

# Synthesis of a Chiral Stationary Phase with Poly[styrene-*b*-cellulose 2,3-bis(3,5-dimethylphenylcarbamate)] by Surface-Initiated Atom Transfer Radical Polymerization and Its Chiral Resolution Efficiency

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**ABSTRACT:** A chiral stationary phase (CSP) with poly[styrene-*b*-cellulose 2,3-bis(3,5-dimethylphenylcarbamate)] was synthesized by the surface-initiated atom transfer radical polymerization (SI-ATRP) of cellulose 2,3-bis(3,5-dimethylphenylcarbamate)-6-acrylate after the SI-ATRP of styrene on the surface of silicon dioxide supports in pyridine. The successful preparation of the CSP with poly[styrene-*b*-cellulose 2,3-bis(3,5-dimethylphenylcarbamate)] was confirmed via Fourier transform infrared spectroscopy, field emission scanning electron microscopy, X-ray photoelectron spectroscopy, elemental analysis, and thermal analysis. The applicability for the chiral resolution of the CSP with poly[styrene-*b*-cellulose 2,3-bis(3,5-diphenylcarbamate)] was evaluated with high-performance liquid

chromatography with 10 racemates under various mobile phases of hexane/alcohol, hexane/tetrahydrofuran (THF), and hexane/chloroform. The results show that the CSP with poly[styrene-*b*-cellulose 2,3-bis(3,5-diphenylcarbamate)] could be used in THF and chloroform as eluents. The chiral resolutions of the commercial Chiracel OD, the CSP with cellulose 2,3-bis(3,5-dimethylphenylcarbamate), and the CSP with poly[styrene-*b*-cellulose 2,3-bis(3,5-dimethylphenylcarbamate)] prepared by SI-ATRP were examined. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 3016–3022, 2011

**Key words:** atom transfer radical polymerization (ATRP); chiral; high performance liquid chromatography (HPLC)

## INTRODUCTION

Atom transfer radical polymerization (ATRP) is a convenient and useful method for synthesizing polymers with well-controlled molecular weights and molecular weight distributions.<sup>1–4</sup> ATRP has been used to synthesize not only linear homopolymers but also many polymers with elaborate architectures, such as block copolymers,<sup>5,6</sup> graft copolymers,<sup>7–9</sup> branched polymers,<sup>10,11</sup> and brush polymers.<sup>12</sup> Graft polymerization via ATRP is a useful method because various functional groups are easily introduced on rigid solid substrates. The rigidity of the solid substrates is a very important factor for column packing materials used in high-performance liquid chromatography (HPLC) because packing materials with soft properties cannot be packed in an HPLC column.

Polysaccharide derivatives with phenylcarbamate groups are known to exhibit high chiral recognition

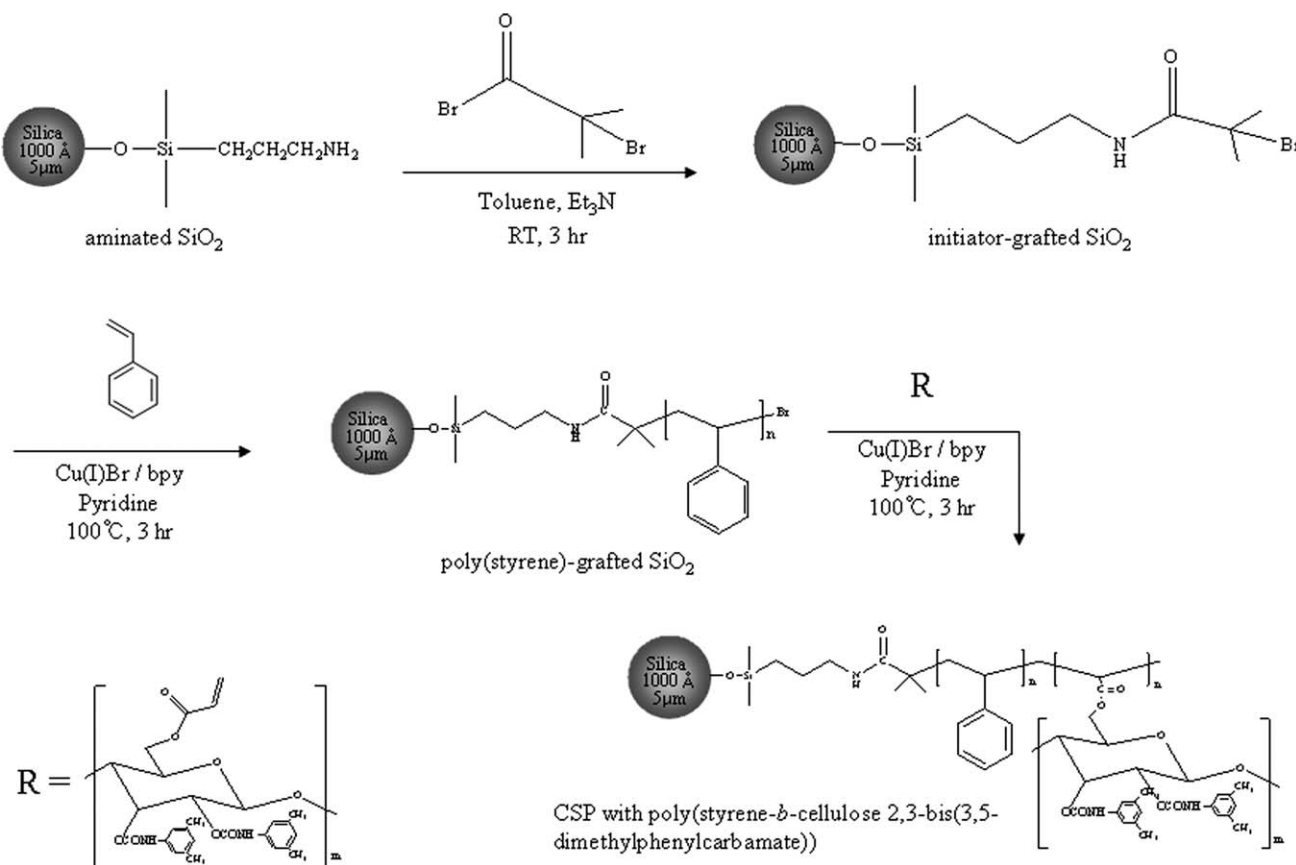
as chiral stationary phases (CSPs)<sup>13–17</sup> for HPLC. Among the polysaccharides with phenylcarbamate derivatives, cellulose 2,3-bis(3,5-dimethylphenylcarbamate) and amylose 2,3-bis(3,5-dimethylphenylcarbamate) have particularly high resolution powers for many racemates. These packing materials based on polysaccharide derivatives have long been prepared with a physical coating method on silicon dioxide (SiO<sub>2</sub>) supports. However, polar solvents, such as tetrahydrofuran (THF) and chloroform, cannot be used as eluents because polysaccharide derivatives are soluble in those polar organic solvents.

To improve upon this defect, several immobilization methods of polysaccharide derivatives have been examined by Okamoto and coworkers.<sup>18–23</sup> Immobilization methods have been applied to the radical polymerization of vinylated polysaccharide derivatives and vinylated SiO<sub>2</sub> supports with 2,2'-azobisisobutyronitrile as an initiator. This immobilization method has posed challenges because of its low immobilization efficiency because radical polymerization is performed on a solid surface at high temperature.

In a previous study,<sup>24</sup> we performed the surface-initiated atom transfer radical polymerization (SI-ATRP) of glycidyl methacrylate on the surface of Wang resin and SiO<sub>2</sub> as supports. Subsequently, the metal ions

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**Figure 1** Synthesis of a novel CSP with poly[styrene-*b*-cellulose 2,3-bis(3,5-dimethylphenylcarbamate)] prepared by SI-ATRP (RT = room temperature).

(Zr<sup>4+</sup>, Fe<sup>3+</sup>, and Pd<sup>2+</sup>) were introduced onto the Wang resin and SiO<sub>2</sub> surface after phosphonation of the epoxy group in the grafted poly(glycidyl methacrylate). Affinities appeared on the Zr<sup>4+</sup>-ion-immobilized stationary phase when we performed the isolation of phosphonated casein and casein.

We prepared the CSP by SI-ATRP of cellulose 2,3-bis(3,5-dimethylphenylcarbamate) with a vinyl group of the 6-position glucose unit on the surface of SiO<sub>2</sub> supports in pyridine.<sup>25–27</sup> We also tested the chiral resolution by HPLC using 10 racemates under various mobile phases of hexane/2-propanol, hexane/THF, and hexane/chloroform. As a result, the CSP prepared by SI-ATRP could be used in THF and chloroform as eluents.

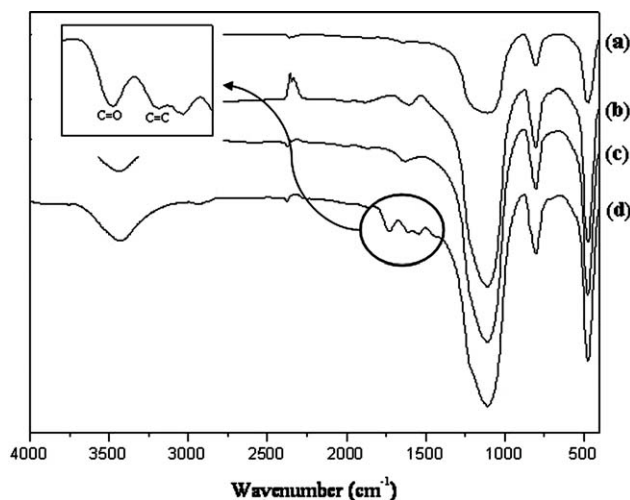
In this study, we prepared a CSP with poly[styrene-*b*-cellulose 2,3-bis(3,5-dimethylphenylcarbamate)] by SI-ATRP with polystyrene on the surface of SiO<sub>2</sub> supports to obtain a hydrophobic CSPs for chiral HPLC application. The prepared CSP was evaluated via Fourier transform infrared (FTIR) spectroscopy, field emission scanning electron microscopy, X-ray photoelectron spectroscopy (XPS), elemental analysis (EA), and thermal analysis. The chiral resolution of the prepared CSP was performed with 10 model racemates under various mobile

phases of hexane/alcohol, hexane/THF, and hexane/chloroform. Furthermore, the chiral resolution of the commercial Chiracel OD, the CSP with cellulose 2,3-bis(3,5-dimethylphenylcarbamate), and the prepared CSP with poly[styrene-*b*-cellulose 2,3-bis(3,5-dimethylphenylcarbamate)] by SI-ATRP was examined for 10 model racemates.

## EXPERIMENTAL

### Chemicals

Cellulose (Avicel; degree of polymerization ≈ 200) was obtained from Merck (Seoul, Republic of Korea). 2-Bromoisobutyryl bromide, triethylamine (Et<sub>3</sub>N), triphenylmethyl chloride, 3,5-dimethylphenyl isocyanate, acryloyl chloride, copper(I) bromide (CuBr), styrene, and 2,2'-bipyridine (bpy; 99%) were purchased from Sigma-Aldrich. The dehydrated solvents, such as pyridine and toluene, were also purchased from Sigma-Aldrich. The macroporous silica gel (Daiso gel SP-100, with a 100-nm pore size and a 5-μm particle size) was purchased from Daiso Chemical (Japan). The solvents used in the chromatographic experiments were HPLC grade. The racemates were purchased from Sigma-Aldrich and TCI Co. (Japan).



**Figure 2** FTIR spectra of (a) aminated SiO<sub>2</sub>, (b) initiator-grafted SiO<sub>2</sub>, (c) polystyrene-grafted SiO<sub>2</sub>, and (d) a CSP with poly[styrene-*b*-cellulose 2,3-bis(3,5-dimethylphenylcarbamate)] prepared by SI-ATRP.

### Synthesis of cellulose 3,5-dimethylphenylcarbamate with a vinyl group

The cellulose derivatives with the vinyl group cellulose 2,3-bis(3,5-dimethylphenylcarbamate)-6-methacrylate were prepared according to Bae et al.<sup>25</sup> Specifically, cellulose (3.00 g) was reacted with a large excess of triphenylmethyl chloride (10.32 g) to form a trityl ether only at position 6 of the hydroxyl group in pyridine (60 mL) at 90°C for 24 h. Subsequently, the reaction mixture precipitated in a large amount of methanol solution and formed a white powder. Next, we obtained cellulose derivatives by the reaction of trityl ether modified cellulose and an excess of 3,5-dimethylphenyl isocyanate (9.55 g) in pyridine (60 mL) at 90°C for 24 h. The cellulose derivatives with 6-position hydroxyl groups were synthesized by suspension in a large excess of methanol containing a small amount of hydrochloric acid to remove the trityl group at room temperature for 24 h. To introduce the vinyl group, the cellulose derivatives with 6-position hydroxyl groups were reacted with acryloyl chloride (1.02 mmol) in pyri-

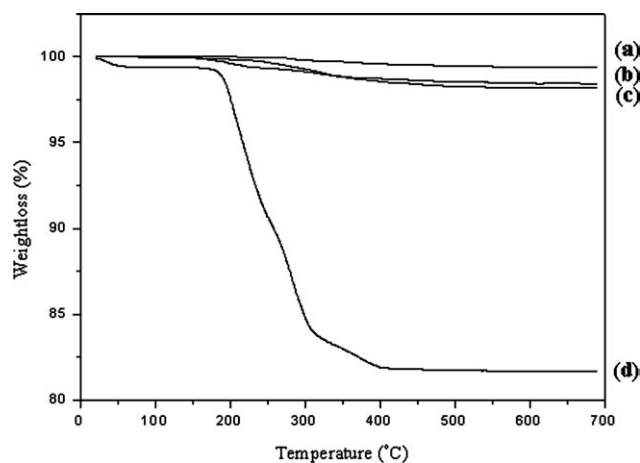
dine at 80°C for 12 h. Then, the solution was precipitated in a large amount of methanol, and insoluble fractions were collected by centrifugation. As a result, we obtained cellulose 2,3-bis(3,5-dimethylphenylcarbamate)-6-methacrylate with a 6-position vinyl group.

### Synthesis of the CSP with poly[styrene-*b*-cellulose 2,3-bis(3,5-dimethylphenylcarbamate)] via SI-ATRP

Figure 1 shows the synthesis procedure of a CSP with poly[styrene-*b*-cellulose 2,3-bis(3,5-dimethylphenylcarbamate)] on the surface of the aminated SiO<sub>2</sub> supports. First, the initiator-grafted SiO<sub>2</sub> was obtained by reaction of the aminated SiO<sub>2</sub> and 2-bromoisobutyryl bromide as follows: aminated SiO<sub>2</sub> (1.75 mmol) was added to toluene (30 mL) containing Et<sub>3</sub>N (7.0 mmol), and then, the polymerization initiator 2-bromoisobutyryl bromide (3.5 mmol) was added, drop by drop, into the solution containing aminated SiO<sub>2</sub> at 0°C under nitrogen. The mixture was left at 0°C for 1 h and at room temperature for 2 h. Afterward, the solution was filtered, and the collected initiator-grafted SiO<sub>2</sub> was thoroughly washed with toluene and methanol several times and then dried *in vacuo*. Second, the polystyrene-grafted SiO<sub>2</sub> was prepared by SI-ATRP of styrene (0.3 g) on the initiator-grafted SiO<sub>2</sub> (3.0 g) with bpy (4.0 mmol) and CuBr (2.0 mmol) in pyridine (20 mL) at 100°C for 3 h under nitrogen.<sup>27</sup> The CSP with poly[styrene-*b*-cellulose 2,3-bis(3,5-dimethylphenylcarbamate)] was prepared by SI-ATRP of the cellulose 2,3-bis(3,5-dimethylphenylcarbamate)-6-methacrylate (0.75 g) on the polystyrene-grafted SiO<sub>2</sub> supports (3.0 g) with bpy (4 mmol) and CuBr (2 mmol) in pyridine (20 mL) at 100°C for 3 h under nitrogen. The reaction mixture was poured into a large excess of methanol for precipitation, centrifuged at 3000 rpm for 10 min, and then washed thoroughly with methanol and THF several times to remove unreacted cellulose derivatives and catalyst residues. The precipitate was dried *in vacuo* overnight.

**TABLE I**  
XPS Surface Compositions of the Aminated SiO<sub>2</sub>, Initiator-Grafted SiO<sub>2</sub>, Polystyrene-Grafted SiO<sub>2</sub>, and CSP with Poly[styrene-*b*-cellulose 2,3-bis(3,5-dimethylphenylcarbamate)] Prepared by SI-ATRP

	Elemental surface compositions determined by XPS (atom %)				
	C1s	O1s	N1s	Si2p	Br3d
Aminated SiO <sub>2</sub>	23.5	42.3	1.39	32.8	—
Initiator-grafted SiO <sub>2</sub>	26.8	43.4	1.53	27.9	0.31
Polystyrene-grafted SiO <sub>2</sub>	25.9	43.3	1.80	28.6	0.20
CSP with poly[styrene- <i>b</i> -cellulose 2,3-bis(3,5-dimethylphenylcarbamate)]	46.5	35.1	2.05	16.3	—



**Figure 3** TGA curves of (a) aminated SiO<sub>2</sub>, (b) initiator-grafted SiO<sub>2</sub>, (c) polystyrene-grafted SiO<sub>2</sub>, and (d) a CSP with poly[styrene-*b*-cellulose 2,3-bis(3,5-dimethylphenylcarbamate)] prepared by SI-ATRP.

### Column packing

The resulting CSP was suspended in a hexane/2-propanol (90/10, v/v) mixture and packed in a stainless-steel column (25 × 0.46 cm i.d.) at 300–400 kg/cm<sup>2</sup> with hexane/2-propanol (90/10) by a slurry packing method for use in HPLC.

### Instrumentation

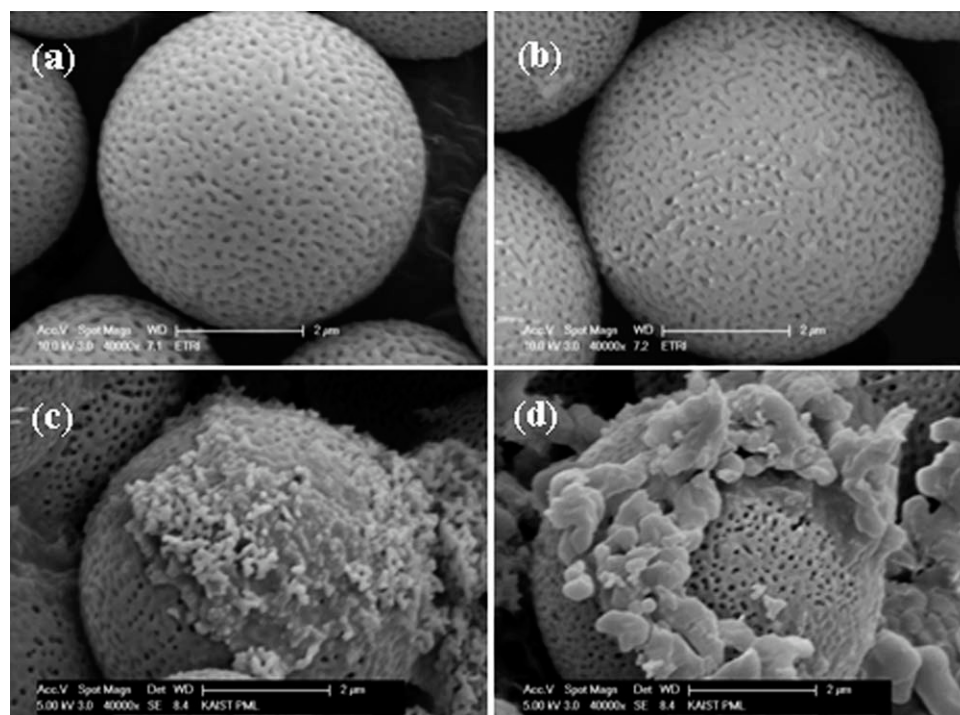
The surface morphology of the samples was determined by field emission scanning electron micros-

copy (S-4800, Hitachi Science System, Ltd., Tokyo, Japan). FTIR spectra were recorded in the range 400–4000 cm<sup>-1</sup> with a 4-cm<sup>-1</sup> resolution from KBr pellets on a PerkinElmer Spectrum 1000 system (PerkinElmer Life and Analytical Sciences). The X-ray photoelectron spectra of the samples were obtained with a Thermo Fisher Scientific instrument (MultiLab ESCA2000). Thermal analysis of the samples was determined with a thermogravimetric analyzer (TGA N-1000/1500, SCINCO, Seoul, Republic of Korea). EA of samples was determined with an automatic elemental analyzer (Thermo Fisher Scientific, Flash EA 1112 series). Also, the separation efficiency of the prepared column was determined by HPLC (Agilent, 1100 series) with a UV detector. The resolution condition was as follows: column = 25 × 0.46 cm i.d.; mobile phase = hexane/2-propanol, THF, or chloroform; flow rate = 0.5 mL/min; room temperature; and detector = UV 254 nm.

## RESULTS AND DISCUSSION

### Synthesis of a CSP with poly[styrene-*b*-cellulose 2,3-bis(3,5-dimethylphenylcarbamate)] via SI-ATRP

The cellulose 2,3-bis(3,5-dimethylphenylcarbamate)-6-acrylate with a 6-position vinyl group was synthesized according to the same method as reported by Bae et al.<sup>25</sup> This vinyl group could be polymerized via SI-ATRP on the surface of polystyrene-grafted SiO<sub>2</sub>, shown in Figure 1. Figure 2 shows the



**Figure 4** Scanning electron microscopy images of (a) aminated SiO<sub>2</sub>, (b) initiator-grafted SiO<sub>2</sub>, (c) polystyrene-grafted SiO<sub>2</sub>, and (d) a CSP with poly[styrene-*b*-cellulose 2,3-bis(3,5-dimethylphenylcarbamate)] prepared by SI-ATRP.



TABLE II  
EA of the Aminated SiO<sub>2</sub>, Initiator-Grafted SiO<sub>2</sub>, Polystyrene-Grafted SiO<sub>2</sub>,  
and CSP with Poly[styrene-*b*-cellulose 2,3-bis(3,5-dimethylphenylcarbamate)]  
Prepared by SI-ATRP

	Nitrogen (%)	Carbon (%)	Hydrogen (%)
Aminated SiO <sub>2</sub>	0.54	0.38	0.12
Initiator-grafted SiO <sub>2</sub>	0.41	0.77	0.14
Polystyrene-grafted SiO <sub>2</sub>	0.41	0.80	0.14
CSP with poly[styrene- <i>b</i> -cellulose 2,3-bis(3,5-dimethylphenylcarbamate)]	1.35	13.3	1.14

FTIR spectra of the aminated SiO<sub>2</sub>, initiator-grafted SiO<sub>2</sub>, polystyrene-grafted SiO<sub>2</sub>, and CSP with poly[styrene-*b*-cellulose 2,3-bis(3,5-dimethylphenylcarbamate)]. The strong absorbance at 1170 cm<sup>-1</sup> was reasonably attributed to the Si—O—Si stretch of silica. In Figure 2(b), the absorption band of 1650 cm<sup>-1</sup> corresponded to the >C=O (carbonyl group) of 2-bromoisobutyryl group, the initiating group, bonded to the silica via the amidation of the surface amine group of aminated silica. The C=O peak shifted to 1680 cm<sup>-1</sup>, and C=C of the aromatic ring in styrene appeared at 1510 cm<sup>-1</sup> due to the formation of polystyrene-grafted SiO<sub>2</sub>, shown in Figure 2(c). The absorption bands at 3420 cm<sup>-1</sup> [ν(NH)] and 1730 cm<sup>-1</sup> [ν(C=O)] became stronger and the peak of C=C divided into two (1650 and 1620 cm<sup>-1</sup>) because of the presence of phenyl groups from styrene and 3,5-dimethylphenylcarbamate of poly[styrene-*b*-cellulose 2,3-bis(3,5-dimethylphenylcarbamate)] prepared by SI-ATRP, shown in Figure 2(d). The results confirm the successful preparation of the CSP for the resolution of the racemates.

Table I lists the XPS surface compositions (percentages) of the aminated SiO<sub>2</sub>, initiator-grafted SiO<sub>2</sub>, polystyrene-grafted SiO<sub>2</sub>, and CSP with poly[styrene-*b*-cellulose 2,3-bis(3,5-dimethylphenylcarbamate)]. The characteristic Br3d value at 70 eV appeared after the surface modification of SiO<sub>2</sub> with 2-bromoisobutyryl bromide. This implied that the bromine was successfully introduced on the surface of the SiO<sub>2</sub> microsphere. On the other hand, after the synthesis of CSP with poly[styrene-*b*-cellulose 2,3-bis(3,5-dimethylphenylcarbamate)], the Br3d value dramatically decreased compared to that of the initiator-grafted SiO<sub>2</sub>. Also, both the N1s value and C1s value gradually increased, whereas both the O1s value and Si2p value gradually decreased. The results suggest that the poly[styrene-*b*-cellulose 2,3-bis(3,5-dimethylphenylcarbamate)] was successfully grafted onto the surface of the SiO<sub>2</sub> microsphere by SI-ATRP.

Figure 3 shows the TGA curves of the aminated SiO<sub>2</sub>, initiator-grafted SiO<sub>2</sub>, polystyrene-grafted SiO<sub>2</sub>, and CSP with poly[styrene-*b*-cellulose 2,3-bis(3,5-dimethylphenylcarbamate)]. A considerable change

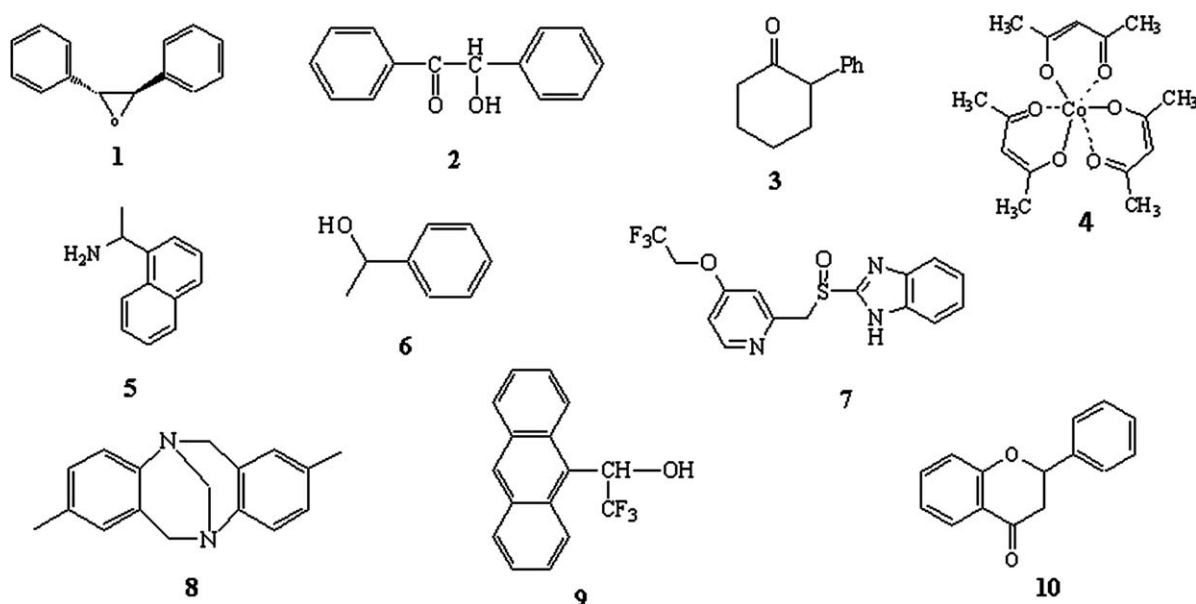
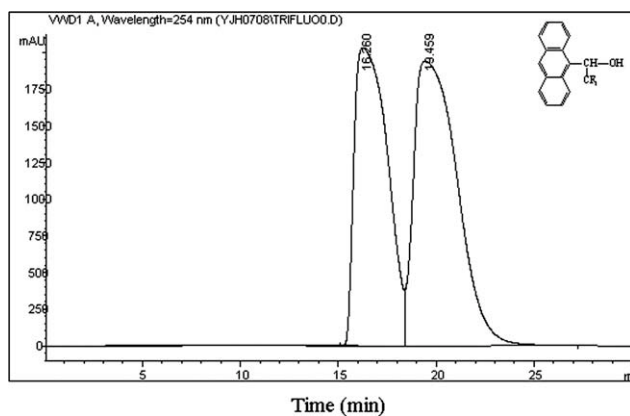


Figure 5 Racemic compounds for the determination of chiral resolution [2 = benzoin; 5 = 1-(1-naphthyl)ethylamine; 6 = DL-sec-phenethyl alcohol; 7 = lansoprazol; 8 = Tröger's base; 10 = flavanone].



**Figure 6** HPLC chromatograms of **9** for the chiral column ( $25 \times 0.46$  i.d.). Flow rate = 0.5 mL/min, eluent = *n*-hexane/2-propanol (90/10), and UV detector = 254 nm.

in the thermal behavior of CSP with poly[styrene-*b*-cellulose 2,3-bis(3,5-dimethylphenylcarbamate)] is shown in Figure 3(d). Weight loss through the degradation of the grafted polymers was seen at 300°C. We considered that the poly[styrene-*b*-cellulose 2,3-bis(3,5-dimethylphenylcarbamate)] was successfully immobilized on the surface of the SiO<sub>2</sub> microsphere with the SI-ATRP technique. The yield was calculated at about 16% by TGA data. As a result, a CSP with poly[styrene-*b*-cellulose 2,3-bis(3,5-dimethylphenylcarbamate)] was successfully synthesized by SI-ATRP.

Figure 4 shows the scanning electron microscopy images of the aminated SiO<sub>2</sub>, initiator-grafted SiO<sub>2</sub>, polystyrene-grafted SiO<sub>2</sub>, and CSP with poly[styrene-*b*-cellulose 2,3-bis(3,5-dimethylphenylcarbamate)]. After the surface modification of the 2-bromoisobutyryl bromide on the surface of the SiO<sub>2</sub> microsphere, the surface morphology of the SiO<sub>2</sub> microsphere was not changed, as shown in Figure 4(b). After the SI-ATRP of styrene, a new particle appeared on the surface of the SiO<sub>2</sub> microsphere, as

shown in Figure 4(c). It appeared that the polystyrene was successfully immobilized on the surface of the SiO<sub>2</sub> microsphere via SI-ATRP. The morphology of the prepared CSP with poly[styrene-*b*-cellulose 2,3-bis(3,5-dimethylphenylcarbamate)] indicated an amorphous structure, as shown in Figure 4(d). The size of poly[styrene-*b*-cellulose 2,3-bis(3,5-dimethylphenylcarbamate)] on the surface of the SiO<sub>2</sub> microsphere was greater than that of polystyrene on the SiO<sub>2</sub> microsphere.

Table II shows the EA of the aminated SiO<sub>2</sub>, initiator-grafted SiO<sub>2</sub>, polystyrene-grafted SiO<sub>2</sub>, and CSP with poly[styrene-*b*-cellulose 2,3-bis(3,5-dimethylphenylcarbamate)] prepared by SI-ATRP. The contents of the cellulose 2,3-bis(3,5-dimethylphenylcarbamate) on the packing materials (CSP) were estimated to be approximately 9.4% by EA (see Table II). FTIR, XPS, TGA, transmission electron microscopy, and EA results from the SI-ATRPs of styrene and cellulose 2,3-bis(3,5-dimethylphenylcarbamate)-6-methacrylate proved the feasibility of polymer grafting strategy for the successful preparation of polystyrene-grafted SiO<sub>2</sub> and the desired final product of CSP.

#### Chiral resolution of the CSP with poly[styrene-*b*-cellulose 2,3-bis(3,5-dimethylphenylcarbamate)] prepared by SI-ATRP

To use a chiral column for the resolution of the racemates, the prepared CSP was packed in stainless steel columns, and the resolution of 10 racemates (see Fig. 5) was performed by HPLC.

Figure 6 shows the chromatogram of the resolution of racemic 2,2,2-trifluoro-1-(9-anthryl) ethanol (**9**; Fig. 5) on the CSP with poly[styrene-*b*-cellulose 2,3-bis(3,5-dimethylphenylcarbamate)]. The (–)-enantiomer was first eluted at retention time  $t_1$  and was followed by the (+)-enantiomer, eluted at retention

**TABLE III**  
Chiral Resolution for the 10 Racemates with the Commercial Chiralcel OD (1), CSP with Cellulose 2,3-Bis(3,5-dimethylphenylcarbamate) (2), and CSP with Poly[styrene-*b*-cellulose 2,3-bis(3,5-dimethylphenylcarbamate)] Prepared by SI-ATRP (3)

Racemate	$t_1$			$t_2$			$\alpha$			$R_s$		
	1	2	3	1	2	3	1	2	3	1	2	3
1	9.00	11.9	8.67	10.7	14.3	9.20	2.67	1.20	1.25	1.02	1.26	1.16
2	1.66	20.7	18.7	18.8	24.7	19.8	1.28	1.62	1.09	0.75	1.40	0.70
3	8.84	15.2	11.3	8.75	16.6	11.9	1.38	1.26	1.14	1.08	0.89	0.92
4	8.84	11.5	10.7	8.81	12.3	11.7	1.22	1.14	1.26	1.58	0.64	1.18
5	ND	10.8	8.66	—	—	8.86	—	—	1.39	—	—	1.17
6	9.58	13.8	9.49	13.8	15.2	—	4.40	1.18	—	1.03	0.70	—
7	ND	14.6	11.1	—	—	12.4	—	—	1.30	—	—	1.31
8	8.08	13.0	10.2	18.9	14.6	11.0	5.68	1.10	1.24	1.07	0.86	1.19
9	29.5	22.4	16.3	40.7	40.6	19.5	4.50	1.82	1.34	2.03	5.42	1.25
10	11.9	16.5	13.0	13.3	18.4	—	2.00	1.12	—	0.75	0.69	—

Eluent = *n*-hexane-2-propanol (90 : 10 v/v), flow rate = 0.5 mL/min, detector = UV 254 nm.

**TABLE IV**  
Effect of the Eluents for Chiral Resolution with the CSP with Poly[styrene-*b*-cellulose 2,3-bis(3,5-dimethylphenylcarbamate)] Prepared by SI-ATRP

Racemate	$\alpha$ values		C
	A	B	
1	1.25	1.35	1.32
3	1.14	1.13	1.08
4	1.26	1.32	1.37

The eluents were (A) hexane/2-propanol (90/10), (B) hexane/CHCl<sub>3</sub> (95/5), and (C) hexane/THF (95/5). Flow rate = 0.5 mL/min; detector = UV 254 nm.

time  $t_2$ . On the basis of the retention times of each enantiomer and the dead time, the capacity factors  $\{k_1' [(t_1 - t_0)/t_0]$  and  $k_2' [(t_2 - t_0)/t_0]\}$  (where  $t_0$  is unretained peak) were estimated to be 1.34 and 1.25, respectively. The separation factor ( $\alpha = [k_2'/k_1']$ ) and resolution factor  $\{Rs = [2(t_2 - t_1)/(w_1 + w_2)]\}$  (where  $w_1$  and  $w_2$  is peak width) were determined to be 1.34 and 1.25, respectively. Table III summarizes the chiral resolution results for the 10 racemates under the mobile phase of the hexane/2-propanol (90/10 v/v) mixture with commercial Chiral OD, CSP with cellulose 2,3-bis(3,5-dimethylphenylcarbamate),<sup>25</sup> and CSP with poly[styrene-*b*-cellulose 2,3-bis(3,5-dimethylphenylcarbamate)]. As shown in Table III,  $\alpha$  of the prepared CSP with poly[styrene-*b*-cellulose 2,3-bis(3,5-dimethylphenylcarbamate)] was lower than that of the commercial Chiral OD because a smaller amount of the chiral selector was used for the prepared CSP compared to the commercial Chiral OD.

As mentioned earlier, traditionally coated CSPs have a challenge because of their solubility in some solvents, such as chloroform and THF. The selection of suitable eluents is very important for improving chiral resolution. Consequently, we also tested the chiral resolution under various mobile phases of hexane/2-propanol, hexane/THF, and hexane/chloroform. Table IV shows the chiral resolution results on the immobilized CSP prepared by SI-ATRP with the addition of THF and chloroform in the mobile phase. The chiral resolution ability of racemic *trans*-stilbene oxide (**1**; Fig. 5) and racemic cobalt(III) trisacetylacetonate (**4**; Fig. 5) increased when hexane/CHCl<sub>3</sub> (95/5) was used over hexane/2-propanol (90/10) as the mobile phase. Also, the chiral resolution through racemic 2-phenylcyclohexanone (**3**; Fig. 5) decreased when hexane/THF (95/5) and hexane/CHCl<sub>3</sub> (95/5) were used over hexane/2-propanol (90/10) as the mobile phase. The results suggest that this CSP with poly[styrene-*b*-cellulose 2,3-bis(3,5-dimethylphenylcarbamate)] prepared by SI-ATRP was very stable and useful, even when THF and chloroform were used as the mobile phases. The SI-ATRP method was an effective method for the preparation of immobilization-type chiral columns for HPLC.

## CONCLUSIONS

A CSP with poly[styrene-*b*-cellulose 2,3-bis(3,5-dimethylphenylcarbamate)] was efficiently synthesized with SI-ATRP. The preparation of the chiral material was achievable, and considerably high column efficiency was observed for the resolution of the test enantiomers. In addition, the prepared CSP with poly[styrene-*b*-cellulose 2,3-bis(3,5-dimethylphenylcarbamate)] was very stable with the addition of some solvents, such as THF and chloroform, to the mobile phase. This made it possible to extend the application range on the prepared CSP for the resolution of enantiomers.

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