) (PACVE), they first used living cationic polymerization initiated by 1,3-dioxane pendant groups to grow arms of poly(methyl vinyl ether) (PMVE) (“grafting from”) and then attached PS onto the PCEVE block (“grafting onto”) through the

anionic coupling reaction.⁶ Although the strategy allows for the preparation of high molar mass and narrow PDI samples, very strict experimental conditions are necessary for living ionic polymerization and coupling reaction, and removal of uncoupled polymer chains or purification following the formation of the first brush was needed before making the second brush. In this paper, we present a robust, one-pot synthetic method for preparing brush diblock copolymers via the combined use of “grafting from” and “grafting onto”.

RESULTS AND DISCUSSION

Synthetic Approach. As schematized in Figure 1, the synthetic method is based on using a precursor diblock copolymer of which one block contains pendant initiator groups for atom transfer radical polymerization (ATRP) of a monomer and the other block bears pendant azide groups ready for “click” coupling with an alkynyl-terminated polymer. We show that with all the ingredients in the same solution formation of two brushes can proceed simultaneously and orthogonally through ATRP and click reaction. It should be emphasized that for the synthesis of one single brush all chemical approaches including living/controlled ionic and radical polymerizations and “click” coupling are known.^{10–17} The novelty of the present study is the designed use of ATRP and click reaction for the one-pot formation of brush diblock copolymers. In addition to polymer synthesis and characterization, the self-assembly behaviors in solution and in the solid state of our brush diblock copolymers were also investigated.

Scheme 1 shows the synthetic route to our brush diblock copolymer. Reversible addition–fragmentation chain transfer polymerization (RAFT) was first utilized to prepare a precursor diblock copolymer of 2-(2-bromoisobutyryloxy)ethyl methacrylate and 2-(2-azideisobutyryloxy)ethyl methacrylate, namely PBIEMA-*b*-PAIEMA, with bromo and azide functionalities on the side chain of each block. Afterward, in a THF solution at 70 °C, one-pot ATRP of styrene and click coupling of alkynyl-terminated poly(ethylene glycol) methyl ether (MPEG) were carried out to produce PS chains on the PBIEMA backbone and PEO chains on the PAIEMA backbone, yielding the target brush diblock copolymer (PBIEMA-*g*-PS)-*b*-(PAIEMA-*g*-PEO). It should be noted that PS and PEO were chosen to test a new

Received: April 1, 2011

Revised: May 24, 2011

Published: June 15, 2011

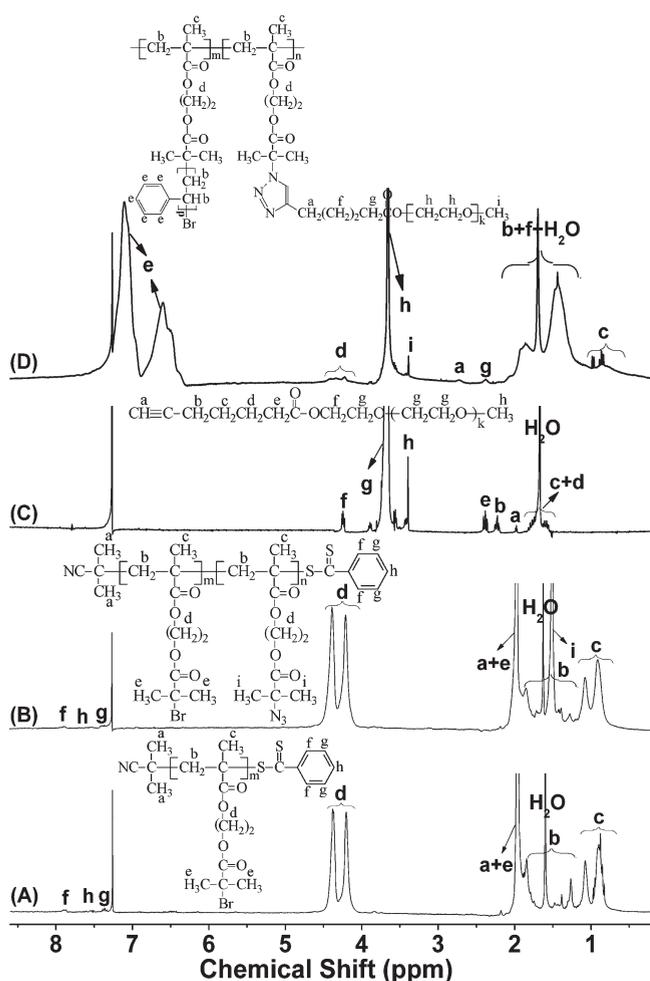


Figure 2. ^1H NMR of (A) PBIEMA₃₀-CTA, (B) PBIEMA₃₀-*b*-PAIEMA₃₆, (C) alkynyl-MPEG2000, and (D) (PBIEMA₃₀-*g*-PSt₆₀)-*b*-(PAIEMA₃₆-*g*-PEO₄₅).

Table 1. Characteristics of Synthesized Polymers

sample	$M_{n,\text{NMR}}^a$ (g/mol)	$M_{n,\text{GPC}}^b$ (g/mol)	M_w/M_n^b
PBIEMA ₃₀ -CTA	8300	8800	1.19
PBIEMA ₃₀ - <i>b</i> -PAIEMA ₃₆	17000	18500	1.18
(PBIEMA ₃₀ - <i>g</i> -PSt ₆₀)- <i>b</i> -(PAIEMA ₃₆ - <i>g</i> -PEO ₄₅)	254600 ^c	165200	1.16
(PBIEMA ₃₀ - <i>g</i> -PSt ₅₆)- <i>b</i> -(PAIEMA ₃₆ - <i>g</i> -PEO ₁₁₂)	285300 ^d	170800	1.13

^aBased on ^1H NMR (in CDCl_3). ^bBased on size exclusion chromatography (SEC) (in THF with polystyrene standards). ^cBased on a "click" graft efficiency of 70% for MPEG2000. ^dBased on a "click" graft efficiency of 52% for MPEG5000.

of alkynyl-terminated MPEG.¹⁸ These NMR-determined compositions were in turn used to calculate the average molecular weights of the two brush diblock copolymers. The characterization results are summarized in Table 1. While all samples have a low polydispersity index (PDI) according to SEC measurements, ^1H NMR-based M_n s of brush diblocks are significantly higher than the values obtained with SEC using PS standards. It is possible that the architecture of brush diblock copolymers leads to more compact conformation and smaller hydrodynamic

volume, resulting in apparently lower molecular weights.^{19,20} Moreover, comparing the infrared spectra of PBIEMA₃₀-*b*-PAIEMA₃₆ and (PBIEMA₃₀-*g*-PS₆₀)-*b*-(PAIEMA₃₆-*g*-PEO₄₅) (Supporting Information), the characteristic azide absorption peak at 2109 cm^{-1} is largely reduced in intensity relative to the carbonyl band indicating coupling of PEO chains, while the appearance of phenyl bands in the $1450\text{--}1600\text{ cm}^{-1}$ region is clearly observed in the brush diblock.

To further confirm the simultaneous growth of PS chains from PBIEMA and the click coupling of PEO onto PAIEMA, the two brush diblock copolymer samples were subjected to hydrolysis (Supporting Information). Both cleaved PS and PEO chains were observed, and they were separated from the mixture and analyzed with SEC and ^1H NMR. Using PS standards, PS chains cleaved from (PBIEMA₃₀-*g*-PS₆₀)-*b*-(PAIEMA₃₆-*g*-PEO₄₅) have $M_n \sim 9600$ and $M_w/M_n = 1.17$, while those from (PBIEMA₃₀-*g*-PS₅₆)-*b*-(PAIEMA₃₆-*g*-PEO₁₁₂) have $M \sim 7800$ and $M_w/M_n = 1.15$. These results are in reasonably good agreement with the NMR results considering the uncertainty in comparing the integrals of the resonance peaks (Figure 2) and the fact that 100% of bromo groups on PBIEMA were assumed to initiate the polymerization in calculating the PS chain length using the ^1H NMR spectra, which is unlikely to be the case.

One-pot synthesis of brush diblock copolymers through the simultaneous use of two types of reactions requires that the two reactions could proceed orthogonally without mutual interference. This is the case with ATRP and click coupling. In order to get some insight into the kinetic process of the one-pot synthesis and to obtain information on how ATRP and click coupling could proceed from the precursor diblock copolymer, the synthesis was monitored through SEC at various reaction times. The results are shown in Figures 3 and 4 for the reactions with MPEG5000 and MPEG2000, leading to respectively (PBIEMA₃₀-*g*-PS₅₆)-*b*-(PAIEMA₃₆-*g*-PEO₁₁₂) and (PBIEMA₃₀-*g*-PS₆₀)-*b*-(PAIEMA₃₆-*g*-PEO₄₅). From the SEC curves, the formation of brush diblock copolymer and the continuous increase in its molecular weight can be noticed from the evolution over time of the peak at shorter elution times. Since the relative amount of the precursor diblock copolymer in the two reactions is very small, its elution peak in the reaction mixture is hardly discernible. By contrast, the amount of styrene monomer is large, and its elution peak at longer times is dominant (not shown for the sake of clarity). At a first approximation, considering that the increase in the peak area of the brush diblock copolymer relative to the peaks of alkynyl-MPEG and styrene reflects its growing amount in the reaction mixture at the expense of alkynyl-MPEG and styrene monomer, changes in the weight fractions of the three components over reaction time were calculated from the SEC curves, and the results are shown in the figures. (The very small fraction of PBIEMA₃₀-*b*-PAIEMA₃₆, 1.6 and 1.5 wt % in the reaction mixtures with MPEG2000 and MPEG5000, respectively, was ignored.) In both cases, the amount of the brush diblock copolymer increases continuously over the used period of 72 h. This is due to the continuous increase in its molecular weight as the number and length of PS chains on PBIEMA and the number of PEO chains attached to PAIEMA increase, since the number of the precursor polymer chains remains unchanged. On the other hand, the ATRP of styrene and the click coupling of alkynyl-MPEG proceed simultaneously as revealed by their decreasing weight fractions over the entire reaction period. After 72 h of reaction, the weight fraction of unreacted

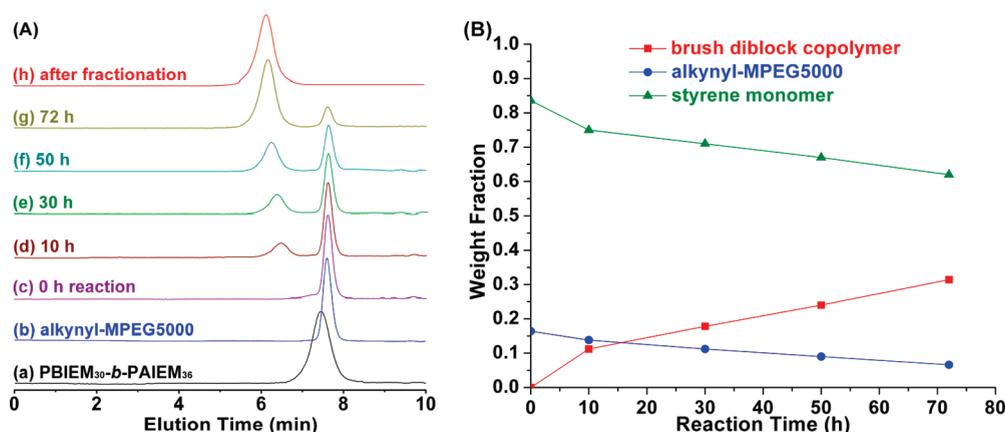


Figure 3. (A) Evolution of SEC curves over reaction time for the synthesis of the brush diblock copolymer using alkynyl-MPEG5000. (B) Plots of weight fraction vs reaction time for three components in the reaction mixture (estimated from the SEC curves).

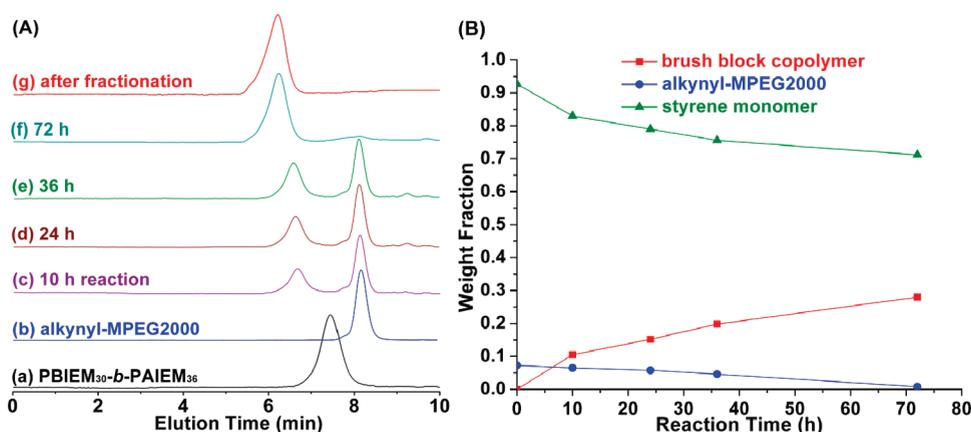


Figure 4. (A) Evolution of SEC curves over reaction time for the synthesis of the brush diblock copolymer using alkynyl-MPEG2000. (B) Plots of weight fraction vs reaction time for three components in the reaction mixture (estimated from the SEC curves).

alkynyl-MPEG5000 in the whole reaction mixture is larger than that of alkynyl-MPEG2000, which is in agreement with the click coupling degree estimated from ^1H NMR. This result indicates effect of the molecular size of alkynyl-MPEG on the efficiency of click coupling. It is logical to expect that MPEG5000 would experience a greater effect of steric hindrance than MPEG2000 from the growing brush diblock copolymer (especially PS chains), which renders the clicking more difficult to proceed.

We also performed a control experiment by increasing the feed ratios of styrene and alkynyl-MPEG2000 to the PBIEM₃₀-*b*-PAIEM₃₆ precursor (Supporting Information). The experiment was designed for two purposes: (1) to examine the ability to grow PS chains of higher molecular weights and to increase the click coupling degree of MPEG and (2) to demonstrate that unreacted alkynyl-MPEG can easily be removed without the need for fractionation. In this case, after 72 h reaction, azide-functionalized Merrifield resin was added in the reaction mixture under stirring.²¹ Purification of the polymer by passing the mixture through a column of neutral alumina and subsequently precipitation in hexane gave rise to a brush diblock copolymer sample of (PBIEM₃₀-*g*-PS₁₃₀)-*b*-(PAIEM₃₆-*g*-PEO₄₅) which contains no unreacted alkynyl-MPEG2000 and has a click coupling degree of $\sim 75\%$ for alkynyl-

MPEG2000. The result indicates that the molecular weight of PS brushes can readily be increased by increasing the amount of monomer, but a higher molar ratio of alkynyl-MPEG to azide groups on PAIEMA can only increase slightly the grafting density (from 70% to 75%).

Microphase Separation and Self-Assembly Behaviors.

The brush diblock samples were characterized with DSC. Figure 5 shows the heating curves of PBIEM₃₀-*b*-PAIEM₃₆, (PBIEM₃₀-*g*-PS₆₀)-*b*-(PAIEM₃₆-*g*-PEO₄₅), and (PBIEM₃₀-*g*-PS₅₆)-*b*-(PAIEM₃₆-*g*-PEO₁₁₂). The precursor diblock copolymer displays a single T_g at about 25 °C, indicating the miscibility between the two blocks that differ only in the terminal side groups (bromo and azide). In the case of brush diblock copolymers, the microphase separation between the PS and PEO brushes can be noticed from the T_g of PS at ~ 93 °C for (PBIEM₃₀-*g*-PS₆₀)-*b*-(PAIEM₃₆-*g*-PEO₄₅) and ~ 98 °C for (PBIEM₃₀-*g*-PS₅₆)-*b*-(PAIEM₃₆-*g*-PEO₁₁₂) and the melting endotherm of PEO at lower temperatures. With (PBIEM₃₀-*g*-PS₆₀)-*b*-(PAIEM₃₆-*g*-PEO₄₅), the crystallization of short PEO chains in the brush diblock copolymer is not prominent; only a small melting peak can be observed. By contrast, the crystallization of PEO is clear in (PBIEM₃₀-*g*-PS₅₆)-*b*-(PAIEM₃₆-*g*-PEO₁₁₂), displaying a prominent PEO melting peak at about 50 °C.

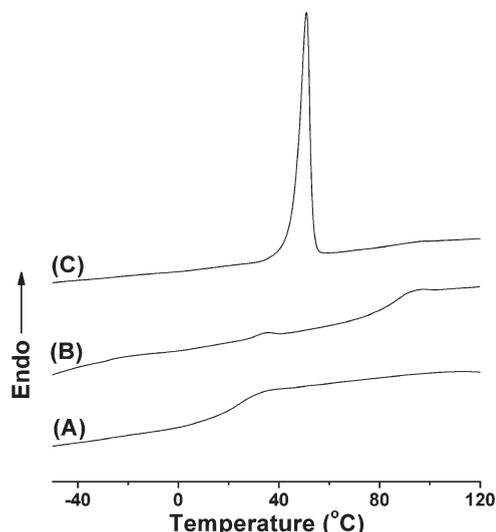


Figure 5. DSC heating curves (second scan) of (A) $\text{PBIEMA}_{30}\text{-}b\text{-PAIEMA}_{36}$, (B) $(\text{PBIEMA}_{30}\text{-}g\text{-PS}_{60})\text{-}b\text{-}(\text{PAIEMA}_{36}\text{-}g\text{-PEO}_{45})$, and (C) $(\text{PBIEMA}_{30}\text{-}g\text{-PS}_{56})\text{-}b\text{-}(\text{PAIEMA}_{36}\text{-}g\text{-PEO}_{112})$.

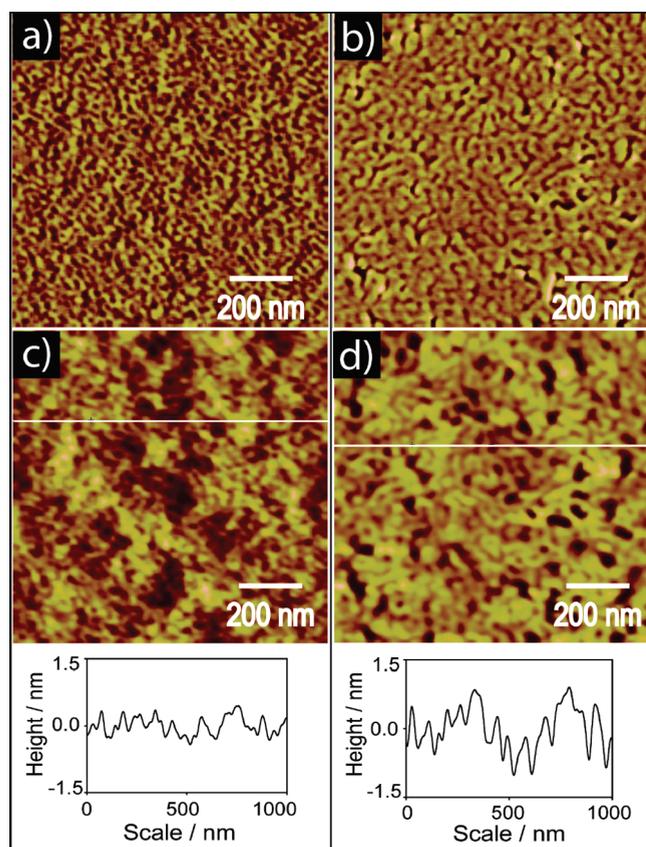


Figure 6. AFM phase (a, b) and height images (c, d) for thin films of $(\text{PBIEMA}_{30}\text{-}g\text{-PS}_{60})\text{-}b\text{-}(\text{PAIEMA}_{36}\text{-}g\text{-PEO}_{45})$ (a, c) and $(\text{PBIEMA}_{30}\text{-}g\text{-PS}_{56})\text{-}b\text{-}(\text{PAIEMA}_{36}\text{-}g\text{-PEO}_{112})$ (b, d). The height profiles correspond to the marked lines.

The self-assembly of the brush diblock copolymers in the solid state arising from the microphase separation was examined by AFM. Figure 6 shows the recorded phase and height images of

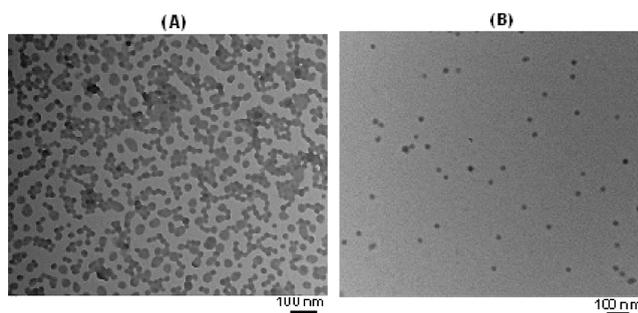


Figure 7. TEM images of micelles of (A) $(\text{PBIEMA}_{30}\text{-}g\text{-PS}_{60})\text{-}b\text{-}(\text{PAIEMA}_{36}\text{-}g\text{-PEO}_{45})$ and (B) $(\text{PBIEMA}_{30}\text{-}g\text{-PS}_{56})\text{-}b\text{-}(\text{PAIEMA}_{36}\text{-}g\text{-PEO}_{112})$.

their thin films spin-coated from toluene solution (2 wt % polymer) onto mica. Before AFM observations at room temperature, the films (~ 100 nm in thickness) were annealed at 110 °C for 3 days. Since toluene is a good solvent for both PS and PEO brushes and a homogeneous film was obtained, the phase images should indicate a microphase-separated morphology for the two samples. As PEO nanodomains in linear diblock copolymers of PEO-*b*-PS appear bright,²² the bright wormlike domains are presumed to come from the PEO brushes, the average domain width being about 23 ± 5 nm for $(\text{PBIEMA}_{30}\text{-}g\text{-PS}_{60})\text{-}b\text{-}(\text{PAIEMA}_{36}\text{-}g\text{-PEO}_{45})$ and 34 ± 4 nm for $(\text{PBIEMA}_{30}\text{-}g\text{-PS}_{56})\text{-}b\text{-}(\text{PAIEMA}_{36}\text{-}g\text{-PEO}_{112})$, with a surface roughness smaller than 2 nm. The low aspect ratio of the wormlike nanodomains contrasts with the long cylinders of PEO in linear diblock copolymers of PS-*b*-PEO. At this point, we do not know how the arrangement of the two brush blocks could lead to the observed morphology. Nevertheless, the difference in the average domain size appears to be related to the different chain lengths of the used alkylnyl-MPEG for the two samples.

Finally, since the brush diblock copolymers are amphiphilic, they can also self-assemble into micelles in a block-selective solvent. For this experiment, either $(\text{PBIEMA}_{30}\text{-}g\text{-PS}_{60})\text{-}b\text{-}(\text{PAIEMA}_{36}\text{-}g\text{-PEO}_{45})$ or $(\text{PBIEMA}_{30}\text{-}g\text{-PS}_{56})\text{-}b\text{-}(\text{PAIEMA}_{36}\text{-}g\text{-PEO}_{112})$ was first dissolved in DMF (10 mg/mL); water was then added slowly in the DMF solution (600% in volume with respect to DMF) to induce the micelle formation. After removal of DMF through dialysis against water (cutoff molecular weight 1000), an aqueous solution of micelles was obtained. Figure 7 shows the TEM images of the micelles of the two brush diblock copolymers, observed after casting the micellar solution on TEM grid, followed by drying. Despite some aggregation observable in the case of $(\text{PBIEMA}_{30}\text{-}g\text{-PS}_{56})\text{-}b\text{-}(\text{PAIEMA}_{36}\text{-}g\text{-PEO}_{45})$ due to a higher concentration, it is visible that both samples form uniformly sized sphere micelles. Measurements with over 50 micelles from the TEM images resulted in diameters of 25.0 ± 1.8 nm for $(\text{PBIEMA}_{30}\text{-}g\text{-PS}_{56})\text{-}b\text{-}(\text{PAIEMA}_{36}\text{-}g\text{-PEO}_{45})$ and 30.0 ± 1.2 nm for $(\text{PBIEMA}_{30}\text{-}g\text{-PS}_{60})\text{-}b\text{-}(\text{PAIEMA}_{36}\text{-}g\text{-PEO}_{112})$. Likewise, the difference in the micelle size seems to be related to the difference in the length of PEO chains that form the water-soluble micelle corona.

CONCLUSIONS

We presented a new and robust one-pot synthetic method for preparing brush diblock copolymers. It consists in synthesizing a precursor diblock copolymer of $\text{PBIEMA}\text{-}b\text{-PAIEMA}$ of which

one block contains terminal bromo groups and the other block azide groups. With this design of diblock copolymer initiator, growing of PS chains from PBIEMA via ATRP of styrene and linking of alkynyl-functionalized MPEG chains onto PAIEMA through click reaction could proceed simultaneously and orthogonally, giving rise to brush diblock copolymers (PBIEMA-g-PS)-*b*-(PAIEMA-g-PEO) with a low polydispersity. Alkynyl-MPEG2000 and MPEG5000 were utilized, and after 72 h of reaction their click coupling degree onto PAIEMA were found to be about 70 and 52%, respectively, revealing the effect of MPEG molecular weight on the click coupling efficiency in the one-pot synthetic process. Because of the amphiphilic nature of the brush diblock copolymers, they could self-assemble into micelles in solution. The microphase separation in thin films between the two molecular brushes was observed on AFM, with PEO brushes forming wormlike domains. This method, based on simultaneous use of ATRP and click coupling, is general and can be applied to prepare other brush diblock copolymers.

■ ASSOCIATED CONTENT

S **Supporting Information.** More details on the synthesis and characterization of brush diblock copolymers. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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■ ACKNOWLEDGMENT

We acknowledge financial support from the Natural Sciences and Engineering Research Council of Canada (NSERC) and le Fonds québécois de la recherche sur la nature et les technologies of Québec (FQRNT). Y.Z. is a member of the FQRNT-funded Center for Self-Assembled Chemical Structures.

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Supporting Information

One-Pot Synthesis of Brush Diblock Copolymers through Simultaneous ATRP and Click Coupling

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1. Materials

All chemicals were purchased from Aldrich unless otherwise stated. Prior to use, tetrahydrofuran (THF, 99%) was refluxed with sodium and a small amount of benzophenone and distilled, triethylamine (TEA) ($\geq 99\%$) was refluxed with *p*-toluenesulfonyl chloride (Fluka, $\geq 99\%$) and distilled, dichloromethane was distilled from CaH₂. Copper(I) bromide (CuBr, 99.999%), Copper(II) bromide (CuBr₂, 99.999%), α -bromoisobutyryl bromide (98%), 2,2'-bipyridyl ($\geq 99\%$), 6-heptynoic acid (97%), anhydrous toluene (99.8%) and 2-hydroxyethyl methacrylate ($\geq 99\%$) were purchased from Aldrich and used directly. Two poly(ethylene glycol) methyl ethers, MPEG2000 ($M_n=2000$ g/mol) and MPEG5000 ($M_n=5000$ g/mol), were dried by azeotropic distillation using anhydrous toluene before use. The starting chain transfer agent (CTA), 2-(2-cyanopropyl)dithiobenzoate (CPDB), was synthesized using a literature method.¹

2. Characterization

¹H NMR spectra were recorded on a Bruker 300 MHz spectrometer using deuterated chloroform as solvent and tetramethylsilane as internal standard. The spectra were used to determine the number-average molecular weights (M_n) of the linear precursors and brush diblock copolymers. A Waters size exclusion chromatograph (SEC) instrument, equipped with a Waters 410 differential refractometer detector and a Waters 996 photodiode array detector, was also utilized to measure the number- and weight-average molecular weights (M_n and M_w) as well as the polydispersity index (PDI). The SEC measurements were conducted at 35 °C using one column (Waters Styragel HR4E, 7.8 mm×300 mm, 5 μ m beads), PS standards for calibration, and THF as the eluent (flow rate: 1.0 mL min⁻¹). A TA Q200 differential scanning calorimeter (DSC) was used to investigate the thermal phase transition behaviors, using indium as the calibration standard and a heating or cooling rate of 10 °C min⁻¹. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet AVATAR 370 DTGS FTIR spectrometer. A Hitachi H-7500 transmission electron microscope (TEM) operating at 60 KV was used to examine micelles self-assembled by the brush amphiphilic diblock copolymer in solution. Observation using a tapping-mode atomic force microscope was performed on a Veeco's NanoscopeV (Dimension Icon) with a TESPA cantilever having a force constant of 20-80 N/m and resonance frequency of 343-399 kHz.

3. Synthesis

3.1 Synthesis of Monomer 2-(2-Bromoisobutyryloxy)ethyl Methacrylate

This monomer was synthesized by using a method reported in the literature.² Into a 250 mL round-bottom flask with a magnetic stirrer, 2-hydroxyethyl methacrylate (16.0 g, 0.12 mol), TEA (17.5 mL, 0.13 mol), and CH₂Cl₂ (100 mL) were added. After the mixture was cooled to 0°C, α -bromoisobutyryl bromide (28.8 g, 130 mmol) was added dropwise over a period of 30 min. The reaction mixture was then cooled back to room temperature and stirred for 24 h. The salt formed was removed by filtration, and the filtrate was washed with 0.5 M NaHCO₃ (3×100 mL) and saturated NaCl solution (3×100 mL). The organic phase was dried over MgSO₄. After filtering off MgSO₄ and

removing dichloromethane under vacuum, the yellow liquid residue was purified by silica-gel column chromatograph (EtOAc/hexane=10/90) to yield a clear light yellow liquid product with 90% yield. ^1H NMR (300 MHz, CDCl_3), δ (TMS, ppm): 6.16 (1H, $\text{CH}_2=\text{C}(\text{CH}_3)-$), 5.62 (1H, $\text{CH}_2=\text{C}(\text{CH}_3)-$), 4.46 (2H, $-\text{COOCH}_2-$); 1.97 (3H, $\text{CH}_2=\text{C}(\text{CH}_3)-$); 1.95-1.96 (6H, $-\text{C}(\text{CH}_3)_2-\text{Br}$).

3.2 Synthesis of Monomer 2-(2-Azideisobutyryloxy)ethyl Methacrylate

Into a 250 mL round-bottom flask were added BIEMA (8.0 g, 28.6 mmol) and sodium azide (11.2 g, 0.17 mol) in 100 mL of anhydrous DMF. After being stirred at room temperature for 24 h, a small amount of water was added to quench the reaction, during which the solution temperature was increased slightly. After being cooled to room temperature, the solution was extracted with 30 mL of dichloromethane five times. The organic phase was collected, washed with distilled water (3 \times 100 mL) and saturated NaCl solution (3 \times 100 mL), and then dried over MgSO_4 overnight. The latter was filtered off and dichloromethane was removed under vacuum. The light yellow liquid residue was purified by silica-gel column chromatograph (EtOAc/hexane=10/90) to yield a colorless liquid product with 86% yield. ^1H NMR (300 MHz, CDCl_3), δ (TMS, ppm): 6.16 (1H, $\text{CH}_2=\text{C}(\text{CH}_3)-$), 5.62 (1H, $\text{CH}_2=\text{C}(\text{CH}_3)-$), 4.46 (2H, $-\text{COOCH}_2-$); 1.97 (3H, $\text{CH}_2=\text{C}(\text{CH}_3)-$); 1.48 (6H, $-\text{C}(\text{CH}_3)_2-\text{N}_3$).

3.3 Synthesis of Macromolecular Chain Transfer Agent of PBIEMA

As shown in Scheme 1, the macromolecular CTA of PBIEMA was obtained by RAFT polymerization of monomer **1** using CPDB as chain transfer agent. For this reaction, BIEMA (2.0 g, 7.2 mmol), AIBN (1.6 mg, 0.01 mmol), and CPDB (20.0 mg, 0.09 mmol) were added into a 10 mL one-necked flask, followed by the addition of 4.0 mL of anhydrous toluene. After the solution under stirring was purged by nitrogen flow for 20 min, the flask was sealed and placed into an oil bath for polymerization at 65 °C for 3 h. The reaction flask was quickly put into liquid nitrogen to stop the polymerization. After three times of polymer precipitation from THF solution in cold hexane, the red-colored polymer was obtained and then dried under vacuum overnight (0.82 g, yield: 41%). ^1H NMR spectrum of the macromolecular CTA was shown in Figure 2(A). In addition to the resonance peaks of PBIEMA, the signal at $\delta=7.85$ ppm (peak *f*) is from CPDB, being ascribed to the phenyl protons ortho to the dithiobenzoate group. Comparing the integral of peak *d* at $\delta=4.0$ -4.5 ppm with that of peak *f*, the polymerization degree of PBIEMA was calculated to be about 30. PBIEMA_{30} has a $M_n(\text{NMR})\sim 8300$ g/mol.

3.4 Synthesis of Precursor Diblock Copolymer PBIEMA-*b*-PAIEMA

The macromolecular CTA PBIEMA was then used to grow PAIEMA to produce the precursor diblock copolymer. For this reaction, AIEMA (1.38 g, 5.73 mmol), AIBN (1.18 mg, 0.007 mmol), and PBIEMA_{30} (0.6 g, 0.072 mmol) were added into a 10 mL one-necked flask. Anhydrous toluene (4.0 mL) was added to dissolve the mixture. After 20 min nitrogen purge, the flask was sealed and placed in a preheated oil bath. The reaction was conducted at 65 °C for 3 h before the flask was put into liquid nitrogen to halt the reaction. After dilution with THF, the reaction solution was added dropwise in cold hexane for precipitation of the diblock copolymer PBIEMA-*b*-PAIEMA. This purification procedure was repeated three times, and the collected sample was dried in a vacuum oven for 24 h at room temperature, yielding a red viscous solid (0.80 g, 40%). ^1H NMR spectrum of PBIEMA-*b*-PAIEMA is shown in Figure 2(B). On the basis of the known number of BIEMA units, the polymerization degree of PAIEMA was determined to be about 36. Thus, the precursor diblock copolymer is denoted as $\text{PBIEMA}_{30}\text{-}b\text{-PAIEMA}_{36}$.

3.5 Synthesis of Alkynyl-functionalized MPEG

Before carrying out the one-pot synthesis of the brush diblock copolymer, alkynyl-functionalized

MPEG was needed. Samples of two molecular weights, 2000 and 5000, were prepared. As example, freshly dried MPEG2000 (3.0 g, 1.5 mmol) was dissolved in anhydrous THF (60 mL) and placed in a 250 ml three-necked flask. After adding 6-heptynoic acid (0.8 g, 6.3 mmol), the flask was sealed with septum and cool to 0 °C with ice-water bath. In the presence of argon, DCC (0.62 g, 3.0 mmol) and DMAP (36.6 mg, 0.30 mmol) were added quickly into the reaction system. The mixture was stirred at room temperature for 48 h. During this period, the reaction mixture slowly turned yellow and insoluble DCC urea precipitated. After filtration to remove the solid, the polymer was precipitated in diethyl ether to remove the excessive 6-heptynoic acid. After being redissolved in THF, the polymer was precipitated again in hexane to remove the excessive DCC and DCC urea. This purification procedure was repeated three times, and the polymer collected by filtration was dried in a vacuum oven for 24 h at room temperature, yielding light yellow powder (2.6 g, 85%). The polymer structure was confirmed by ¹H NMR analysis, as shown in Figure 2(C). The same method was used to synthesize alkynyl-terminated MPEG5000.

3.6 One-Pot Synthesis of Brush Diblock Copolymer (PBIEMA_{30-g}-PS₆₀)-*b*-(PAIEMA_{36-g}-PEO₄₅)

A typical synthetic procedure is as follows. PBIEMA_{30-b}-PAIEMA₃₆ (50 mg, 0.088 mmol of bromide groups, 0.11 mmol of azide groups), styrene (2.8 g, 0.027 mol), MPEG2000 (0.22 g, 0.11 mmol) or MPEG5000 (0.55 g, 0.11 mmol), CuBr (0.01 g, 0.07 mmol), CuBr₂ (3.96 mg, 0.018 mmol), bipyridyl (0.033 g, 0.21 mmol) and THF (4.0 mL) were added successively into a 10mL flask. The reaction mixture was degassed by three pump-thaw cycles, backfilled with argon, and placed in an oil bath thermostated at 70 °C for 72 h. During the polymerization, a small amount of the sample was collected at various reaction times for SEC measurements. At the end of the polymerization, the mixture was diluted with THF and then passed through a column of neutral alumina to remove the metal salt. After precipitation by adding the polymer solution of THF into hexane, a light-yellow powder was collected by filtration and then dried under vacuum overnight (0.80 g with 42% yield when using alkynyl-functionalized MPEG2000 and 1.10 g with 32% yield with MPEG5000). From SEC measurements, a small amount of un-reacted MPEG2000 or MPEG5000 remained after 72 h polymerization, but they could easily be removed by fractionation precipitation. Using the one-pot reaction involving MPEG2000 as example, 0.50 g of crude brush diblock copolymer was dissolved in 50 mL of THF; then 80 mL of hexane was added dropwise to the solution until it just turned cloudy. The solution was left standing overnight at room temperature to yield two phases. The denser bottom layer was collected and added into hexane to precipitate the polymer. The polymer collected by filtration was dried in vacuum oven at room temperature overnight to yield 0.28 g of brush diblock copolymer free of MPEG2000 homopolymer.

3.7 One-Pot Synthesis of Brush Diblock Copolymer (PBIEMA_{30-g}-PS₁₃₀)-*b*-(PAIEMA_{36-g}-PEO₄₅)

By increasing the ratios of styrene and alkynyl-MPEG2000 to PBIEMA_{30-b}-PAIEMA₃₆ precursor, higher molecular weight of PS brush and slightly higher grafting density of PEO could be obtained. And by using azide-functionalized Merrifield resin, brush diblock copolymer could be collected after purification free of unreacted alkynyl-MPEG2000 without the need for fractionation. For this synthesis, PBIEMA_{30-b}-PAIEMA₃₆ (10 mg, 0.018 mmol of bromide groups, 0.022 mmol of azide groups), styrene (1.68 g, 0.016 mol), MPEG2000 (0.13 g, 0.065 mmol), CuBr (0.002 g, 0.014 mmol), CuBr₂ (0.80 mg, 0.0036 mmol), bipyridyl (0.007 g, 0.04 mmol) and THF (4.0 mL) were added successively into a 10 mL flask. The reaction mixture was degassed by three pump-thaw cycles, backfilled with argon, and placed in an oil bath thermostated at 70 °C for 72 h. Afterward, azide-functionalized Merrifield resin³ (0.06 g, 0.18-0.21 mmol azide moieties) was added. The

suspension was kept stirring for another 24 h at 70 °C. It was then diluted with THF and passed through a column of neutral alumina to remove the metal salt and Merrifield resin. The polymer THF solution was concentrated and then precipitated into an excess of hexane. After being dried in a vacuum oven overnight, a light-yellow powder was collected (0.2 g, $M_{n, GPC}=223600$, $M_w/M_n=1.15$). The removal of unreacted alkynyl-MPEG2000 can be noticed from the SEC curves in Figure S1. ^1H NMR was used to confirm the polymer structure, as shown in Figure S2. According to the integrals of resonance peaks, the DP of PS brush is about 130 and the grafting density of PEO chains is estimated to be 75%.

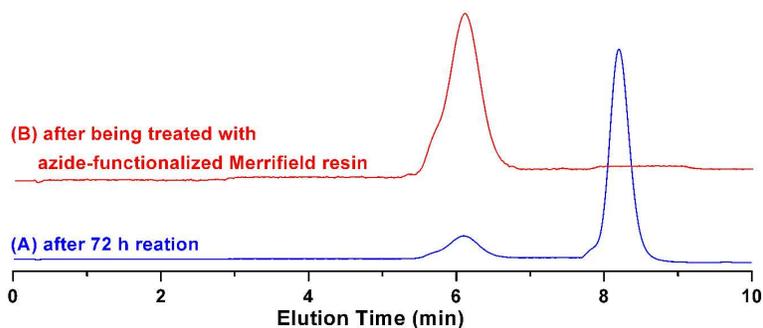


Figure S1. SEC curves of (A) after reaction for 72 h for control experiment and (B) after treated with azide-functionalized Merrifield resin.

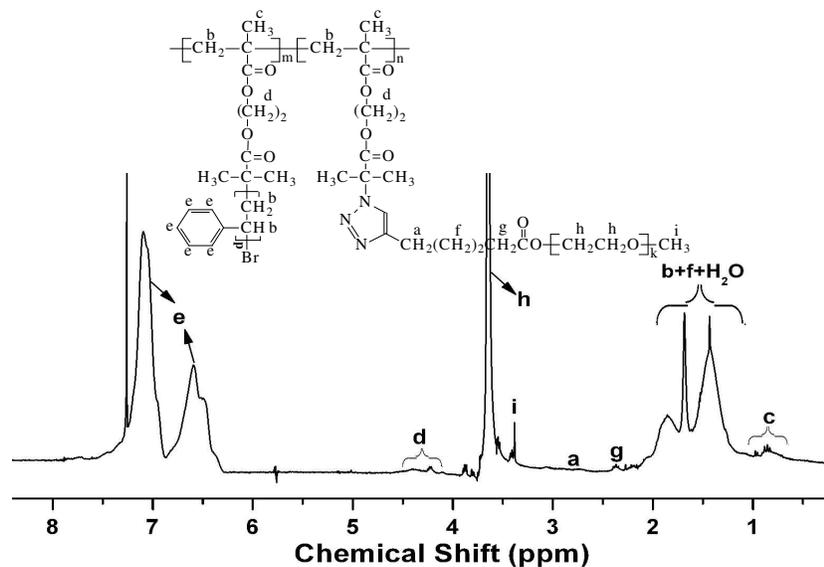


Figure S2. ^1H NMR spectrum (in CDCl_3) of the brush diblock copolymer (PBIEMA₃₀-g-PSt₁₃₀)-*b*-(PAIEMA₃₆-g-PEO₄₅).

4. Infrared Spectra

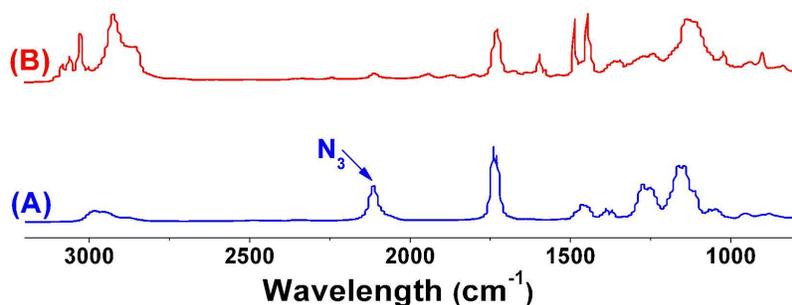


Figure S3. Infrared spectra of (A) PBIEMA₃₀-*b*-PAIEMA₃₆ and (B) (PBIEMA₃₀-*g*-PSt₆₀)-*b*-(PAIEMA₃₆-*g*-PEO₄₅).

5. Hydrolysis of Brush Diblock Copolymer

The brush diblock copolymer (PBIEMA₃₀-*g*-PS₆₀)-*b*-(PAIEMA₃₆-*g*-PEO₄₅) or (PBIEMA₃₀-*g*-PS₅₆)-*b*-(PAIEMA₃₆-*g*-PEO₁₁₂) (0.5 g) was dissolved in THF (20 mL) in a 50 mL round-bottomed flask fitted with a refluxing condenser. Into the polymer solution was added a potassium hydroxide solution in water (10 mL, 1 M), and the mixture was refluxed for 48 h. After removing the volatiles in the reaction mixture with rotary evaporator, the residue was extracted with CH₂Cl₂ three times. The extracts were combined, dried with MgSO₄ and passed through a short column of neutral alumina to remove MgSO₄ and other possible salt side-products. After the removal of CH₂Cl₂ under reduced pressure, a small amount of the sample was collected for SEC measurements (Figures S4 and S5) and the residue was dissolved in cyclohexane, and then filtered to remove the undissolved solid. The filtrate was concentrated and then precipitated into an excess of methanol, the hydrolyzed product precipitated was collected by filtration and then dried under a vacuum oven for 24 h to afford the product PS ($M_{n, GPC}=9600$, $M_w/M_n=1.17$, PS chains cleaved from (PBIEMA₃₀-*g*-PS₆₀)-*b*-(PAIEMA₃₆-*g*-PEO₄₅) and $M_{n, GPC}=7800$, $M_w/M_n=1.15$, PS chains cleaved from (PBIEMA₃₀-*g*-PS₅₆)-*b*-(PAIEMA₃₆-*g*-PEO₁₁₂)). The solid undissolved in cyclohexane and collected by filtration was re-dissolved in water, and then filtered. After evaporation of water in the filtrate under reduced pressure, PEG2000 and PEG5000 cleaved from the brush diblocks were obtained, as revealed by SEC curves in Figures S4 and S5. ¹H NMR was used to confirm the polymer structures as shown in Figure S6 using cleaved PS and MPEG2000 from as example. (A) δ (ppm): 6.30-7.32 (aromatic protons); 1.29-2.21 (methylene and methine protons). (B). δ (ppm): 3.70 (-OCH₂CH₂O-).

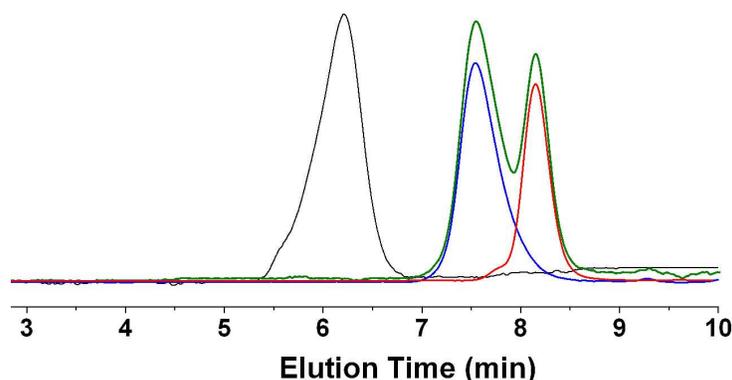


Figure S4. SEC curves: brush diblock before hydrolysis (PBIEMA₃₀-*g*-PS₆₀)-*b*-(PAIEMA₃₆-*g*-PEO₄₅)

(black line at shorter evolution time), the mixture of cleaved PS and PEO chains after hydrolysis (green line at longer evolution time), cleaved PS chains (blue line) and PEO2000 (red line) after being separated from the mixture.

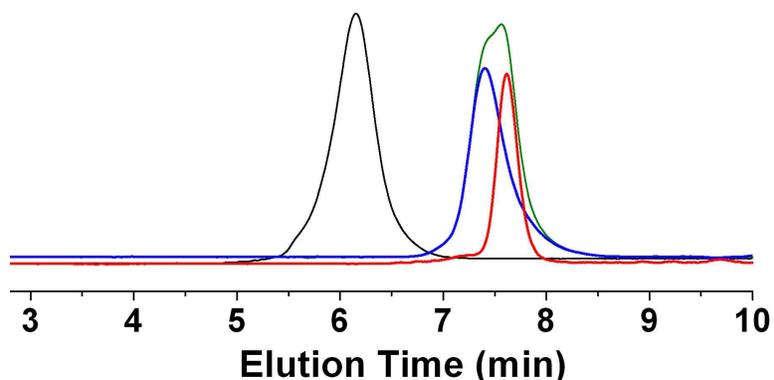


Figure S5. SEC curves: brush diblock before hydrolysis (PBIEMA₃₀-*g*-PS₅₆)-*b*-(PAIEMA₃₆-*g*-PEO₁₁₂) (black line at shorter evolution time), the mixture of cleaved PS and PEO chains after hydrolysis (green line at longer evolution time), cleaved PS chains (blue line) and PEO5000 (red line) after being separated from the mixture. The peak of MPEG5000 appears at shorter elution times than MPEG2000. The monomodal elution peak of cleaved PS chains also indicates the absence of free PS chains prior to the hydrolysis reaction.

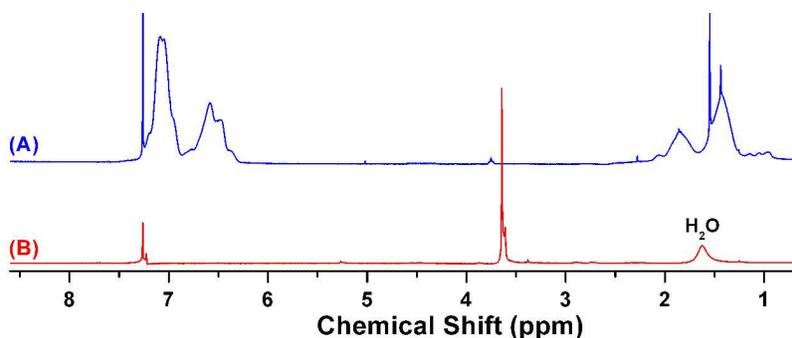


Figure S6. ¹H NMR spectra (in CDCl₃) of separated PS chains (A) and PEO (B) after hydrolysis of the brush diblock copolymer.

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