

# Synthesis of Functionalized Double-Cylinder-Type Copolymer Brushes and Crosslinking of Internal Cylindrical Domains

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**ABSTRACT:** Photoinduced atom transfer radical polymerization (ATRP) was applied to the synthesis of double-cylinder-type copolymer brushes. The procedure included the following steps: (1) photoinduced ATRP of multifunctional polystyrene (PSDC) having *N,N*-diethyldithiocarbamate (DC) pendant groups with *t*-butyl acrylate (BA) and (2) subsequent photoinduced ATRP of methyl methacrylate (MMA) with this PBA brush polyinitiator provided double-cylinder-type brushes [PSDC-*graft*-(PBA-*block*-PMMA)]. Solution properties of such double-cylinder-type brushes were investigated by dynamic

light scattering. As a result, these copolymer brushes exhibited an isotropic conformation in solution. After hydrolysis of PBA blocks, we obtained amphiphilic copolymer brushes: PSDC-*graft*-[poly(acrylic acid) (PAA)-*block*-PMMA]. Crosslinking of PAA internal cylindrical domains was performed by the reaction of PAA blocks with ethylenediamine. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 3994–4000, 2007

**Key words:** photoinduced ATRP; living radical polymerization; copolymer brushes; crosslinking

## INTRODUCTION

It is well known that comb polymers with densely arranged 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.<sup>1–4</sup> The construction of such nanocylinders has been recently achieved in the synthesis of linear polymers with dendritic side groups. There are three approaches that can be used to prepare polymers with dendron side groups: (A) divergent construction, analogous to divergent dendrimer synthesis, with a multifunctional linear polymers;<sup>5–7</sup> (B) attachment of prefabricated dendron building blocks onto a reactive polymer chain by a polymer-analogous reaction;<sup>8,9</sup> and (C) polymerization of dendron monomers.<sup>10,11</sup> For a recent treatment of dendrimer fragments shape polymer chains, the reader is referred to reviews.<sup>11,12</sup> On the basis of these backgrounds, we presented the novel construction of nanocylinders with hyperbranched side groups via living radical mechanism.<sup>13</sup> These nanocylinders took rigid rod conformation even in a good solvent.

More recently, we have systematically investigated the architecture of multicomponent copolymer brushes (double-cylinder-type, prototype, and block-type).<sup>14,15</sup> We have reported the synthesis and dilute-solution properties of double-cylinder-type copolymer brushes by free-radical polymerization of the corresponding diblock macromonomers.<sup>16–18</sup> It was found from their solution properties that these double-cylinder-type copolymer brushes were molecularly dissolved in a dilute solution and took geometrically anisotropic conformation, such as a cylinder with an increasing aspect ratio. Matyjaszewski and coworkers<sup>19</sup> and Müller and coworkers<sup>20</sup> have also synthesized the double-cylinder-type copolymer brushes by the *grafting from* approach, with atom transfer radical polymerization (ATRP). We have also established a preparation method of double-cylinder-type copolymer brushes by *grafting from* photoinduced ATRP of multifunctional polystyrene (PSDC) having *N,N*-diethyldithiocarbamate (DC) pendant groups with vinyl monomers [first monomer, *t*-butyl methacrylate; second monomer, styrene or methyl methacrylate (MMA)].<sup>21</sup> On the basis of the earlier experimental results, we speculate that the rigid nanocylinders will be able to construct by crosslinking of internal cylindrical domains of functionalized double-cylinder-type copolymer brushes.

In this article, we synthesized the double-cylinder-type copolymer brushes by photoinduced ATRP of PSDC having DC pendant groups with vinyl

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monomers [*t*-butyl acrylate (BA) and MMA] under UV irradiation. Subsequently, we derived to functionalize double-cylinder-type copolymer brushes [grafted chain: polyacrylic acid (PAA)-*block*-poly(methyl methacrylate) (PMMA)] by hydrolysis of poly(*t*-butyl acrylate) (PBA) blocks. Internal PAA cylindrical domains were crosslinked in tetrahydrofuran (THF), with ethylenediamine (EDA) and *N,N'*-dicyclohexyl carbodiimide as the crosslinking reagents. We studied the solution properties and morphology of these crosslinked copolymer brushes in detail.

## EXPERIMENTAL

### Materials

Inimer 4-vinylbenzyl *N,N*-diethyldithiocarbamate (VBDC) was synthesized by the reaction of *p*-chloromethylstyrene (Seimi Chemical Industry, Tokyo, Japan) with *N,N*-diethyl-dithiocarbamate sodium salt (DC; Tokyo Kasei Organic Chemicals, Tokyo, Japan) in acetone. Details concerning the synthesis and purification of VBDC have been given elsewhere.<sup>22</sup> Methyl methacrylate (MMA), *t*-butyl acrylate (BA), styrene (Tokyo Kasei Organic Chemicals) were distilled under high vacuum. 2,2'-Azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70; Wako Pure Chemical Industries, Tokyo, Japan), basic aluminium oxide (Merck, Frankfurt, Germany), tributyltin hydride [(Bu)<sub>3</sub>SnH; Aldrich, Milwaukee, WI], CuCl, bipyridine (bpy), tetrahydrofuran (THF), dioxane, methanol, *N,N*-dimethylformamide (DMF), formic acid, and hydrochloric acid (HCl; Tokyo Kasei Organic Chemicals) were used as received.

### Synthesis of PSDC

PSDC was prepared by free-radical copolymerization of VBDC and styrene (1 : 1 equiv) initiated by V-70 (3 wt % for monomer) in THF at 35°C for 2 days in a dark room. Subsequently, the polymer recovered was fractionated with a THF-methanol system. The content of DC groups (50 mol %) was determined from the integration ratio of the aromatic protons ( $\delta$  6.11–7.20 ppm) of polystyrene (PS) to methylene protons (3.68 and 4.00 ppm) of the DC groups by a <sup>1</sup>H NMR spectrum (500 MHz, JEOL GSX-500 NMR spectrometer in CDCl<sub>3</sub>).

### Synthesis of double-cylinder-type copolymer brushes by photoinduced ATRP

The synthesis route for double-cylinder-type copolymer brushes is outlined in Scheme 1. ATRP operations were carried out in a sealed glass apparatus under high vacuum and UV irradiation (250 W high-pressure mercury lamp, Ushio Denki SXUI 250 HAMQ, Tokyo, Japan; UV intensity 42 mW/cm<sup>2</sup>,

irradiation distance 15 cm). We used higher intensity of UV-lamp to speed-up the reaction, because the propagation rate of photoinduced ATRP was very slow. Typical polymerization conditions for the synthesis of PBA cylinders: PSDC-*graft*-PBA (PBA-C) are as follows. PMAE, BA, CuCl, and bpy ([DC] : [BA] : [CuCl] : [bpy] = 1 : 150 : 1.2 : 2.5, where [DC] indicates DC concentration of PSDC pendant groups) were dissolved in THF (66.7 wt % monomer solution), and the resulting mixture was stirred at room temperature for about 1 h to form a copper complex, CuCl/bpy. After photoinduced ATRP for 10–20 h of UV irradiation, the crude product was recovered by precipitation in water/methanol 1/3 (v/v) containing dilute HCl. The final polymerization mixture was diluted with THF, the solution was filtered through a column filled with aluminium oxide 90 active basic to remove the catalyst, and the polymer was precipitated in excess of the water/methanol mixture and dried *in vacuo* to a constant weight.

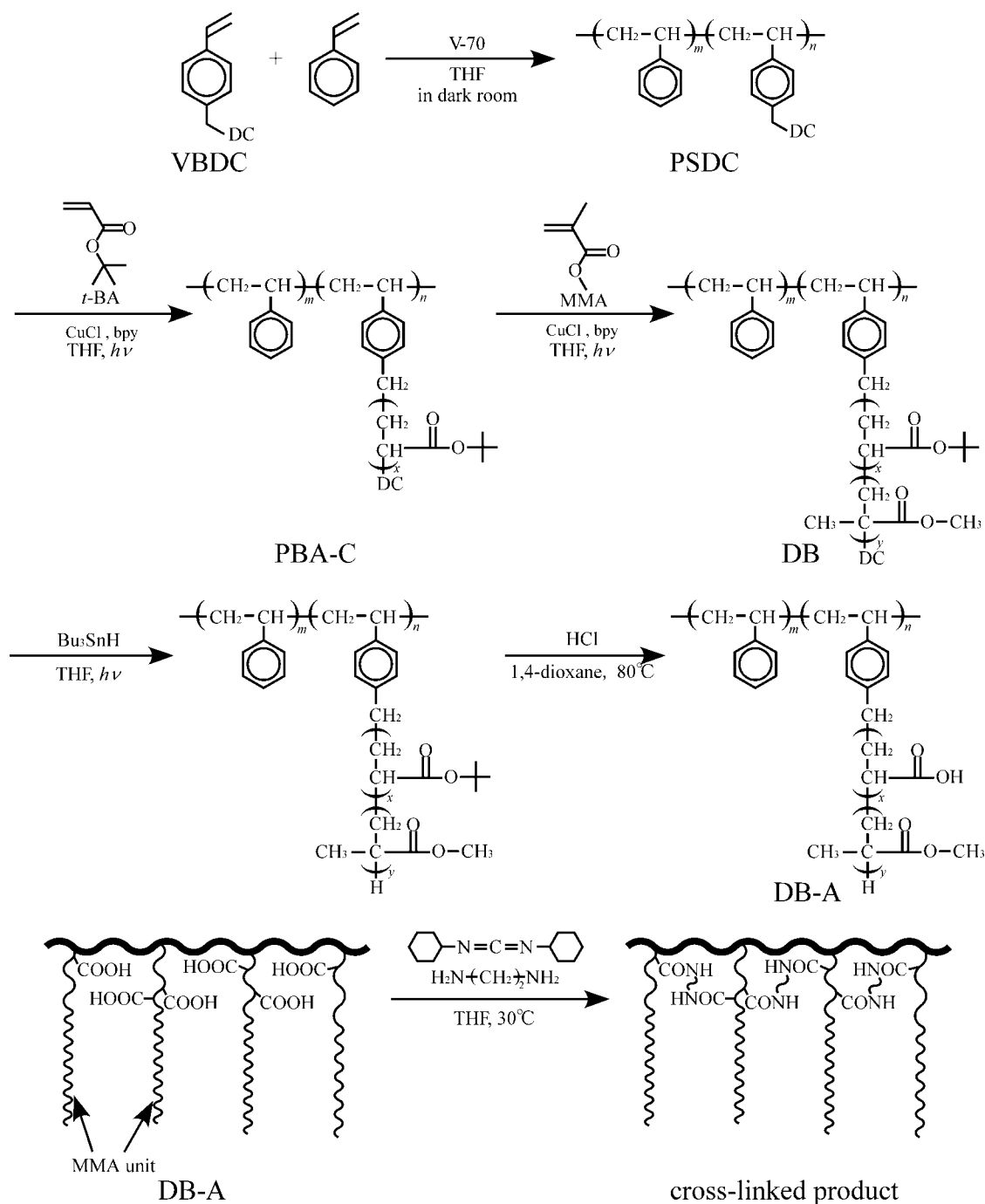
Double-cylinder-type copolymer brushes (DB, grafted chain: PBA-*block*-PMMA) were also synthesized by photoinduced ATRP technique, with PBA-C precursor as a photoinitiator. For example, double-cylinder-type brushes DB were prepared by photopolymerization in THF (66.7 wt % monomer solution) for 20–24 h of UV irradiation under the feed condition: [DC] : [MMA] : [CuCl] : [bpy] = 1 : 300–450 : 1.2 : 2.55, where [DC] indicates DC concentration of PBA-C. After photoinduced ATRP, the crude product was recovered by precipitation in a large excess of methanol. The catalyst was removed by the same column procedure described earlier.

### Reduction of DC groups of double-cylinder-type copolymer brushes

DC groups at grafting chain ends were reduced with (Bu)<sub>3</sub>SnH by radical transfer under 30 min of UV irradiation ([ (Bu)<sub>3</sub>SnH ]/[DC] = 1.2 mol/mol, 0.5 wt % of THF solution). Details concerning reduction have been given elsewhere.<sup>23</sup> Reduction of DC groups was recognized from the disappearance of ethylene protons ( $\delta$  3.68 and 4.00 ppm) of DC groups from <sup>1</sup>H NMR in CDCl<sub>3</sub>.

### Hydrolysis of PBA blocks

Amphiphilic double-cylinder-type copolymer brushes (DB-A, grafted chain: PAA-*block*-PMMA) were obtained by hydrolysis of DB precursors in dioxane at reflux temperature, with an excess of formic acid for 7 h. Details concerning hydrolysis have been given elsewhere.<sup>24</sup> After hydrolysis, the solution was placed in dialysis tubes and dialyzed against distilled water for 2 days and finally freeze-dried. The degree of hydrolysis of PBA chains was determined from the



Scheme 1 Reaction scheme for the synthesis of double-cylinder-type brushes.

disappearance of methyl protons ( $\delta$  1.42 ppm) of *t*-butyl groups by  $^1\text{H}$  NMR in the mixture of  $\text{D}_2\text{O}/\text{DMSO-}d_6$ .

#### Crosslinking of PAA internal cylindrical domains

The copolymer brush (DB-A) and DCCD were dissolved in THF and stirred for 30 min ( $[\text{DCCD}]/[\text{COOH}] = 1.2$  mol/mol, 0.5 wt % of THF solution). Next, EDA was added to this solution and stirred for 3 h at  $35^\circ\text{C}$  ( $[\text{NH}_2]/[\text{COOH}] = 1.0$  mol/

mol). In no case, crosslinked or insoluble materials were observed. After crosslinking, the product was recovered by precipitation with a large excess of methanol.

#### Characterization

The number-average molecular weight ( $M_n$ ) and molecular weight distribution ( $M_w/M_n$ ) of PSDC backbone were determined by gel permeation chromatography (GPC; Tosoh high-speed liquid chromatograph

HLC-8120, Tokyo) using two TSK gel columns, GMH<sub>XL</sub> [excluded-limit molecular weight ( $M_{ELM} = 4 \times 10^8$ )] and G2000H<sub>XL</sub> ( $M_{ELM} = 1 \times 10^4$ ), in series in THF as eluent (flow rate of 1.0 mL/min) at 40°C, using calibration of PS standard samples. The  $M_w/M_n$  of PBA-C and DB brushes were also determined by GPC, using calibration of PMMA standard samples. The  $M_n$  of PBA-C and DB brushes was evaluated from the  $M_n$  of PSDC backbone, and each composition was determined by <sup>1</sup>H NMR.

The hydrodynamic radius ( $R_h$ ) of DB brushes was evaluated using Stokes–Einstein equation from the diffusion coefficient ( $D_0$ ) determined by dynamic light scattering (DLS; Photal TMLS-6000HL: Otsuka Electronics, Tokyo, He-Ne laser:  $\lambda_0 = 632.8$  nm) data with cumulant method in THF or DMF at 25°C (scattering angle of 90°). Sample solutions were filtered through membrane filters with a nominal pore of 0.2  $\mu$ m, just before measurement.

Crosslinking of internal cylindrical domains was recognized from the formation of amido bonds (—NHCO—) by FTIR. FTIR data were recorded on a Shimadzu FTIR-8500 (Kyoto) spectrometer.

## RESULTS AND DISCUSSION

### Synthesis of double-cylinder-type copolymer brushes by photoinduced ATRP

In the previous work,<sup>21</sup> we carried out free-radical homopolymerization of VBDC initiated by V-70. As a result, the probability that a propagating polystyryl radical led to chain transfer was negligible. We obtained the similar result for PSDC synthesis by free-radical copolymerization of VBDC and styrene. The composition of DC groups of PSDC was 50 mol % [from the integration ratio of methylene protons ( $\delta$  3.68 and 4.00 ppm) of the DC groups to the aromatic protons (6.11–7.20 ppm) of PS in <sup>1</sup>H NMR]. This value was identical to the feed monomer ratio. The two monomers (VBDC and styrene) showed almost equal reactivity toward both propagating species, and the copolymer composition was controlled by the feed monomer composition. Characteristics of fractionated PSDC employed in this work are listed in Table I.

**TABLE I**  
Characteristics of PSDC Backbones

Code	$M_n^a$ ( $10^{-4}$ )	$DP_n^b$	$M_w/M_n^a$	DC groups <sup>c</sup> (mol %)
PSDC-1	8.01	485	1.56	50
PSDC-2	10.4	630	1.40	50

<sup>a</sup> Determined by GPC with THF as eluent at 40°C, using calibration of PS standard samples.

<sup>b</sup> Degree of polymerization.

<sup>c</sup> Determined by <sup>1</sup>H NMR in CDCl<sub>3</sub>.

**TABLE II**  
Polymerization Conditions and Results of PBA-C Brushes (PSDC-*graft*-PBA) by Photoinduced ATRP<sup>a</sup>

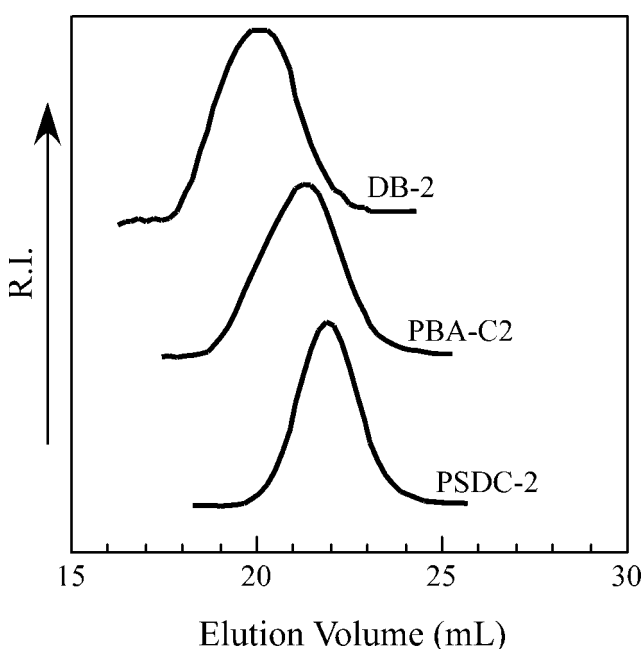
Code	PSDC	Time (h)	PBA-C brushes		
			$M_n^b$ ( $10^{-5}$ )	$M_w/M_n^c$	$DP_n$ of PBA
PBA-C1	PSDC-1	15	2.26	1.69	6
PBA-C2	PSDC-2	20	3.54	1.68	6

<sup>a</sup> Polymerized in THF (66.7 wt % monomer solution) under the feed condition: [DC] : [BA] : [CuCl] : [bpy] = 1 : 150 : 1.2 : 2.5.

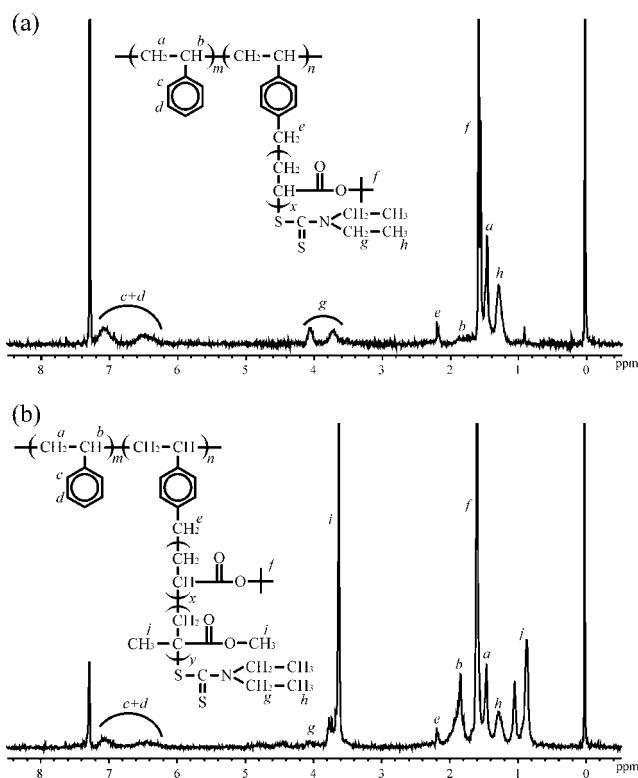
<sup>b</sup> Calculated from  $M_n$  of PSDC backbone and  $DP_n$  of PBA-grafted chains.

<sup>c</sup> Determined by GPC with THF as eluent at 40°C, using calibration of PMMA standard samples.

We performed the PBA-C brush (PSDC-*graft*-PBA) synthesis by photoinduced ATRP of BA, with PSDC as a multifunctional initiator. Reaction conditions and results for PBA-C syntheses are listed in Table II. A typical GPC profile of PBA-C2 is shown in Figure 1. The polymerization of BA occurred, and the GPC curve of PBA-C2 shifts to the high-molecular-weight side compared with that of the PSDC-2 precursor, keeping not only a unimodal distribution but also almost the same polydispersity. The <sup>1</sup>H NMR spectrum also gives support to the PSDC-*graft*-PBA brush having formed ([Fig. 2(a)]. The spectrum displays the expected resonances for aromatic protons (c,d;  $\delta$  6.11–7.20 ppm) of PS and the methylene protons (e; 2.16 ppm) adjacent to the benzene ring, methyl protons (f; 1.58 ppm) of *t*-butyl groups of PBA-grafted chains, and methylene (g; 3.70 and 4.03



**Figure 1** GPC profiles of PSDC-2, PBA-C2, and DB-2 in THF as an eluent at 40°C.



**Figure 2**  $^1\text{H}$  NMR spectra of (a) PBA-C2: PSDC-graft-PBA and (b) DB-2: PSDC-graft-(PBA-block-PMMA) in  $\text{CDCl}_3$ .

ppm) and methyl protons (h; 1.28 ppm) of DC pendant ends. The integration ratio of aromatic protons (c,d) to methylene protons (g) of DC groups was 5 : 4. These results indicate that the PBA-grafted chains had the DC group at the terminal end (the functionality is near unity). Moreover, the methylene protons (4.50 ppm) of benzyl groups adjacent to DC groups (PSDC backbone) shifted completely to e position (2.16 ppm). This means that efficiency of initiation is very high for PBA-C brushes. Table II lists the characteristics of the PBA-C brushes. The  $\text{DP}_n$  of the PBA-grafted chain for PBA-C2 was estimated to be 6 by  $^1\text{H}$  NMR, that is,  $(g/9)/[(c,d)/5]$ . The monomer conversions for PBA-C series were 4–8% from gravimetric method.

Subsequently, the double-cylinder-type brushes [DB; PSDC-graft-(PBA-block-PMMA)] were prepared by similar photoinduced ATRP techniques, with PBA-C precursor as a polyinitiator. Table III listed the polymerization conditions and results for DB syntheses. A typical GPC profile of the copolymerization product DB-2 is also shown in Figure 1. The polymerization of MMA also occurred, and the GPC curve of the DB-2 shifts to the high-molecular-weight side compared with that of the PBA-C2 precursor. Moreover, its GPC curve keeps a unimodal distribution ( $M_w/M_n = 1.61$ ) and becomes narrower than that of the precursor ( $M_w/M_n = 1.68$ ). These results may mean that the DB-2 has a compact structure because of the higher density of branches being composed of double-cylinder domains. The  $^1\text{H}$ -NMR spectrum also gives support to the PSDC-graft-(PBA-block-PMMA) copolymer DB-2 formed [Fig. 2(b)]. This spectrum shows the characteristic signals of the PMMA-grafted chains, that is,  $\alpha$ -methyl (j;  $\delta$  0.92 ppm) and methoxy protons (i; 3.62 ppm) in addition to the signals of the PSDC backbone and PBA inner cylinder chains. The  $\text{DP}_n$  of the PMMA-grafted chain was estimated to be 18 from the composition of the pendant PBA-block-PMMA chain, that is, the integration ratio of the methyl protons (f) of *t*-butyl groups of PBA to the methoxy protons (i) of PMMA. The integration ratio of methoxy protons (i) of PMMA to methyl protons (h) of DC group was 9 : 1. These results also indicate that PMMA-grafted chains had the DC group at each terminal end. Usually, ATRP from acrylate to methacrylate is not a well-defined system, which gives low initiating efficiency. It should be noticed that our photoinduced ATRP overcomes this problem. The monomer conversions for DB series were in the range of 8–13% from gravimetric method.

### Solution properties of double-cylinder-type brushes

To discuss the geometrical anisotropy and intermolecular interaction, we determined the translational diffusion coefficient ( $D_0$ ) of polymer brushes. In gen-

**TABLE III**  
Polymerization Conditions and Results of DB Double-Cylinder-Type Brushes [PSDC-graft-(PBA-block-PMMA)] by Photoinduced ATRP<sup>a</sup>

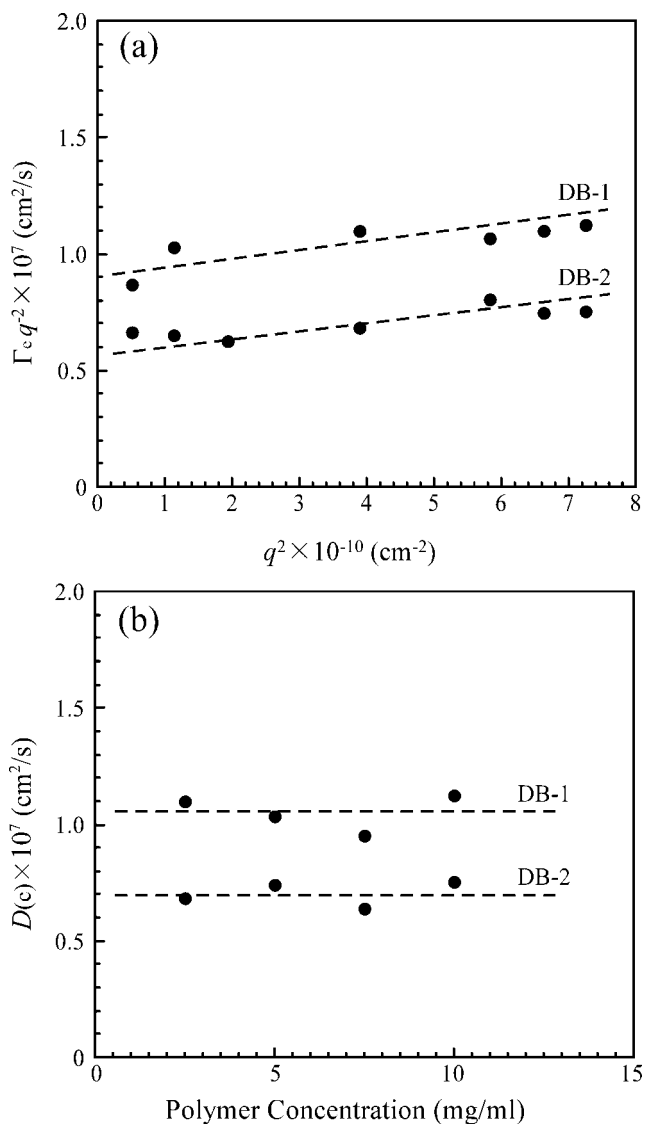
Code	PBA-C	Time (h)	DB brushes				
			$M_n^b(10^{-5})$	$M_w/M_n^c$	$\text{DP}_n$ of PMMA	$D_0^d(10^8\text{cm}^2/\text{s})$	$R_h^d$ (nm)
DB-1	PBA-C1	20	4.13	1.65	8	9.38	21.7
DB-2	PBA-C2	24	9.11	1.61	18	6.29	35.0

<sup>a</sup> Polymerized in THF (66.7 wt % monomer solution) under the feed condition: [DC] : [MMA] : [CuCl] : [bpy] = 1 : 300 : 1.2 : 2.5 for DB-1; [DC] : [MMA] : [CuCl] : [bpy] = 1 : 450 : 1.2 : 2.5 for DB-2 and DB-3.

<sup>b</sup> Calculated from  $M_n$  of PSDC backbone and  $\text{DP}_n$  of PBA- and PMMA-grafted chains.

<sup>c</sup> Determined by GPC with THF as eluent at 40°C, using calibration of PMMA standard samples.

<sup>d</sup> Determined by DLS in THF at 25°C.



**Figure 3** DLS data for DB-2 brush in THF at 25°C; (a) angular dependence  $\Gamma_e q^{-2}$  versus  $q^2$  ( $R_h q < 1$ ) and (b) plot of diffusion coefficient  $D(C)$  against polymer concentration  $C$ .

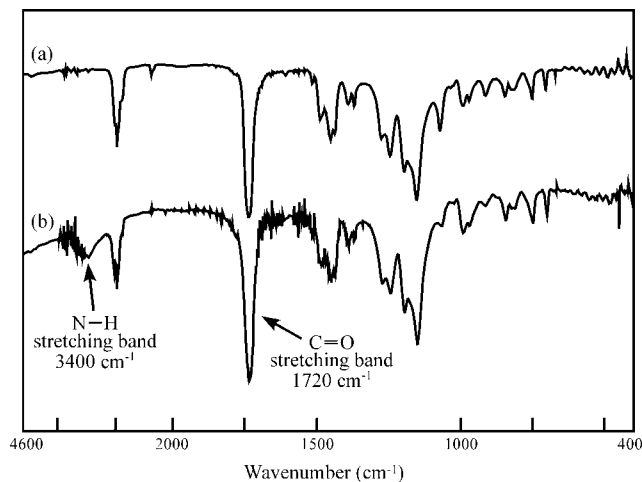
eral, the mutual diffusion coefficient  $D(C)$  is defined as  $D(C) \cong \Gamma_e q^{-2} \theta \rightarrow 0$ , where  $\theta$ ,  $\Gamma_e$ , and  $q$  are the scanning angle, decay rate (the first cumulant), and scattering vector, respectively. Typical angular dependence of  $\Gamma_e q^{-2}$  ( $qR_h < 1$ , where  $R_h$  is hydrodynamic radius) for DB-1 and DB-2 brushes is shown in Figure 3(a). In the case of a spherical shape, it is well known that the slope of the line is zero. It is found that these brushes show somewhat angular dependence. The weak dependence of  $\Gamma_e q^{-2}$  on  $q^2$  shows that there is only a single diffusion mode. Figure 3(b) shows the relationship between the translational diffusion coefficient  $D(C)$  and the polymer concentration  $C$  for DB-1 and DB-2. Each  $D(C)$  has an almost constant value in the range of 2.5–10 mg/mL polymer concentrations. This suggests that these

copolymer brushes form a single molecule in such polymer concentration. The translational diffusion coefficient  $D_0$  can be estimated by extrapolation of the polymer concentration  $C$  to zero. The values of  $D_0$  and  $R_h$  are also listed in Table III.  $R_h$  is defined as the Stokes–Einstein equation:  $R_h = kT/6\pi\eta_0 D_0$ , where  $k$ ,  $T$ , and  $\eta_0$  are the Boltzmann constant, the absolute temperature, and viscosity of the solvent, respectively. Both DB-1 and DB-2 brushes also showed similar solution properties. Because these copolymer brushes were stabilized sterically with densely high-grafted chains, such comb-shaped brushes formed a single molecule in THF.

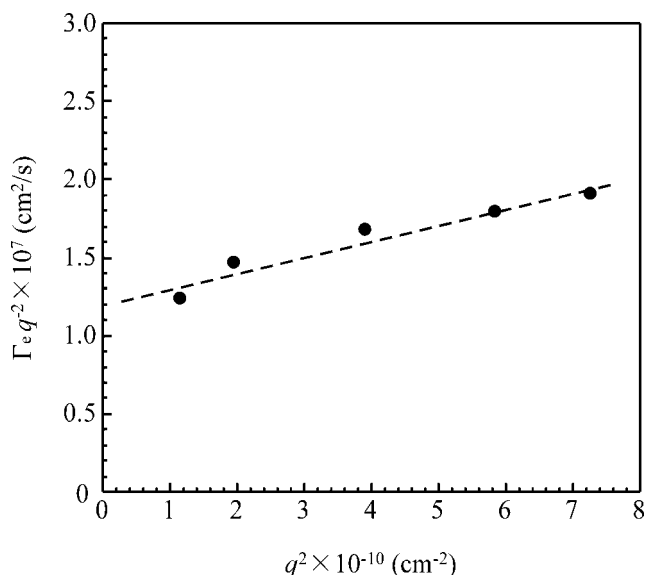
### Reduction of DC groups and hydrolysis of PBA blocks

These copolymer brushes exhibited DC groups at each grafted chain end. The DC groups were reduced with  $(\text{Bu})_3\text{SnH}$ . After reduction, the methylene (g) and methyl protons (h) of DC groups at the grafted chain ends [refer to Fig. 2(b)] disappeared completely from the  $^1\text{H}$  NMR spectra. These results indicated that  $(\text{Bu})_3\text{SnH}$  was one of the most effective reductants for DC groups.

The hydrolysis of PBA blocks was carried out using formic acid.  $^1\text{H}$  NMR spectrum showed the amphiphilic brush structure (DB-A) consisting of PAA internal and PMMA external cylinders. It was found that the peak of *t*-butyl groups (f) of PBA blocks decreased extremely compared with that of the corresponding starting material DB. For example, the hydrolysis of PBA blocks for DB-2 brush achieved 90% from the integration ratio of methyl protons (f) of *t*-butyl groups to methoxy protons (i) of PMMA-grafted chains in such reaction condition [refer to Fig. 2(b)].



**Figure 4** FTIR spectra of (a) DB-A1 and (b) its crosslinked product.



**Figure 5** DLS data for crosslinked product of DB-1A in DMF at 25°C.

### Crosslinking of internal PAA cylindrical domains

Crosslinking of PAA internal cylinders of DB-A1 (degree of hydrolysis of PBA blocks = 100%) was carried out in dilute THF solution, using DCCD and EDA as crosslinking reagents. Insoluble materials were not observed during reaction. This means that crosslinking may occur within the PAA domain of a brush molecule. Figure 4(a,b) shows the FTIR spectra of starting material DB-A1 and its crosslinked product, respectively. After crosslinking of PAA cylinders, new peaks at  $3400 \text{ cm}^{-1}$  due to the  $N-H$  symmetric stretching band and for amide bonds ( $-NHCO-$ ) were observed, in addition to characteristic absorbance of  $C=O$  stretching band ( $1720 \text{ cm}^{-1}$ ). Then, the existence of amide bonds formed by crosslinking was recognized qualitatively.

This crosslinked product was not so soluble in THF. Therefore, DLS measurement was performed in DMF at 25°C. The angular dependence of  $\Gamma_e q^{-2}$  ( $qR_h < 1$ ) for crosslinked product is shown in Figure 5. The crosslinked product also shows angular dependence. The translational diffusion coefficient  $D_0$  was evaluated to be  $1.9 \times 10^{-7} \text{ cm}^2/\text{s}$ . This value was somewhat larger than that of DB-1 precursor ( $D_0 = 9.38 \times 10^{-8} \text{ cm}^2/\text{s}$ ), because the crosslinked product exhibited the rigid nature by crosslinking of internal cylindrical domains.

### CONCLUSIONS

We have explored the scope of the synthetic approach to double-cylinder-type copolymer brushes [PSDC-graft-(PBA-block-PMMA)] with photoinduced ATRP. These brushes exhibited an isotropic conformation. Amphiphilic copolymer brushes [PSDC-graft-(PAA-block-PMMA)] were derived by hydrolysis of PBA blocks. Crosslinking of PAA internal cylinders was carried out in dilute THF solution, using DCCD and EDA as crosslinking reagents. The crosslinked product showed larger  $D_0$  than that of brush precursor because of the rigid nature.

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