3056 *Macromolecules* **2007,** *40,* 3056−3061

Architecture of Prototype Copolymer Brushes by Grafting-from ATRP Approach from Functionalized Alternating Comb-Shaped Copolymers

Koji Ishizu* and Hiroe Yamada

Department of Organic Materials and Macromolecules, International Research Center of Macromolecular Science, Tokyo Institute of Technology, 2-12-1-H-133, Ookayama, Meguro-ku, Tokyo 152-8552, Japan

Received November 22, 2006; Revised Manuscript Received February 15, 2007

ABSTRACT: Atom transfer radical polymerization (ATRP) was applied to a novel synthesis of prototype copolymer brushes. The procedure included the following steps: (1) free-radical copolymerization of vinylbenzyl-terminated polystyrene (PS-VB) macromonomer and *N*-(4-hydroxyphenyl)maleimide gave well-defined alternating comb-shaped copolymers, (2) subsequent esterification reaction [*N*-(4-hydroxyphenyl)maleimide sites] of such comb-shaped copolymer with 2-bromoisobutyryl bromide yielded a comb-shaped polyinitiator, and (3) the grafting-from ATRP method of methyl methacrylate (MMA) using comb-shaped polyinitiator provided PS/poly(methyl methacrylate) (PMMA) alternating copolymer brushes. Dilute solution properties and morphological results of both comb-shaped polyinitiator and prototype copolymer brushes were investigated by static and dynamic light scattering and transmission electron microscopy. As a result, prototype copolymer brush composed of short aspect ratio changed the shape from ellipsoid to starlike conformation because both polystyrene (PS) and PMMA side chains were stretched by introduction of PMMA grafted chains.

Introduction

Nanostructured polymers are of rapidly growing interest because of their sized-coupled properties. The interest in branched polymers arises from their compactness and their enhanced segment density. Recently, a new class of branched architectural polymers, nanocylinders (often called polymer brushes), is attracting attention because their unique structures may result in unusual properties.

Comb polymers with densely grafted side chains in a good solvent can adopt a wormlike cylinder brush conformation, in which the side chains are stretched in the direction normal to the backbone owing to the excluded-volume interaction. More recently, we systematically investigated the architecture of multicomponent copolymer brushes.[1,2] Figure 1 shows the illustration of three types of multicomponent copolymer brushes, i.e., double-cylinder type, prototype, and block type. Herein, we focus on prototype copolymer brushes. Two strategies can be designed to construct such structures. Schlüter et al.[3] reported the synthesis of the prototype amphiphilic nanocylinders by polycondensation of Suzuki-type dendron (having both hydrophilic and hydrophobic pendant chains in a molecule) with diboronic acid ester. As another synthetic strategy reported by Ishizu's group,[4] an alternating copolymerization of a mixture of two macromonomers is an elegant approach for the architecture of prototype copolymer brushes. Free-radical copolymerization of binary macromonomers will form copolymers with comb-shaped structure. In this preparation process, the relevant copolymerization parameters are very important in determining the branch distribution in the resulting comb-shaped copolymers. The reactivity ratios [r_1(PS-VB) = 0.25 and r_2(PEO-MC) = 0.02] obtained for free-radical copolymerization of vinylbenzyl-terminated polystyrene (PS-VB) and methacryloyl-terminated poly(ethylene oxide) (PEO-MC)/tin tetrachloride ($SnCl_4$) macromonomers showed strong alternation.[4] It was suggested that alternation results from homopolymerization of 1:1 complexes (PS-VB, donor; PEO-MC/$SnCl_4$, acceptor) formed between the electron donor and acceptor monomers.

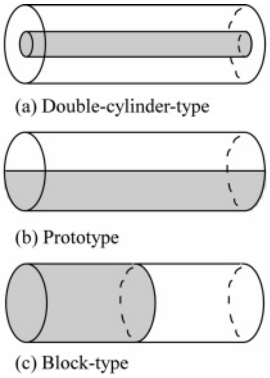


Figure 1. Illustration of multicomponent copolymer brushes: (a) double-cylinder type, (b) prototype, and (c) block type.

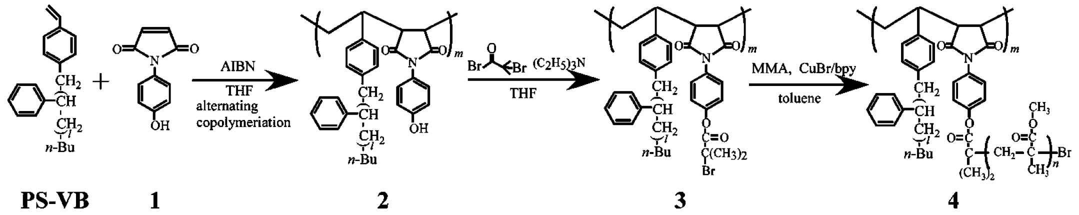
These alternating copolymer brushes with long aspect ratios (the ratio of diameter to the length of rodlike molecule) should form phase-separated cylindrical domains (prototype as sketched in Figure 1b) because incompatible alternating PS and PEO side chains align densely on the main chain. Dilute-solution properties and structural analysis demonstrate that such alternating copolymer brushes formed large aggregates in an aqueous solution.[5] In this self-assembly process, hierarchical generation, i.e., aggregate formation from small rods to large rods, was observed. Moreover, in the self-assembly of prototype amphiphilic copolymer brushes consisting of PEO and poly(propylene oxide) (PPO),[6] an interesting morphology such as cascade, i.e., treelike, generation of rods was observed. Since the hydrophobicity of PPO domains is weaker than that for PS domains in water, PPO/PEO copolymer brushes may self-assemble to three-dimensional supramolecules. The PS/PEO prototype copolymer brushes were converted into sulfonated PS (PSS)/PEO brushes (anionic/nonionic polyelectrolyte prototype) by sulfonation. We studied the binding behaviors of PSS/PEO brush to linear quaternized poly(4-vinylpyridine) (P4VPQ)

---

* Corresponding author. E-mail: kishizu@polymer.titech.ac.jp.

10.1021/ma062685e CCC: $37.00

Scheme 1. Synthesis Route for Prototype Copolymer Brushes (AIBN = 4,4′-Azobis(isobutyronitrile), MMA = Methyl Methacrylate)



in an aqueous solution.[7] As a result, rod-shaped prototype brush aggregate/P4VPQ complexes were formed, because of PSS/PEO brushes abundantly bound to P4VPQ due to electrostatic interaction. More recently, Schmidt et al.[8] prepared statistical copolymer brushes consisting of statistically arranged P2VPQ and poly(methyl methacrylate) (PMMA) side chains. They found the supermolecular structure formation (supermolecular order of a few polymer molecules into filament-like structures) of such statistical copolymer brushes in the solid state due to intramolecular phase separation of PMMA and P2VPQ side chains.

A more general synthetic method is required to prepare the prototype copolymer brushes consisting of various chemical components. As mentioned earlier, an alternating copolymer can be easily obtained by free-radical copolymerization of an electron-rich monomer and an electron-deficient monomer through the formation of charge-transfer complexes. One of the extensively studied systems is maleimide (MI) and styrene.[9] We can expect to synthesize easily prototype copolymer brushes by alternating copolymerization of VB-terminated and MI-terminated macromonomers or grafting-from atom transfer radical polymerization (ATRP) approach from alternating comb-shaped copolymers having functionalized MI groups.

In this article, we present a novel synthesis of prototype copolymer brushes by the grafting-from ATRP approach from alternating comb-shaped copolymers having functionalized MI groups. The procedure included the following steps: (1) free-radical copolymerization of PS-VB and *N*-(4-hydroxyphenyl)-maleimide gave well-defined alternating comb-shaped copolymers, (2) subsequent esterification reaction of such comb-shaped copolymer with 2-bromoisobutyryl bromide yielded a comb-shaped polyinitiator, and (3) grafting-from ATRP method of MMA using comb-shaped polyinitiator provided PS/PMMA alternating copolymer brushes.

Experiments

Materials. PS-VB was synthesized by the coupling reaction of polystyryllithium with an excess amount of *p*-chloromethylstyrene (CMS) in a benzene−tetrahydrofuran (THF) mixed solvent. Details of the synthesis and characterization are given elsewhere.[5] MMA (>99.8%, Tokyo Kasei Organic Chemicals, Tokyo) was distilled under high vacuum. 4-Aminophenol (>99%), 4,4′-azobis(isobutyronitrile) (AIBN, >99.5%), 2,2′-bipyridine (bpy, >99.0%), 2-bromoisobutyryl bromide (>97%), *N,N*-dimethylformamide (DMF, >99.5%), maleic anhydride (>99.0%), methanol (99.8%), THF (99.5%), triethylamine (Et_3N, >99.0%), toluene (99.5%), *p*-xylene (>98%) (the commercial souce of these materials; Tokyo Kasei Organic Chemicals, Tokyo), copper(I) bromide (CuBr, 95%), hydrochloric acid (HCl, 35.0−37.0%), sodium metal, zinc acetate, (>99%) (the commercial souce of these materials; Kanto Kagaku Reagent Division, Tokyo), and aluminum oxide active base (Aldrich, Milwaukee) were used as received.

Synthesis of *N*-(4-Hydroxyphenyl)maleimide (1).[10] *N*-(4-Hydroxyphenyl)maleimide (**1**) was followed by the method reported by Rao et al.[11] In brief, maleic anhydride was reacted with 4-aminophenol in *p*-xylene and DMF. Subsequently, zinc acetate was added as a catalysis, and the reaction was allowed to provide **1** (orange crystal; mp 182 °C, yield 56%).

Synthesis of Functionalized Comb-Shaped Copolymers 2. Scheme 1 shows the synthesis routes for prototype copolymer brushes. Alternating copolymerizations of PS-VB ($M_n = 5000$, $M_w/M_n = 1.04$) with **1** were carried out in THF initiated by AIBN at 60 °C for 5 h in a sealed glass ampule under vacuum (the polymerization has been degassed), varying the feed monomer ratios (feed mole fraction of PS-VB = 0.25−0.75). Typical polymerization conditions of CP3 (feed mole fraction of PS-VB = 0.5) were as follows: PS-VB (0.2 g, 0.04 mmol), **1** (0.0074 g, 0.04 mmol), AIBN (0.0026 g, 0.016 mmol) in THF (1.2 mL). After polymerization, the resulting solution was poured into a large excess of methanol. The conversion (15−25%) was estimated from peak areas of gel permeation chromatograph (GPC) chart for the recovered polymers (the mixture of alternating copolymer **2** and unreacted PS-VB). The reactivity ratio is the ratio of the rate constant for a propagating species adding to its own monomer to the rate constant for its addition to the other monomer. In order to determine the reactivity ratios, r_1 (PS-VB) and r_2 (**1**), the copolymerization product was separated by precipitation fractionation in a THF-methanol system.

Preparation of Comb-Shaped Polyinitiators 3. A mixture of **2** (hydroxyphenyl groups = 0.53 mmol), 2-bromoisobutyryl bromide (0.37 g, 1.59 mmol), and Et_3N (0.17 g, 1.59 mmol) as an acid acceptor was stirred in THF (dried over with Na chips; 20 mL) for 3 h at 0 °C, followed by stirring at room temperature for 18 h. Reaction product **3** [derivation to functional groups: *N*-(4-(2-bromobutyryloxy)phenyl)maleimide] was poured into a large excess of methanol and separated by filtration (degree of esterification; 100%).

Synthesis of Prototype Copolymer Brushes 4. ATRP operations were carried out in a sealed glass apparatus under high vacuum (the polymerization has been degassed). Typical polymerization conditions for the synthesis of PS/PMMA prototype copolymer brushes **4** are as follows. Comb-shaped polyinitiator **3** (0.5 g, 0.1 mmol), MMA (0.668 g, 6.67 mmol), CuBr (0.014 g, 0.1 mmol), and bpy (0.027 g, 0.17 mmol) ([Br]:[MMA]:[CuBr]:[bpy] = 1:67:1:1.7, where [Br] indicates Br concentration of functionalized MI groups) were dissolved in toluene (0.38 mL) (67 wt % monomer solution), and the resulting mixture was stirred at room temperature for a certain time to form a copper complex, CuBr/bpy (we observed color change of solution). After ATRP polymerization at 40 °C for 2.5 h, the crude product was recovered by precipitation in methanol containing dilute HCl to remove roughly the copper complex. The final polymerization mixture was diluted with THF, the solution was filtered through a column filled with aluminum oxide 90 active basis to remove the catalyst, and the polymer was precipitated in excess of methanol and dried in vacuo to a constant weight (conversion of MMA; 17.1%).

Characterization. Polydispersities (M_w/M_n) of comb-shaped polyinitiator **3** and prototype copolymer brush **4** were determined by GPC (Tosoh high-speed liquid chromatograph HLC-8120, Tokyo) using two TSK gel columns, GMH_{XL} [excluded-limit molecular weight ($M_{ELM} = 4 \times 10^8$)] and $G2000H_{XL}$ ($M_{ELM} = 1 \times 10^4$), in series in THF as eluent (flow rate of 1.0 mL/min) at 40 °C using PS standard samples. The weight-average molecular weights (M_w) of **3** and **4** were determined by static light scattering (SLS; Photal DLS-8000PNA: Otsuka Electronics, Tokyo, He−Ne laser: $\lambda_0 = 632.8$ nm, 10 mW) using Zimm mode in THF ($n_D = 1.40$, $\eta = 0.456$ cP) at 25 °C. The refractive index increment d*n*/d*c* of each polymer was determined by a differential refractometer (Photal DRM-1021; $\lambda_0 = 632.8$ nm). Sample solutions were filtered through membrane filters with a norminal pore of 0.2 μm just before measurement. The diffusion coefficient (D_0) was determined by the extrapolation to zero concentration on dynamic light scattering (DLS; Otsuka Electronics) data with cumulant method at 25 °C in 2−10 mg/mL THF solution of comb-shaped polyinitiator **3** and prototype copolymer brush **4**. The scattering angle was in the range 30°−150°.

In order to evaluate the reactivity ratios (r_1 and r_2), the composition of comb-shaped polyinitiators **3** was determined by Fourier transform infrared (FT-IR) spectroscopy (Shimadzu FTIR-8500, Tokyo). Calibration curve was constructed using the mixture of PS and *N*-(4-hydroxyphenyl)maleimide (characteristic absorbance of PS, 735 cm^{-1}, and carbonyl moiety, 1700 cm^{-1}). Two monomers, M_1 and M_2, are defined as the PS-VB macromonomer and *N*-(4-hydroxyphenyl)maleimide, respectively. The reactivity ratios, r_1 and r_2, were estimated by a graphical r_1-r_2 determination and curve-fitting procedure.[12]

Proton nuclear magnetic resonance (^{1}H NMR) spectra (500 MHz, JEOL GSX-500 NMR spectrometer, Tokyo) for **3** and **4** were performed in $CDCl_3$.

Morphological behavior of polymer brushes was obtained as follows. THF solution of 0.1 wt % concentration was dropped on a microscope mesh coated with carbon film for taking transmission electron microscopy (TEM). The specimen was stained with rutenium tetraoxide (RuO_4) vapor. Morphological results were obtained on a Hitachi H-500 TEM at 100 kV.

Results and Discussion

Synthesis of Functionalized Comb-Shaped Copolymers. Highly alternating copolymers are prepared by copolymerizing electron-accepting monomers such as maleic anhydride or MI with electron-donating monomers such as styrene.[9] It has been suggested that alternation results from the homopolymerization of 1:1 complexes formed between the donor and acceptor monomers. So, it can also be expected that macromonomer PS-VB and maleimide derivative **1** form 1:1 complexes.

To demonstrate this concept, free-radical copolymerizations of PS-VB with **1** were carried out varying the feed comonomer concentration (feed mole fraction of PS-VB = 0.25−0.75, monomer concentration = 45 wt % THF solution). In order to estimate the reactivity ratios, the yield of copolymers was in the range 15−25%. Normally these conversions should not be higher than 10% to minimize compositional drift. A typical GPC profile of the copolymer produced (CP3; feed mole fraction of PS-VB = 0.5) is shown in Figure 2. In this copolymerization, a new peak appears at the high-molecular-weight side compared to PS-VB macromonomer. This peak corresponds to alternating comb-shaped copolymer. The conversion was evaluated to be 23% from the peak areas of GPC chart. To determine the composition of copolymer produced, the copolymerization product CP3F was fractionated by the precipitation method (THF−methanol system), as shown in Figure 2.

A typical FT-IR spectrum of the copolymerization product CP3F is shown in Figure 3. The spectrum showed the expected absorbance for carbonyl groups (1700 cm^{-1}) of **1** and aromatic ring (1600 and 735 cm^{-1}) of PS comb chains. In order to determine the composition of the copolymers, the calibration curve was constructed using the mixture of PS and **1** (aromatic ring at 735 cm^{-1} and carbonyl groups at 1700 cm^{-1}). Figure 4 shows the graphical r_1-r_2 determination plot for copolymerization series. Reactivity ratios ($r_1 = 0.08$ and $r_2 = 0$) were derived from this plot. On the other hand, each copolymer composition F_1 (PS-VB [M_1]; **1** [M_2]) on the comonomer feed composition, f_1, for experimental series is shown in Figure 5. The line c indicates the curve for model compounds of styrene and MI ($r_1 = 0.1$ and $r_2 = 0.1$[9]). Reactivity ratios $r_1 = 0.08$ and $r_2 = 0$ (line b; estimated from graphical r_1-r_2 determination) were fitted somewhat below from the observed values. Then, reactivity ratios r_1 and r_2 were estimated by the curve-fitting procedure. Reactivity ratios $r_1 = 0.15$ and $r_2 = 0$ (line a) were well fitted on the observed values. It is found that copolymerization reactivity of PS-VB with **1** shows a strong alternation. However, maleimides are not as strong electron acceptors as their maleic anhydride counterpart. They may not form the molecular complex with styrene that maleic anhydride easily forms. It has been left unsolved whether the propagating copolymer radicals proceed always with homopolymerization of 1:1 complexes formed.

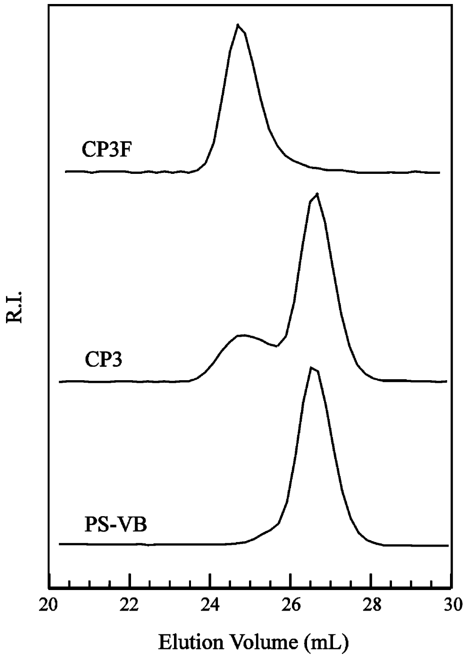


Figure 2. Gel permeation chromatograph (GPC) profiles of vinylbenzyl-terminated PS macromonomer (PS-VB), copolymer produced: feed mole fraction of PS-VB = 0.5 (**CP3**) and fractionated copolymer **CP3F**.

Derivation to Comb-Shaped Polyinitiators 3. To synthesize the prototype copolymer brushes, we prepared newly alternating comb-shaped copolymer **2B** ($M_w = 6.88 \times 10^5$, $M_w/M_n = 1.41$; PS−VB: $M_n = 5000$) with a large scale (conversion: 85.7%). The esterification of hydroxyphenyl groups in alternating comb-shaped copolymers was carried out with 2-bromoisobutyryl bromide in THF solution. Figure 3 also shows the FT-IR spectrum of comb-shaped polyinitiator **3B**. The spectrum of **3B** shows the expected absorbance for the aromatic ring (1600 and 735 cm^{-1}) and characteristic both absorbances for carbonyl groups of maleimide at 1700 cm^{-1} and for carbonyl groups of ester bonds at 1750 cm^{-1}. To determine the esterification yield of hydroxyphenyl groups, we synthesized the model compound, i.e., esterification compound of **1** with 2-bromoisobutyryl bromide. The spectrum of this model compound indicated the same intensity ratios of absorbance at 1750 cm^{-1} to that at 1700 cm^{-1}. This indicated the successful esterification of hydroxyphenyl groups with 2-bromoisobutyryl bromide. Usually such esterification employed the introduction of initiating groups in ATRP approaches and proceeded quantitatively.[13−16] In the FT-IR spectrum, the −OH resonance (broad band at 3500 cm^{-1}) looks more intense in the supposedly esterified product. This may be due to a small amount of water in the sample.

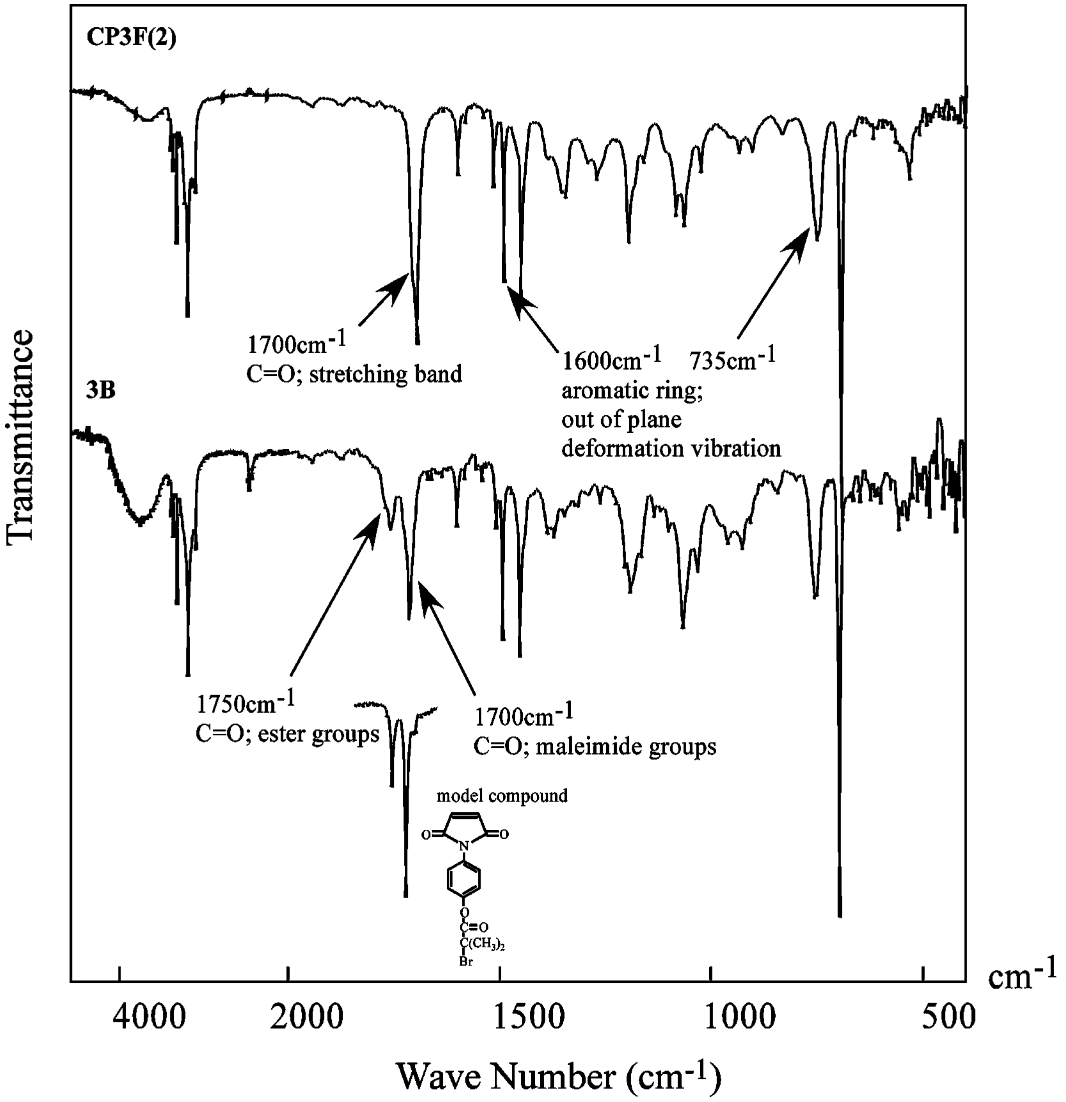


Figure 3. FT-IR spectra of copolymerization product **CP3F** and comb-shaped polyinitiator **3B**.

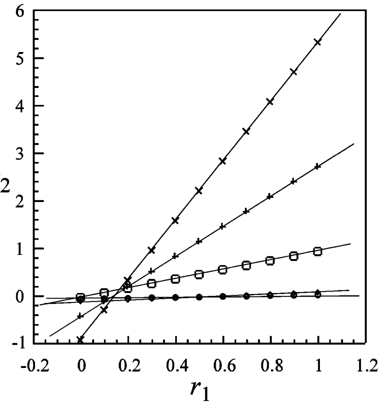


Figure 4. Graphical r_1–r_2 determination plot for copolymerization series.

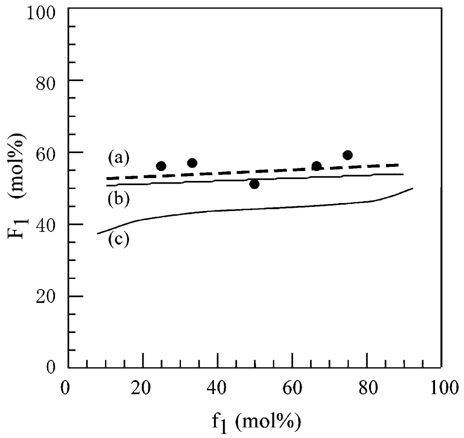


Figure 5. Plot of the dependence of instantaneous copolymer composition F_1 on the comonomer feed composition f_1 for **CP** copolymerization series: line a: $r_1 = 0.15$ and $r_2 = 0$ (curve-fitting method); line b: $r_1 = 0.08$ and $r_2 = 0$ (graphical r_1–r_2 determination); line c: $r_1 = 0.1$ and $r_2 = 0.1$ (model compounds of styrene and maleimide).

Preparation of Prototype Copolymer Brushes 4 by Grafting-from ATRP. Preliminary experiments concerning the relationship between conversion and time for prototype copolymer syntheses in toluene were performed under the following conditions: [**3B**] = 0.145 mmol/L, [MMA] = 9.75 mol/L, [CuBr] = 0.145 mmol/L, and [bpy] = 0.250 mmol/L. Both polymerizations at 60 °C for 2 h and at 40 °C for 4 h led to gelation due to intermolecular radical couplings. Similar behavior was reported already in the synthesis of double-cylinder-type copolymer brushes via ATRP approaches.[13−15] Then, grafting-from ATRP for prototype copolymer brush **4B** was performed at 40 °C for 2.5 h. The conversion of MMA was 17.1%.

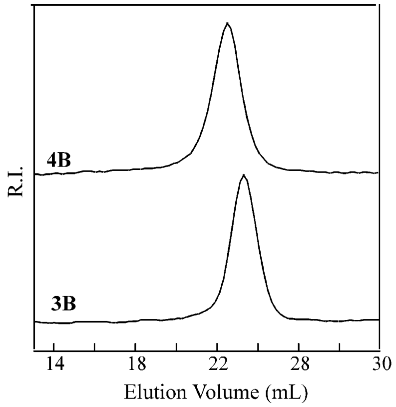


Figure 6. Gel permeation chromatograph (GPC) profiles of prototype copolymer brush **4B** and its precursor **3B**.

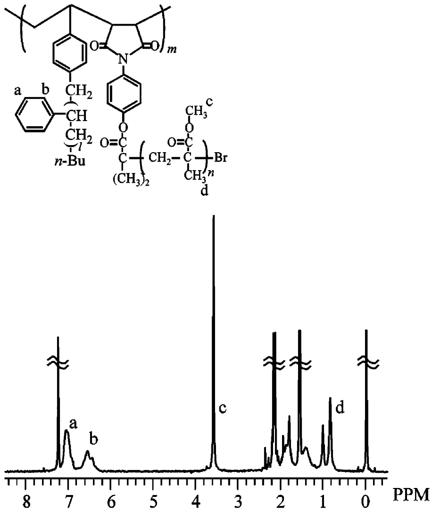


Figure 7. ^{1}H NMR spectrum of prototype copolymer brush **4B** in $CDCl_3$.

Table 1. Characteristics and Solution Properties of Polymer Brushes

code	$10^{-5}M_w{}^a$	$M_w/M_n{}^b$	$R_g{}^a$ (nm)	10^7D_0 (cm^2/s)^c	$R_h{}^c$ (nm)
3B	6.88	1.41	18.5	8.67	6.1
4B	11.0	1.43	32.5	5.13	10.1

[a] R_g = radius of gyration: determined by static light scattering (SLS) with Zimm mode in tetrahydrofuran (THF) at 25 °C. [b] Determined by gel permeation chromatograph (GPC) profiles in THF as eluent using PS standard samples. [c] Translational diffusion coefficient: determined by dynamic light scattering (DLS) in THF at 25 °C.

Figure 6 shows GPC profiles of the prototype brush **4B** and its precursor **3B**. The GPC curve of **4B** shifts to the high-molecular-weight side compared to that of the **3B** precursor, keeping not only a unimodal distribution but also almost the same polydispersity ($M_w/M_n = 1.43$). The ^{1}H NMR spectrum also gives support to the prototype brush formed (see Figure 7). The spectrum displays the expected resonances for aromatic protons of PS (a,b; δ 6.30−7.21 ppm) and the methoxy protons (c; 3.60 ppm) and methyl protons (d; 0.68−1.12 ppm) of PMMA grafted chains. The integration ratio of aromatic protons (a, b) to methoxy protons (c) was 5:3. These results indicate that the PMMA grafted chains had almost the same degree of polymerization ($DP_{n,PMMA} = 48$) as PS side chains. The characteristics of prototype copolymer brushes will be discussed later.

Characterization and Solution Properties of Polymer Brushes. Table 1 lists the characteristics of comb-shaped polyinitiator **3B** and prototype copolymer brush **4B**. The DP_n of the main chain was calculated to be 194 from both M_n of **3B** and PS-VB macromonomer (M_n = 5000). The DP_n of the PMMA grafted chains was also calculated to be 29 from both M_n of **4B** and **3B** (converting from M_w and M_w/M_n of **4B** and **3B**), assuming that all of the initiation sites on the comb-shaped polyinitiator led to propagation of MMA. This value is very small compared to $DP_{n,PMMA} = 48$ determined by ^{1}H NMR data in the former section. The $DP_{n,PMMA}$ determined from SLS data may be contained some experimental error due to polydispersity of comblike polymers. As mentioned earlier, the polydispersities of **4B** and **3B** were almost the same. Then, the M_w/M_n of grafted PMMA chains may be narrow. It was concluded that this sample **4B** has in total 194 main chain units ($DP_{n,PS} + DP_{n,MI}$) as compared to 48 (PS) and 48 (PMMA; employed NMR data) side-chain units, respectively.

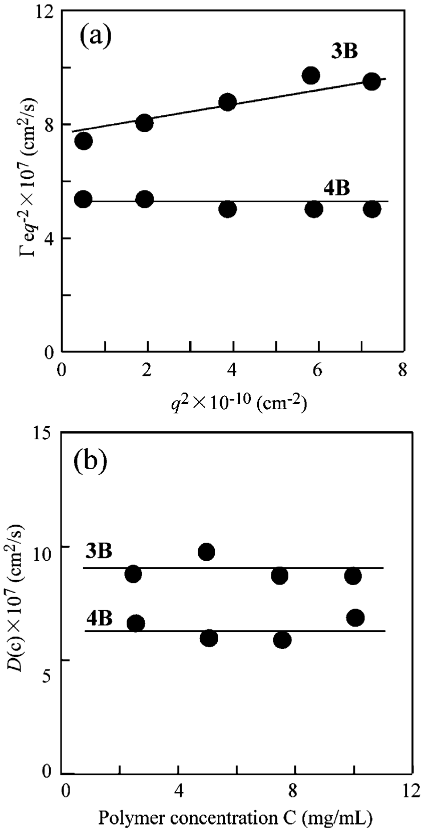


Figure 8. Dynamic light scattering (DLS) data for prototype copolymer brush **4B** and comb-shaped polyinitiator **3B** in tetrahydrofuran (THF): (a) angular dependence $\Gamma_e q^{-2}$ vs q^2 (Γ_e and q are the first cumulant and scattering vector, respectively) and (b) plots of diffusion coefficient against polymer concentration.

To discuss the geometrical anisotropy and intermolecular interaction, we determined the translational diffusion coefficient (D_0) of polymer brushes. In general, the mutual diffusion coefficient D(C) is defined as $D(C) \equiv \Gamma_e q^{-2}{}_{\theta\to 0}$, where Γ_e, q, and θ are the first cumulant, scattering vector, and scattering angle, respectively. Angular dependences of $\Gamma_e q^{-2}$ ($qR_h < 1$, where R_h is hydrodynamic radius) for comb-shaped polyinitiator **3B** and prototype copolymer brush **4B** are shown in Figure 8a. **3B** shows a weak angular dependence. On the other hand, it is found that the observed data on **4B** are fitted on an almost flat line. In the case of a spherical shape, it is well-known that the slope of line shows zero. On the other hand, the weak dependence of $\Gamma_e q^{-2}$ on q^2 shows that there is only a single diffusion mode. In general, polymer brushes composed of long aspect ratio took the wormlike conformation in a good solvent.[17,18] However, these brushes composed of short aspect ratio

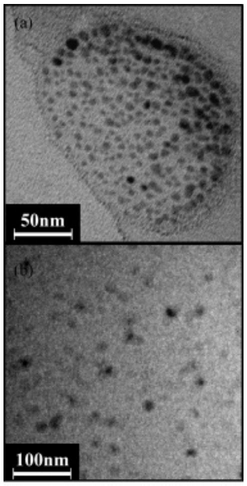


Figure 9. Transmission electron microscopy (TEM) photographs of comb-shaped polyinitiator **3B** (a) and prototype brush **4B** (b).

took ellipsoid or starlike conformation. It seems therefore that the prototype copolymer brush **4B** composed of relatively short aspect ratio changes the shape from ellipsoid (comb-shaped polyinitiator **3B**) to starlike structure because both PS and PMMA chains were stretched by introduction of PMMA grafted chains due to not only dense conformation but also intramolecular repulsion between PS and PMMA side chains. As a result, the cross-sectional diameter of prototype copolymer brush may increase compared to that of comb-shaped polyinitiator.

Figure 8b shows the relationship between the translational diffusion coefficient D(C) and the polymer concentration for **3B** and **4B**. Each D(C) has an almost constant value in the range 2−10 mg/mL of polymer concentration. This suggests that these polymer brushes are molecularly dissolved in the dilute solution. Similar tendencies were also observed in double-cylinder-type copolymer brushes.[1,19−21] The translational diffusion coefficient D_0 can be estimated by extrapolation of polymer concentration C to zero. The values of D_0 and R_h for polymer brushes **3B** and **4B** are also listed in Table 1. R_h is defined by the Stokes−Einstein equation; $R_h = kT/6\pi\eta_0 D_0$, where k, T, and η_0 indicate Boltzmann coefficient, absolute temperature, and viscosity of solvent, respectively. The values of D_0 and R_h for polymer brushes were as follows: **3B**: $D_0 = 8.67 \times 10^{-7}$ cm^2/s, $R_h = 6.1$ nm; **4B**: $D_0 = 5.13 \times 10^{-7}$ cm^2/s, $R_h = 10.1$ nm. The R_h value of **4B** is higher than that of **3B** because the molecular weight of **4B** increased by the introduction of these chains. As mentioned earlier, they may also cause intramolecular repulsion between PS and PMMA side chains.

Morphological Behaviors of Polymer Brushes. Parts a and b of Figure 9 show TEM photographs of polymer brushes **3B** and **4B**, respectively. PS domains were stained selectively with RuO_4. It is found from Figure 9a that ellipsoid or starlike particles are visible clearly on the carbon substrate. The average particle size (D_n) was estimated to be 6.6 nm. This value is small compared to hydrodynamic radius D_h (12.2 nm, see Table 1) in solution due to shrinkage in the solid state. After grafting of PMMA chains, prototype brush **4B** changes to large particles ($D_n = 19.2$ nm, see Figure 9b). However, we could not detect “Janus-type” morphology (intramolecular microphase-separated structure) in this photograph. These morphological results indicate also that the cross-sectional diameter of **4B** increases by introduction of PMMA grafted chains compared to that of **3B**.

Conclusions

Free-radical copolymerization of PS-VB and N-(4-hydroxyphenyl)maleimide gave well-defined alternating comb-shaped copolymers. Subsequent esterification of such comb-shaped copolymer with 2-bromoisobutyryl bromide yoelded a comb-shaped polyinitiator. The grafting-from ATRP approach from functionalized alternating comb-shaped initiator is a new route to construct the prototype copolymer brushes. Two brush side chains were stretched by introduction of PMMA grafted chains due to not only dense conformation but also intramolecular repulsion between PS and PMMA side chains. This work raises the possibility for the architecture of prototype copolymer brushes composed various vinyl monomers.

Supporting Information Available: Synthesis of vinylbenzyl-terminated polystyrene macromonomer (PS-VB). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Ishizu, K.; Tsubaki, K.; Mori, A.; Uchida, S. *Prog. Polym. Sci.* **2003**, *28*, 27−54.

(2) Ishizu, K. *Polym. J.* **2004**, *36*, 775−792.

(3) Bo, Z.; Rabe, J. P.; Schlüter, A. D. *Angew. Chem., Int. Ed.* **1999**, *38*, 2370−2372.

(4) Ishizu, K.; Shen, X. X.; Tsubaki, K. *Polymer* **2000**, *41*, 2053−2057.

(5) Tsubaki, K.; Kobayashi, H.; Satoh, J.; Ishizu, K. *J. Colloid Interface Sci.* **2001**, *241*, 275−279.

(6) Ishizu, K.; Sawada, N.; Satoh, J.; Sogabe, A. *J. Mater. Sci., Lett.* **2003**, *22*, 1219−1222.

(7) Ishizu, K.; Toyoda, K.; Furukawa, T.; Sogabe, A. *Macromolecules* **2004**, *37*, 3954−3957.

(8) Zhang, B.; Zhang, S.; Okrasa, L.; Pakula, T.; Stephan, T.; Schmidt, M. *Polymer* **2004**, *45*, 4009−4015.

(9) Patnaik, B. K.; Gaylord, N. G. *Macromol. Synth.* **1972**, *4*, 129−131.

(10) Ryuichiro, T.; Kanimitsu, F.; Teruo, M. US Patent 5 175 309, CA 115: 8571a, 1992.

(11) Rao, B. S.; Sireesha, R.; Pasala, A. R. *Polym. Int.* **2005**, *54*, 1103−1109.

(12) Ishizu, K.; Takashimizu, C.; Shibuya, T.; Uchida, S. *Polym. Int.* **2003**, *52*, 1010−1015.

(13) Boerner, H. G.; Beers, K.; Matyjaszewski, K.; Sheiko, S. S.; Moeller, M. *Macromolecules* **2001**, *34*, 4375−4383.

(14) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921−2990.

(15) Zhang, M.; Breiner, T.; Mori, H.; Müller, A. H. E. *Polymer* **2003**, *44*, 1449−1458.

(16) Ishizu, K.; Satoh, J.; Sogabe, A. *J. Colloid Interface Sci.* **2004**, *274*, 472−479.

(17) Nemoto, N.; Nagai, M.; Koike, A.; Okada, Y. *Macromolecules* **1995**, *28*, 3854−3859.

(18) Kawaguchi, H.; Matsumoto, H.; Iriany, H.; Ito, K. *Polym. Prepr. Jpn.* **1998**, *47*, 1694−1695.

(19) Ishizu, K.; Tsubaki, K.; Ono, T. *Polymer* **1998**, *39*, 2935−2939.

(20) Tsubaki, K.; Ishizu, K. *Polymer* **2001**, *42*, 8387−8393.

(21) Ishizu, K.; Tsubaki, K.; Satoh, J.; Uchida, S. *Des. Monomers Polym.* **2002**, *5*, 23−38.

MA062685E