

Architecture of Prototype Copolymer Brushes Composed of Alternating Structure and Intramolecular Phase Separation of Side Chains in Solution

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ABSTRACT: Atom transfer radical polymerization (ATRP) was applied to the synthesis of prototype copolymer brushes composed polystyrene/poly(*t*-butyl methacrylate) (PS/PBMA) alternating structure. Dilute solution properties of prototype copolymer brush were investigated by static and dynamic light scattering (SLS and DLS) in tetrahydrofuran (THF). As a result, such prototype copolymer brush composed of short aspect ratio formed a star-like single molecule in THF. To discuss the intramolecular phase separation of PS/PBMA brushes in solution, we determined the radius of gyration (R_g) and cross-sectional radius of gyration ($R_{g,c}$) of prototype copolymer brush by small-angle X-ray

scattering (SAXS) using Guinier's plots in THF and styrene. We used styrene as solvent to cancel each other out with the electron density of PS side chains. Both R_g and $R_{g,c}$ obtained in styrene decreased drastically compared with those obtained in THF. These results indicated strongly that PS and PBMA side chains of prototype brushes formed intramolecular phase separation even in good solvent. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 2298–2304, 2010

Key words: atom transfer radical polymerization (ATRP); prototype copolymer brush; Guinier's plots; phase separation

INTRODUCTION

Branched macromolecules exhibit specific solution properties due to a higher segment density compared to linear chains of equivalent molar mass and same chemical composition. Such a higher segment density not only affects the intrinsic viscosity but also interactions of excluded volume type. It is well-known that comb polymers with densely grafted side chains in a good solvent can adopt a worm-like 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 investigated the architecture of prototype copolymer brushes (see Fig. 1) by alternating free-radical copolymerization of binary macromonomers.^{1,2} Other strategy can be designed to construct such structures. Schlüter and coworkers³ 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.

More general synthetic method is required to prepare the prototype copolymer brushes consisting of

various chemical components. 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.⁴ We can expect to synthesize easily prototype copolymer brushes by alternating copolymerization of vinylbenzyl (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 fact, we have reported recently that ATRP from alternating comb-shaped copolymers having MI groups was applied to a novel synthesis of prototype copolymer brushes.⁵

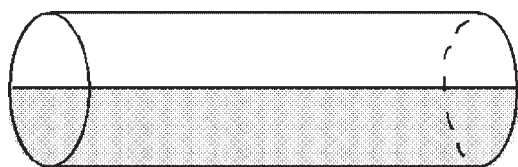
In this article, we present the synthesis of PS/poly(*t*-butyl methacrylate) (PBMA) prototype copolymer brushes by using the grafting-from ATRP approach from alternating comb-shaped copolymers having functionalized MI groups. Especially, the main purpose of this work is to make clear the possibility of intramolecular phase separation of both side chains for prototype copolymer brushes in solution.

EXPERIMENTAL

Materials

Well-defined vinylbenzyl-terminated PS (PS-VB) was synthesized by the coupling reaction of polystyryl

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Prototype Copolymer Brush

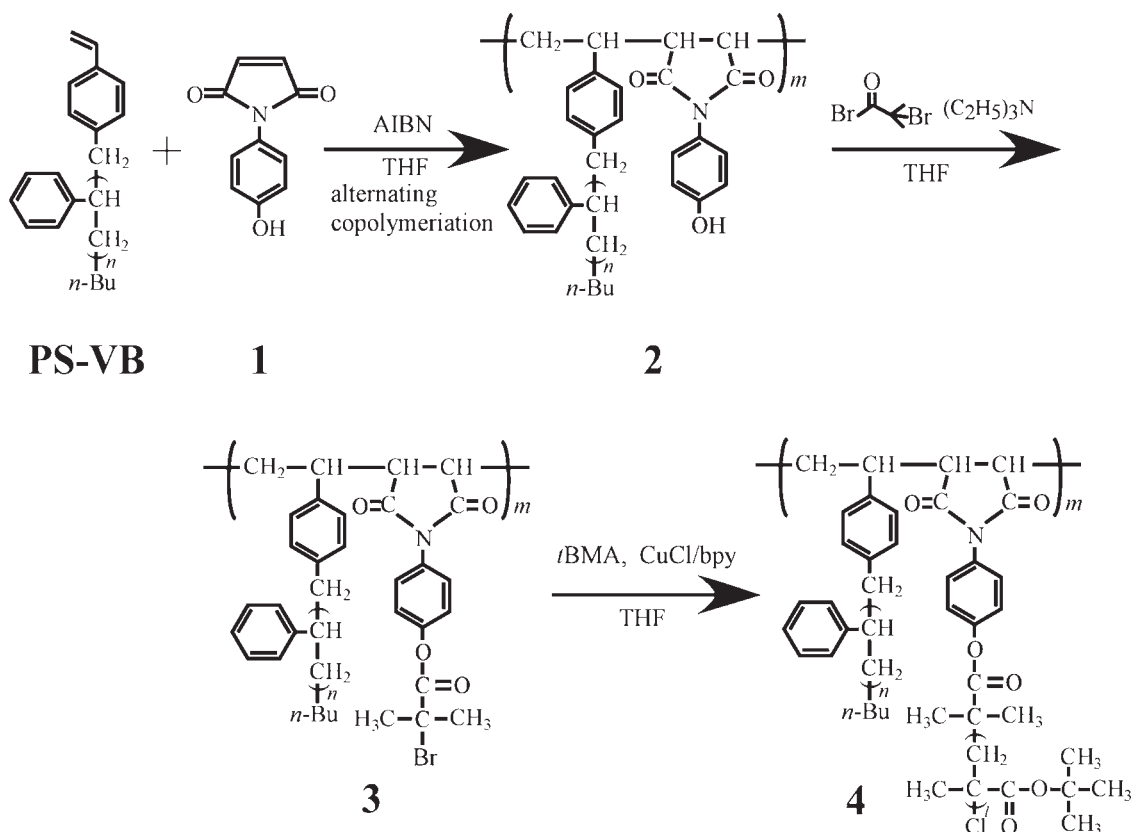
Figure 1 Illustration of prototype copolymer brush.

lithium with an excess amount of *p*-chloromethylstyrene (CMS) in a benzene-tetrahydrofuran (THF) mixed solvent. Details of the synthesis and characterization are given elsewhere.⁶ *N*-(4-Hydroxyphenyl) maleimide (**1**) was followed by the method reported by Rao et al.⁷ In brief, maleic anhydride was reacted with 4-aminophenol in *p*-xylene and *N,N*-dimethylformamide (DMF). Subsequently, zinc acetate was added as a catalyst, and the reaction was allowed to provide **1**. *t*-Butyl methacrylate (BMA; >98.0%, Tokyo Kasei Organic Chemicals, Tokyo) and styrene (>99.0%) were distilled under high vacuum. 4,4'-Azobisisobutyronitrile (AIBN, >99.5%), 2,2'-bipyridine

(bpy, >99.0%), 2-bromoisobutyryl bromide (>97%), methanol (99.8%), THF (99.5%), triethyl amine (Et₃N, >99.0%, the commercial source of these materials; Tokyo Kasei Organic Chemicals, Tokyo), copper(I) chloride (CuCl, 95%), hydrochloric acid (HCl, 35.0–37.0%, the commercial source of these materials; Kanto Kagaku Reagent Division, Tokyo) and aluminum oxide active base (Aldrich, Milwaukee) were used as received.

Preparations of functionalized Comb-shaped copolymers (**2**) and Comb-shaped polyinitiators (**3**)

Scheme 1 shows the synthesis routes for prototype copolymer brushes. Alternating copolymerizations of PS-VB ($M_n = 3600$, $M_w/M_n = 1.09$) with **1** were carried out in THF initiated by AIBN at 60°C for 96 h in a sealed glass ampoule under vacuum (the polymerization has been degassed; more than 70% of conversion for PS-VB and **1**). Copolymerization product **2** ($M_w = 1.23 \times 10^5$, $M_w/M_n = 1.13$) showed alternating structure as mentioned in a previous article.⁵ Comb-shaped polyinitiator **3** was prepared by esterification of **2** with 2-bromoisobutyryl bromide in the presence of Et₃N as an acid acceptor in THF



Scheme 1 Synthesis route for prototype copolymer brushes (AIBN; 4,4'-azobisisobutyronitrile, *t*BMA; *tert*-butylmethacrylate).

for 3 h at 0°C, followed by stirring at room temperature for 18 h. Details of the synthesis and characterization have been given elsewhere.⁵

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/PBMA prototype copolymer brushes **4** are as follows. Comb-shaped polyinitiator **3** (0.2 g, 0.052 mmol), BMA (0.33 g, 2.32 mmol), CuCl (0.0063 g, 0.063 mmol), and bpy (0.016 g, 0.11 mmol) ([Br]:[BMA]:[CuCl]:[bpy] = 1 : 45 : 1.5 : 2.5), where [Br] indicates Br concentration of functionalized MI groups, were dissolved in THF (0.54 mL) (67 wt % monomer solution) and the resulting mixture was stirred at room temperature for a certain time to form a copper complex, CuCl/bpy (we observed color change of solution). After ATRP polymerization at 60°C for 3 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 BMA; 68.5%).

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 **2** 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 dn/dc of each polymer was determined by differential refractometer (Photal DRM-1021; $\lambda_0 = 632.8$ nm). Sample solutions were filtered through membrane filters with a nominal 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 2.5–10 mg/mL THF solution of functionalized comb-shaped copolymer **2** and prototype copolymer brush **4**. The scattering angle was in the range 30–150°.

Proton nuclear magnetic resonance (¹H-NMR) spectra (300 MHz, Bruker GPX300 NMR spectrometer, Frankfurt) for **3** and **4** were performed in CDCl₃.

To discuss the intramolecular phase separation of prototype PS/PBMA copolymer brushes **4** in solution, we determined the radius of gyration (R_g) and cross-sectional radius of gyration ($R_{g,c}$) of **4** by small-angle X-ray scattering (SAXS). The SAXS intensity distribution $I(q)$ was measured with a rotating-anode X-ray generator (Bruker AXS Nanostar, Frankfurt) operated at 50 kV and 100 mA. The X-ray source was monochromatic Cu K α ($\lambda = 15.4$ nm) radiation. In the measurement a THF or styrene solution (0.5 and 1.0 wt %) of the sample, we used the cell sandwiched between mica plates as a holder vessel. The background correction was carried out using polyethylene film. We used styrene as solvent to cancel each other out with the electron density of PS side chains under irradiation of X-ray beam. The values of R_g and $R_{g,c}$ are estimated by Guinier's method from the following equation.⁸

$$\ln I(q) = \text{constant} - (1/3)(R_g^2)q^2 \quad (1)$$

$$\ln qI(q) = \text{constant} - (1/2)(R_{g,c}^2)q^2 \quad (2)$$

where q is the scattering vector.

RESULTS AND DISCUSSION

Synthesis of functionalized Comb-shaped copolymers (2) and polyinitiators (3)

As mentioned in the previous work,⁵ highly alternating comb-shaped copolymer **2** was prepared by copolymerizing electron-accepting monomer such as *N*-(4-hydroxyphenyl) maleimide **1** with electron-donating monomer such as PS-VB. Characteristics of **2** were listed in Table I. The number of grafted PS side chains was calculated to be 30 from M_w and M_w/M_n , because the unit number (N) of the main chain was 60.

The esterification of hydroxyphenyl groups in alternating comb-shaped copolymer **2** was carried out with 2-bromoisobutyryl bromide in THF solution. Usually such esterification was employed the introduction of initiating groups in ATRP approaches and proceeded quantitatively.^{9–12} In fact, it was found from the FTIR spectrum of **3** that such esterification proceeded quantitatively.

Preparation of prototype copolymer brushes (4) by grafting-from ATRP

It is well-known for the block copolymer synthesis that the poly(methacrylate) macroinitiator, having a bromine atom at the end group, effectively initiates the ATRP of methacrylate monomers in the presence

TABLE I
Characteristics and Solution Properties of
Polymer Brushes

Code	$10^{-5} M_w^a$	M_w/M_n^b	R_h^c (nm)
2	1.23	1.13	7.48
4	2.62	1.42	13.3

^a 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 R_h : hydrodynamic radius; determined by dynamic light scattering (DLS) in THF at 25°C.

of the catalyst CuCl; that is a halide exchange should take place.^{13–15} Therefore, we performed a halide exchange equilibrium to achieve a narrow polydispersity for the prototype copolymer brush synthesis initiated by polyinitiator **3** with CuCl in the ATRP method instead of CuBr. Several comprehensive reviews for polymer brushes via a grafting-from ATRP have been published.^{16,17} Grafting from ATRP for prototype copolymer brush **4** was performed at 60°C for 3 h (67 wt % monomer solution). The conversion of BMA was 68.5 %. Figure 2 shows GPC profiles of the prototype brush **4** and its precursor **3**. The GPC curve of **4** shifts to the high-molecular weight side compared to that of the **3** precursor, keeping a unimodal distribution with somewhat broad polydispersity ($M_w/M_n = 1.42$). Moreover, the GPC curve of the PS/PBMA prototype copolymer brush **4** seems to show a tail at the low-molecular weight and a peak at the high-molecular weight. However, they are not due to macroinitiator and PBMA homopolymer, because PBMA is soluble in methanol employed as precipitant. It is better that the polymerization was generally carried out in dilute solution and at low conversion to avoid inter- and intra-molecular reactions.

The ¹H-NMR spectrum also gives support to the prototype brush formed (see Fig. 3). The spectrum displays the expected resonances for aromatic protons of PS (a,b; δ 6.30–7.21 ppm) and the methyl protons (d; 1.40 ppm) of *t*-butyl groups and α -methyl protons (c; 0.68–1.12 ppm) of PBMA grafted chains. However, actually the aromatic region (a,b) also has to take account the contribution from the aromatic protons of the phenyl maleimide. Similarly, the α -methyl proton (c) also has contribution from other types of methyl units and peak has a shoulder in the spectra. The integration ratio of aromatic protons (a,b) to α -methyl protons s(c) was 1 : 0.77. These results indicate that the PBMA grafted chains had somewhat long degree of polymerization [$DP_{n,PBMA} = 45$; i.e., $0.77 \times (5/3) \times 35$] as compared to PS side chains ($DP_{n,PS} = 35$). Therefore, it is not accurate to conclude from the aromatic to methyl proton inten-

sity ratio that the PBMA chain has longer DP_n . The characteristics of prototype copolymer brushes will be discussed later.

Characterization and solution properties of polymer brushes

Characteristics of PS/PBMA prototype copolymer brush **4** are also listed in Table I. The DP_n of the PBMA grafted chain ($DP_{n,PBMA}$) was also calculated to be 25 from both M_n of **4** and **2** (converting from M_w and M_w/M_n of **4** and **2**), assuming that all of the initiation sites on the comb-shaped polyinitiator led to propagation of BMA. This value is smaller compared to $DP_{n,PBMA}$ (45) determined by ¹H-NMR data in the former section. As mentioned earlier, the determination method from NMR for the composition is not accurate. This could be one of the reasons for the mismatch between the DP_n calculated using GPC and NMR. However, the $DP_{n,PBMA}$ determined from SLS data may be also contained some experimental error due to broad polydispersity of brush polymers. It was employed in this work that this sample **4** has in total 60 main chain units ($N_{PS} + N_{MI}$) as compared to 35 ($DP_{n,PS}$) and 45 ($DP_{n,PBMA}$; employed NMR data) side chain units, respectively.

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 $D(C) \equiv \Gamma_e q^{-2} \theta_{\theta=0}$, 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

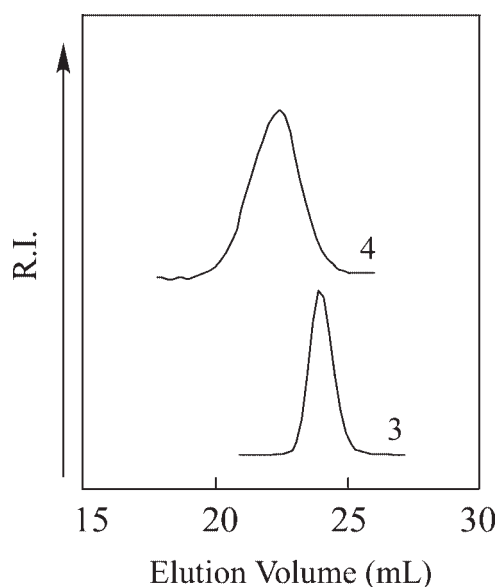


Figure 2 Gel permeation chromatograph (GPC) profiles of comb-shaped polyinitiator **3** and PS/PBMA prototype copolymer brush **4**.

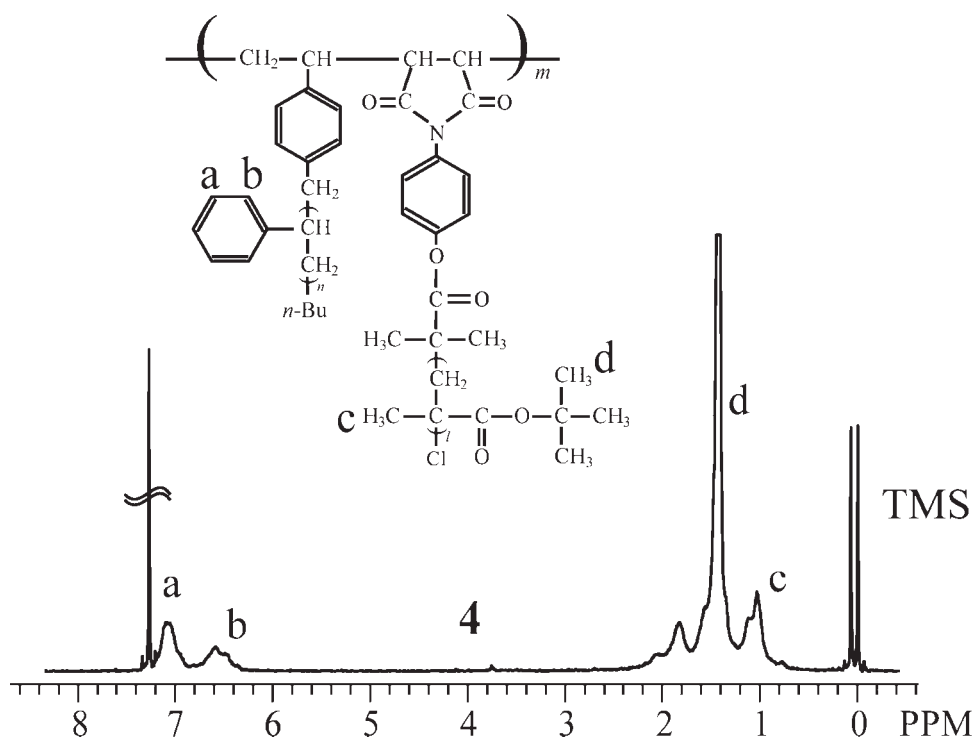


Figure 3 $^1\text{H-NMR}$ spectrum of prototype copolymer brush 4 in CDCl_3 .

functionalized comb-shaped copolymer **2** and prototype copolymer brush **4** are shown in Figure 4(a). Both polymers **2** and **4** show a weak angular dependence. 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 worm-like conformation in a good solvent.^{18,19} However, these brushes composed of short aspect ratio took ellipsoid conformation. Figure 4(b) shows the relationship between the translational diffusion coefficient $D(C)$ and the polymer concentration for **2** and **4**. Each $D(C)$ has an almost constant value in the range 2.5–10 mg/mL of polymer concentration. This suggests that these polymer brushes are molecularly dissolved in the dilute solution.

Intramolecular phase separation of PS/PBMA side Chains in solution

R_g and $R_{g,c}$ of prototype copolymer brush **4** were determined by Guinier's plots on SAXS. Figure 5(a) shows Guinier's plots for prototype brush **4** in THF, varying polymer concentrations (0.5 and 1.0 wt %). The slopes are constant regardless of polymer concentration. Then, R_g can be evaluated to be 10.8 nm from these slopes. On the other hand, Figure 5(b) shows the cross-sectional Guinier's plot for proto-

type brush **4** in THF, varying polymer concentrations (0.5 and 1.0 wt%). The slopes are also constant regardless of polymer concentration. The $R_{g,c}$ can be evaluated to be 9.4 nm from these slopes. These physical values are listed in Table II.

We consider the molecular size of PS/PBMA brush **4** in THF solution. Assuming a polydisperse rodlike shape and neglecting $R_{g,c}$, R_g is given by the following relation

$$R_g = (5/27)^{1/2} L_w \quad (3)$$

for the Schulz-Zimm length distribution

$$(L_w/L_n = 1.5)$$

where L_w denotes the length of a rodlike molecule. Equation (3) allows one to evaluate the rod length as $L_w = 25.1$ nm, because $R_g = 10.8$ nm. The cross-sectional diameter d is calculated from $R_{g,c}$ as

$$d = (\sqrt{8}) R_{g,c} \quad (4)$$

Since eq. (4) yields $d = 26.6$ nm, the aspect ratio L_w/d is about unity. Accordingly, the shape of the prepared PS/PBMA brush **4** is much more similar to a spherical shape. On the other hand, R_h value of **4** is higher than that of **2** as shown in Table I, because the molecular weight of **4** increased by the

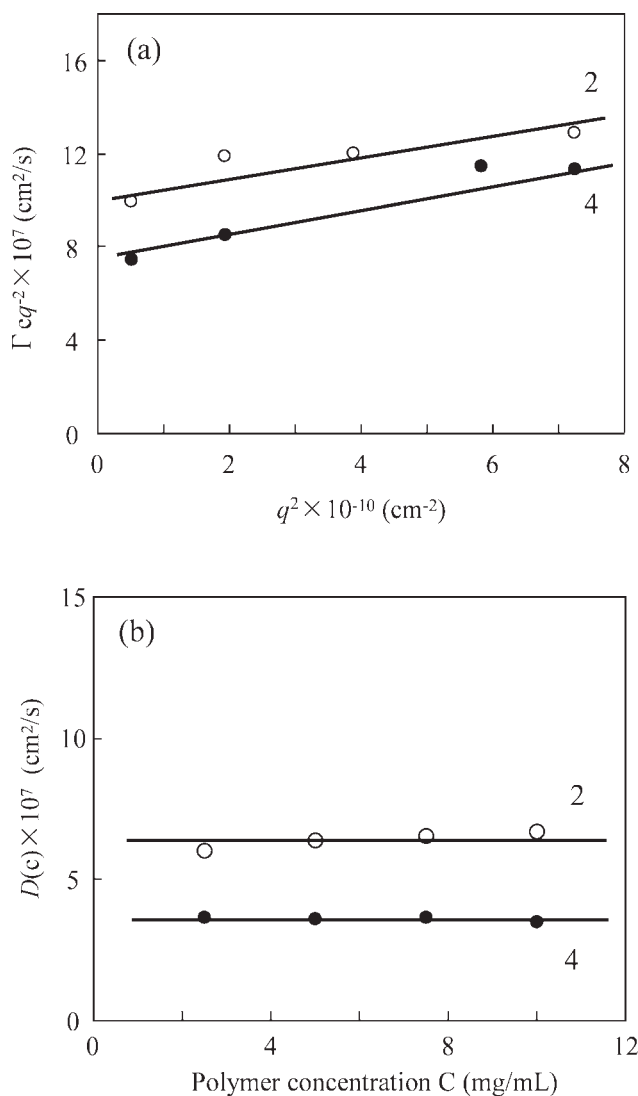


Figure 4 Dynamic light scattering (DLS) data for prototype copolymer brush 4 and functionalized comb-shaped copolymer 2 in tetrahydrofuran (THF): (a) angular dependence $\Gamma_e q^{-2}$ vs q^2 (Γ_e and q are the first cumulant and scattering vector, respectively) and (b) plots of diffusion coefficient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

introduction of these chains. As mentioned earlier, they may also cause intramolecular repulsion between PS and PBMA side chains by assuming a constant electron density across the brush.

Figure 6(a,b) show Guinier's and cross-sectional Guinier's plots of prototype brush 4 in styrene, respectively. R_g and $R_{g,c}$ also can be estimated from each slope. These physical values are also listed in Table II. The cohesive energy density of styrene (δ_{styrene}) is 19.0 (MPa)^{1/2}.²⁰ Then, styrene is good solvent for PBMA block. It is found that both values of R_g and $R_{g,c}$ in styrene decrease drastically compared with those obtained in THF. For example, the observed diameter d of 4 in styrene is estimated to

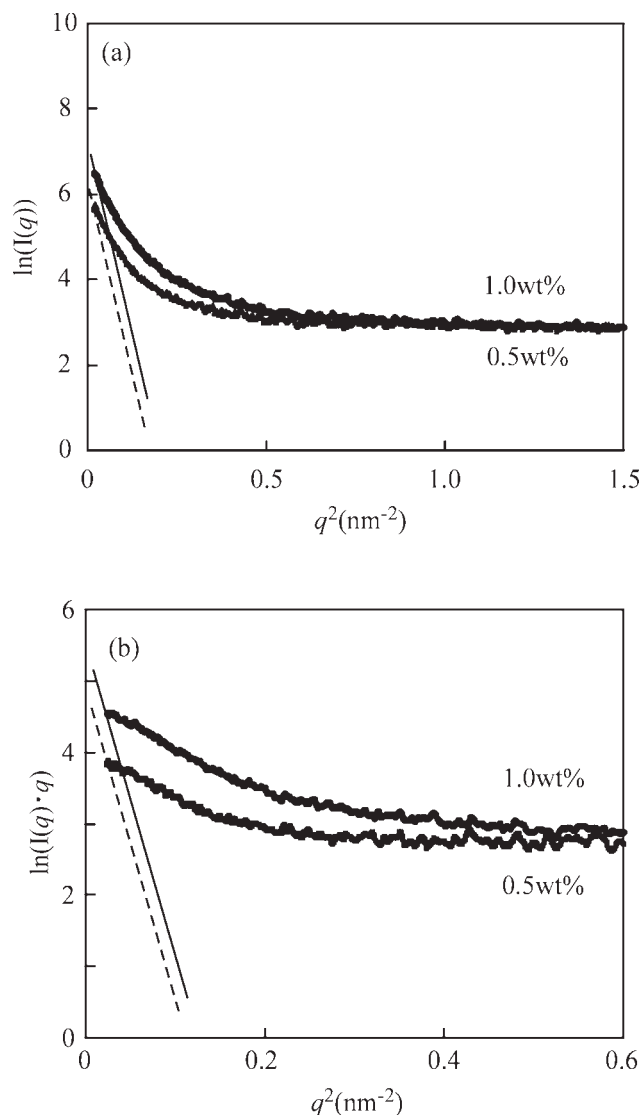


Figure 5 Guinier's and cross-sectional Guinier's plots of prototype copolymer brush 4 for determination of (a) R_g and (b) $R_{g,c}$ in THF, varying polymer concentration.

be 12.1 nm, because $R_{g,c} = 4.3$ nm. This means that the observed diameter of 4 in styrene is smaller compared with d (26.6 nm) in THF due to cancellation of phase-separated PS domain. Cohesive energy densities (δ) of side chains and solvents used as the index for solubility parameters are as follows:²⁰ PS; $\delta = 17.52$ (MPa)^{1/2}, PBMA; 17.9 (MPa)^{1/2} [employed

TABLE II
The Values of R_g and $R_{g,c}$ of PS/PBMA Copolymer Brush 4 from Guinier's Plots in THF or Styrene as Solvents

Solvent	R_g^a (nm)	$R_{g,c}^b$ (nm)
THF	10.8	9.4
Styrene	7.5	4.3

^a Radius of gyration.

^b Cross-sectional radius of gyration.

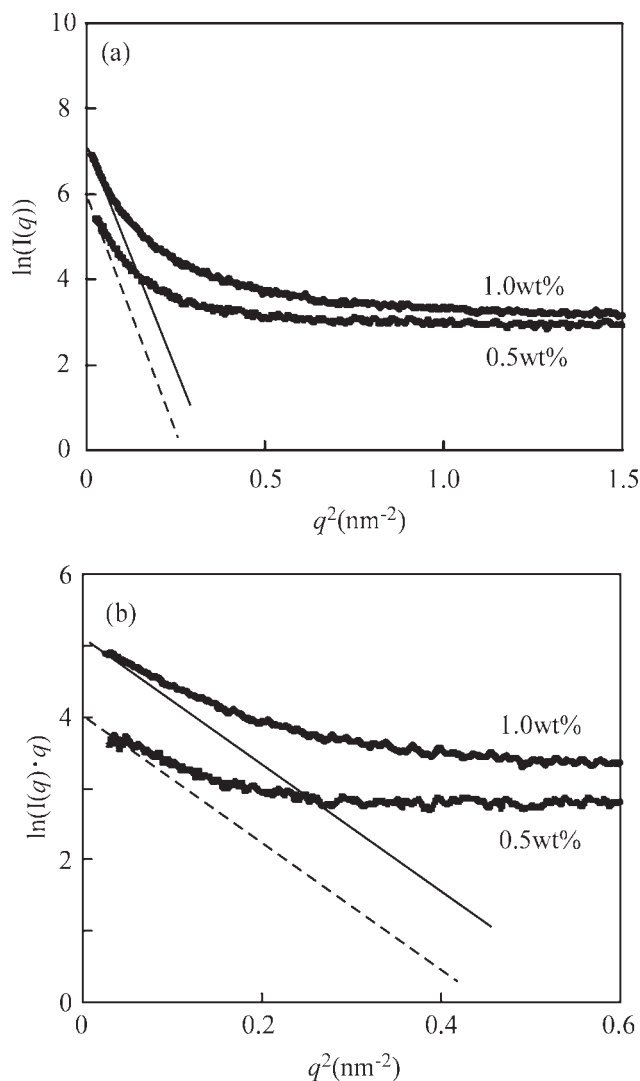


Figure 6 Guinier's and cross-sectional Guinier's plots of prototype copolymer brush 4 for determination of (a) R_g and (b) $R_{g,c}$ in styrene, varying polymer concentration.

the value of poly(*n*-butyl methacrylate) in this work], THF; $19.4 \text{ (MPa)}^{1/2}$, styrene; $19.0 \text{ (MPa)}^{1/2}$. Then, both THF and styrene are good solvent for PS and PBMA segment. This suggests that the electron density of PS side chains was canceled each other out with styrene used as solvent. We can speculate therefore from these results that PS and PBMA side chains lead to phase separation even in good solvent due to alternating structure. The comparative experiment for alternating and random structures of copolymer brushes is the subject for a future study. Moreover, acid hydrolysis of the *t*-butyl ester groups yielding their methacrylic acid counterparts would provide more interesting morphological changes due to the polymer's amphiphilicity. The results obtained will be reported in the near future.

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 yielded a comb-shaped polyinitiator. Grafting-from ATRP approach from functionalized alternating comb-shaped initiator is a new route to construct the prototype copolymer brushes. This work raises the possibility for the architecture of prototype copolymer brushes composed various vinyl monomers. It was found from SLS and DLS data that PS/PBMA prototype brush 4 with short aspect ratio formed a star-like single molecule in solution. R_g and $R_{g,c}$ were determined by Guinier's plots on SAXS in THF or styrene as solvent. Both values of R_g and $R_{g,c}$ in styrene decreased drastically compared with those obtained in THF, because the electron density of PS side chains was canceled each other out with styrene used as solvent. Thus, we succeeded first to discover the intramolecular phase separation of prototype copolymer brushes in solution by means of SAXS techniques. The information obtained in this work will be contributed to technological application of such prototype brush nanomaterials.

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