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

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S 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 "grating 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) (PAcEVE), they first used living cationic polymerization initiated by 1,3-dioxane pendant groups to grow arms of poly(methyl vinyl ether) (PMVE) ("grating 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

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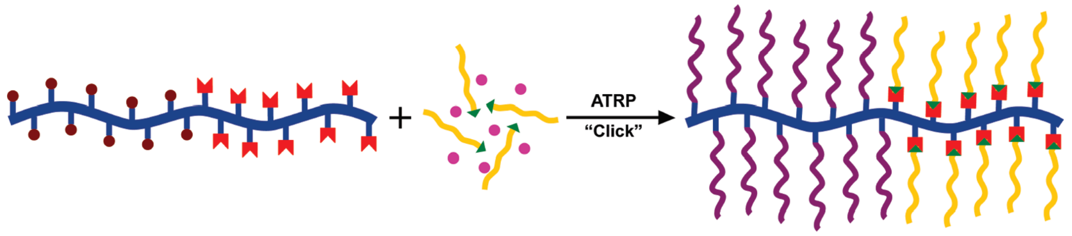
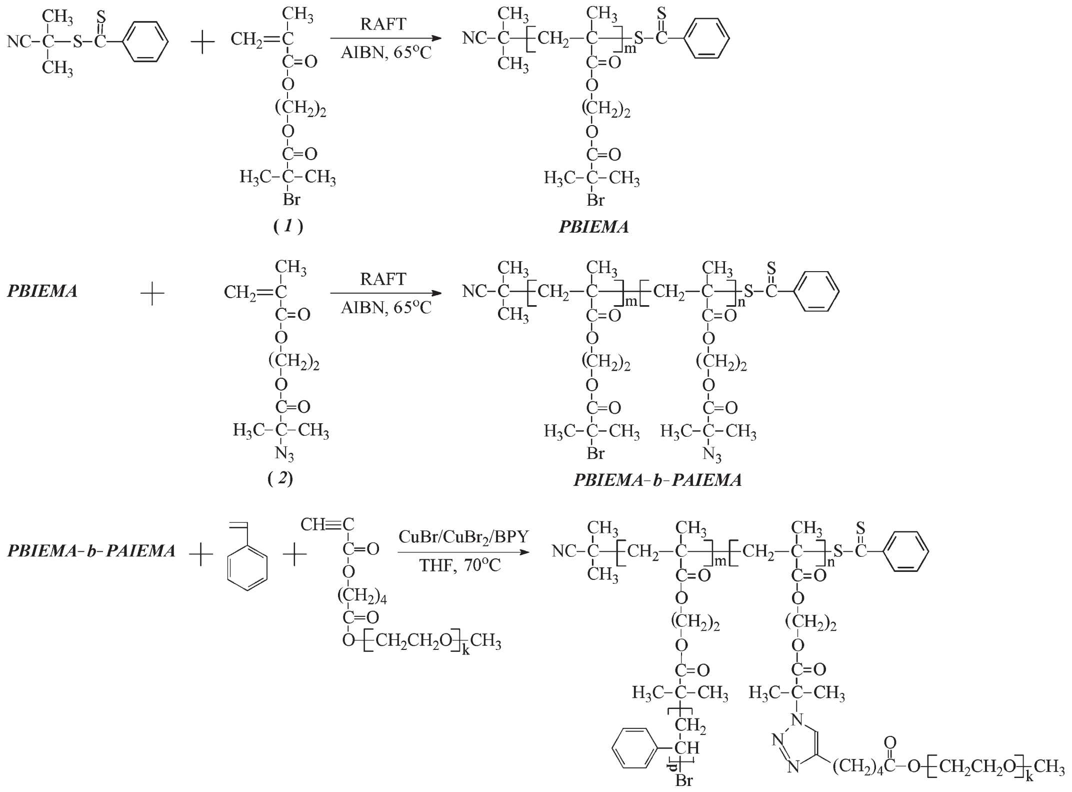


Figure 1. Schematic illustration of the one-pot synthesis of brush diblock copolymers through combined use of ATRP and click coupling.

Scheme 1. One-Pot Synthesis of the Brush Diblock Copolymer by Using Simultaneous ATRP from and Click Coupling onto a Precursor Diblock Copolymer



one-pot synthetic method for brush diblock copolymers, and that although they were used as arms in a previous study,[5] the backbone of our brush diblock copolymer is a polymethacrylate instead of a poly(vinyl ether). Details on the syntheses leading to the brush diblock copolymers are given in the Supporting Information.

Characterizations. A precursor diblock copolymer PBIEMA$_{30}$-*b*-PAIEMA$_{36}$ was used to grow the two brushes simultaneously. ^{1}H NMR spectroscopy was used to determine the composition of the brush diblock. To better explain the measurement, Figure 2 shows the ^{1}H NMR spectra of the starting macromolecular chain transfer agent PBIEMA$_{30}$-CTA, the precursor diblock PBIEMA$_{30}$-*b*-PAIEMA$_{36}$, alkynyl-MPEG2000, and the resulting brush diblock. Examining the spectrum of the brush diblock copolymer, in addition to the characteristic resonance signals of polymethacrylate backbone, signals at δ = 6.30−7.32 (*e*) and δ = 3.75 (*h*) are visible, being ascribed to the side chains of PS and PEO, respectively. First, knowing the numbers of units of BIEMA and AIEMA on the chain backbone (see Supporting Information) and the molecular weight of PEO, comparison of the integral of the resonance peak *d* at 4.0−4.5 ppm (protons of the ethylene units linking the chain backbone and side chains) with that of the characteristic peak *h* of PEO at 3.75 ppm led to a click coupling degree of about 70%. This grafting density is comparable to the reported results in studies using click chemistry to prepare molecular brushes.[16,18] Second, comparing the integral of the same reference peak at 4.0−4.5 ppm with that of the resonance peaks *e* at 6.30−7.32 ppm (aromatic protons of PS), the total number of styrene units could be estimated. Assuming that all bromo groups on the PBIEMA block could initiate polymerization of styrene, the average polymerization degree of PS chains is about 60. Therefore, this brush diblock copolymer is denoted as (PBIEMA$_{30}$-*g*-PS$_{60}$)-*b*-(PAIEMA$_{36}$-*g*-PEO$_{45}$) hereafter. Similar ^{1}H NMR analysis of the brush diblock copolymer obtained with alkynyl-terminated MPEG5000 yielded (PBIEMA$_{30}$-*g*-PS$_{56}$)-*b*-(PAIEMA$_{36}$-*g*-PEO$_{112}$), with a click coupling degree of ~52%. The lower grafting density is likely due to the used larger molecular weight

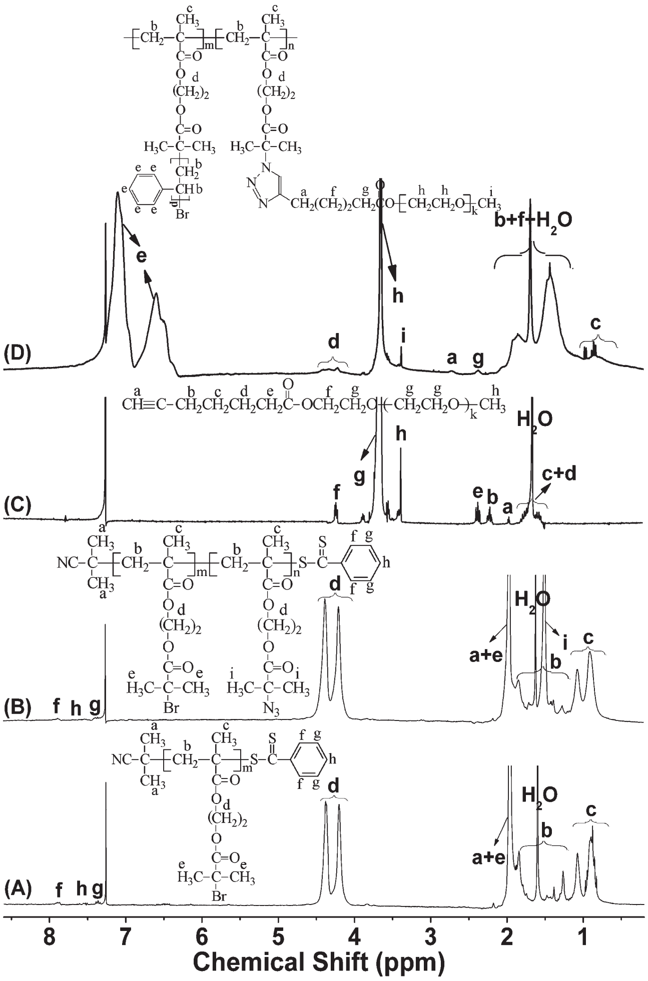


Figure 2. ^{1}H NMR of (A) PBIEMA$_{30}$-CTA, (B) PBIEMA$_{30}$-*b*-PAIEMA$_{36}$, (C) alkynyl-MPEG2000, and (D) (PBIEMA$_{30}$-*g*-PSt$_{60}$)-*b*-(PAIEMA$_{36}$-*g*-PEO$_{45}$).

Table 1. Characteristics of Synthesized Polymers

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

[a] Based on ^{1}H NMR (in CDCl$_3$). [b] Based on size exclusion chromatography (SEC) (in THF with polystyrene standards). [c] Based on a "click" graft efficiency of 70% for MPEG2000. [d] Based 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, ^{1}H NMR-based M_ns 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 PBIEMA$_{30}$-*b*-PAIEMA$_{36}$ and (PBIEMA$_{30}$-*g*-PS$_{60}$)-*b*-(PAIEMA$_{36}$-*g*-PEO$_{45}$) (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 1450−1600 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 ^{1}H NMR. Using PS standards, PS chains cleaved from (PBIEMA$_{30}$-*g*-PS$_{60}$)-*b*-(PAIEMA$_{36}$-*g*-PEO$_{45}$) have $M_n \sim 9600$ and $M_w/M_n = 1.17$, while those from (PBIEMA$_{30}$-*g*-PS$_{56}$)-*b*-(PAIEMA$_{36}$-*g*-PEO$_{112}$) 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 ^{1}H 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 reactions times. The results are shown in Figures 3 and 4 for the reactions with MPEG-5000 and MPEG2000, leading to respectively (PBIEMA$_{30}$-*g*-PS$_{56}$)-*b*-(PAIEMA$_{36}$-*g*-PEO$_{112}$) and (PBIEMA$_{30}$-*g*-PS$_{60}$)-*b*-(PAIEMA$_{36}$-*g*-PEO$_{45}$). 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 vary 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 PBIEMA$_{30}$-*b*-PAIEMA$_{36}$, 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

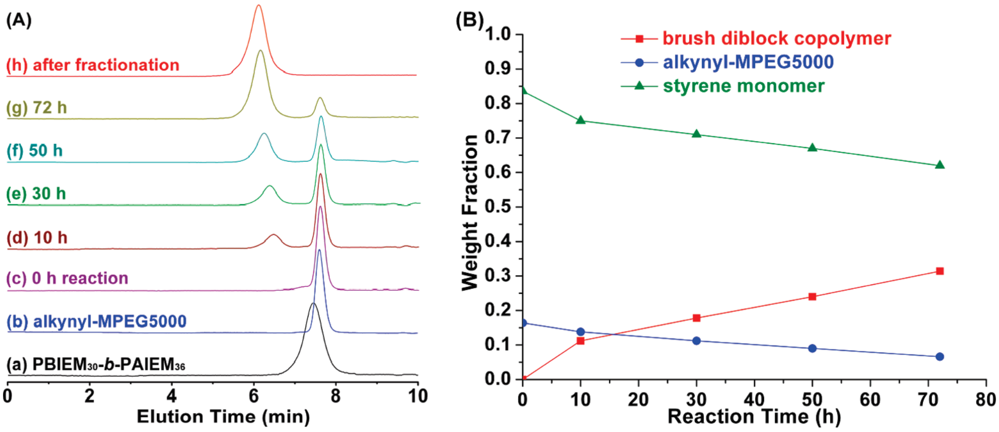


Figure 3. (A) Evolution of SEC curves over reaction time for the synthesis of the brush diblock copolymer using alkynyl-MPEG5000. (B) Plots of weight fraction vs reaction time for three components in the reaction mixture (estimated from the SEC curves).

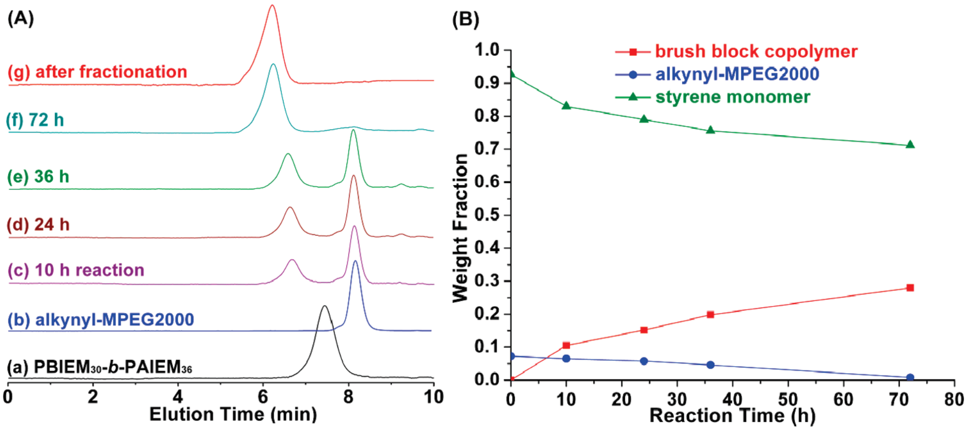


Figure 4. (A) Evolution of SEC curves over reaction time for the synthesis of the brush diblock copolymer using alkynyl-MPEG2000. (B) Plots of weight fraction vs reaction time for three components in the reaction mixture (estimated from the SEC curves).

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 ^{1}H 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 PBIEMA$_{30}$-*b*-PAIEMA$_{36}$ 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 (PBIEMA$_{30}$-*g*-PS$_{130}$)-*b*-(PAIEMA$_{36}$-*g*-PEO$_{45}$) which contains no unreacted alkynyl-MPEG2000 and has a click coupling degree of ~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 PBIEMA$_{30}$-*b*-PAIEMA$_{36}$, (PBIEMA$_{30}$-*g*-PS$_{60}$)-*b*-(PAIEMA$_{36}$-*g*-PEO$_{45}$), and (PBIEMA$_{30}$-*g*-PS$_{56}$)-*b*-(PAIEMA$_{36}$-*g*-PEO$_{112}$). 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 (PBIEMA$_{30}$-*g*-PS$_{60}$)-*b*-(PAIEMA$_{36}$-*g*-PEO$_{45}$) and ~98 °C for (PBIEMA$_{30}$-*g*-PS$_{56}$)-*b*-(PAIEMA$_{36}$-*g*-PEO$_{112}$) and the melting endotherm of PEO at lower temperatures. With (PBIEMA$_{30}$-*g*-PS$_{60}$)-*b*-(PAIEMA$_{36}$-*g*-PEO$_{45}$), 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 (PBIEMA$_{30}$-*g*-PS$_{56}$)-*b*-(PAIEMA$_{36}$-*g*-PEO$_{112}$), displaying a prominent PEO melting peak at about 50 °C.

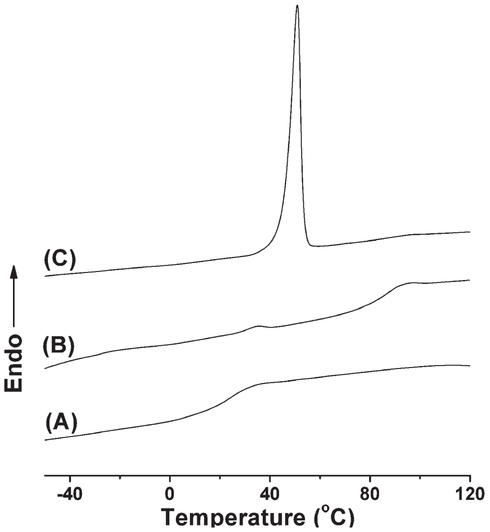


Figure 5. DSC heating curves (second scan) of (A) PBIEMA$_{30}$-*b*-PAIEMA$_{36}$, (B) (PBIEMA$_{30}$-*g*-PS$_{60}$)-*b*-(PAIEMA$_{36}$-*g*-PEO$_{45}$), and (C) (PBIEMA$_{30}$-*g*-PS$_{56}$)-*b*-(PAIEMA$_{36}$-*g*-PEO$_{112}$).

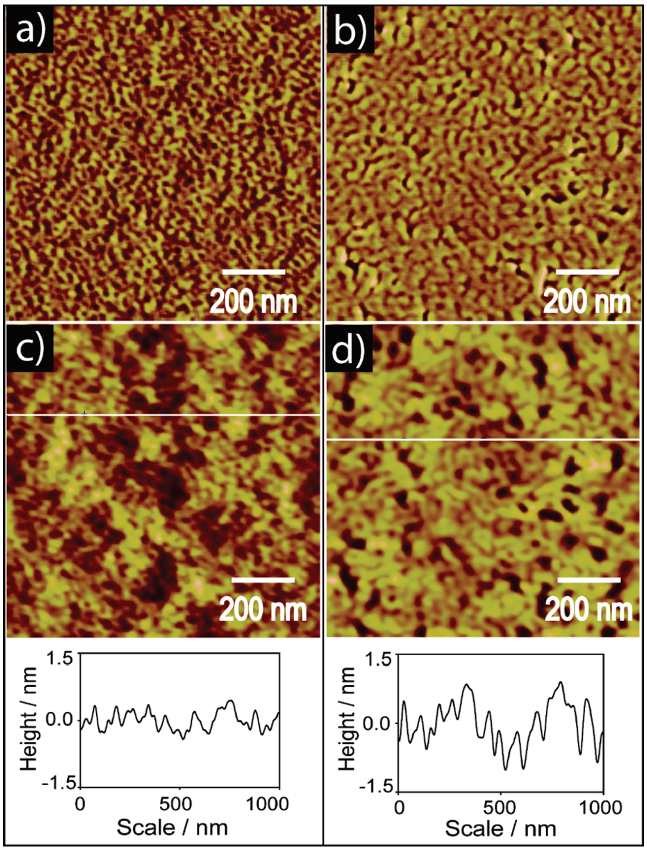


Figure 6. AFM phase (a, b) and height images (c, d) for thin films of (PBIEMA$_{30}$-*g*-PS$_{60}$)-*b*-(PAIEMA$_{36}$-*g*-PEO$_{45}$) (a, c) and (PBIEMA$_{30}$-*g*-PSt$_{56}$)-*b*-(PAIEMA$_{36}$-*g*-PEO$_{112}$) (b, d). The height profiles correspond to the marked lines.

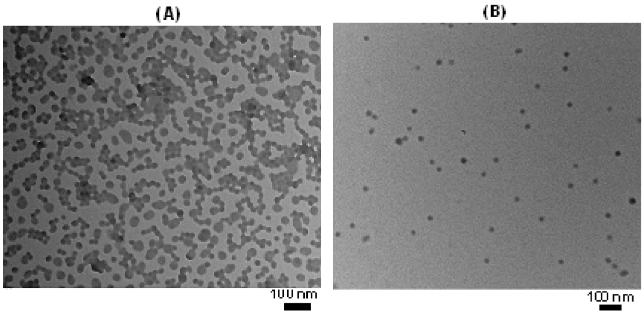


Figure 7. TEM images of micelles of (A) (PBIEMA$_{30}$-*g*-PSt$_{60}$)-*b*-(PAIEMA$_{36}$-*g*-PEO$_{45}$) and (B) (PBIEMA$_{30}$-*g*-PSt$_{56}$)-*b*-(PAIEMA$_{36}$-*g*-PEO$_{112}$).

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 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 (PBIEMA$_{30}$-*g*-PS$_{60}$)-*b*-(PAIEMA$_{36}$-*g*-PEO$_{45}$) and 34 ± 4 nm for (PBIEMA$_{30}$-*g*-PS$_{56}$)-*b*-(PAIEMA$_{36}$-*g*-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 alkynyl-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 (PBIEMA$_{30}$-*g*-PS$_{60}$)-*b*-(PAIEMA$_{36}$-*g*-PEO$_{45}$) or (PBIEMA$_{30}$-*g*-PS$_{56}$)-*b*-(PAIEMA$_{36}$-*g*-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 (PBIEMA$_{30}$-*g*-PS$_{56}$)-*b*-(PAIEMA$_{36}$-*g*-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 (PBIEMA$_{30}$-*g*-PS$_{56}$)-*b*-(PAIEMA$_{36}$-*g*-PEO$_{45}$) and 30.0 ± 1.2 nm for (PBIEMA$_{30}$-*g*-PS$_{60}$)-*b*-(PAIEMA$_{36}$-*g*-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 PBIEMA-*b*-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 amphiphic 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

Ⓢ 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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