

## Comparison Study of a Chiral Stationary Phase Based on Cellulose Derivatives prepared by “Grafting from” and “Grafting to” Methods

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**ABSTRACT:** Chiral stationary phase (CSP) with cellulose derivatives was synthesized using the “grafting from” and “grafting to” methods. The “grafting to” method involves the bonding of a preformed end-functionalized polymer to reactive surface amine groups on the silica gel. The “grafting from” involves the immobilization of initiator onto the aminated silica gel followed by atom transfer radical polymerization (ATRP) to generate the chiral polymer chains. The successful preparation of the CSP with cellulose derivatives prepared by ATRP was confirmed by FE-SEM, XPS, EA, and thermal analysis. The chiral resolution of the CSP with cellulose derivatives was evaluated by high-performance liquid chromatography using 10 racemates with various mobile phases that consisted of hexane/alcohol, hexane/THF, and hexane/chloroform. Furthermore, the CSP with cellulose derivatives prepared by “grafting from” and “grafting to” were compared and discussed. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**KEYWORDS:** chiral stationary phase; cellulose derivatives; atom transfer radical polymerization; grafting from; grafting to; chiral resolution

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### INTRODUCTION

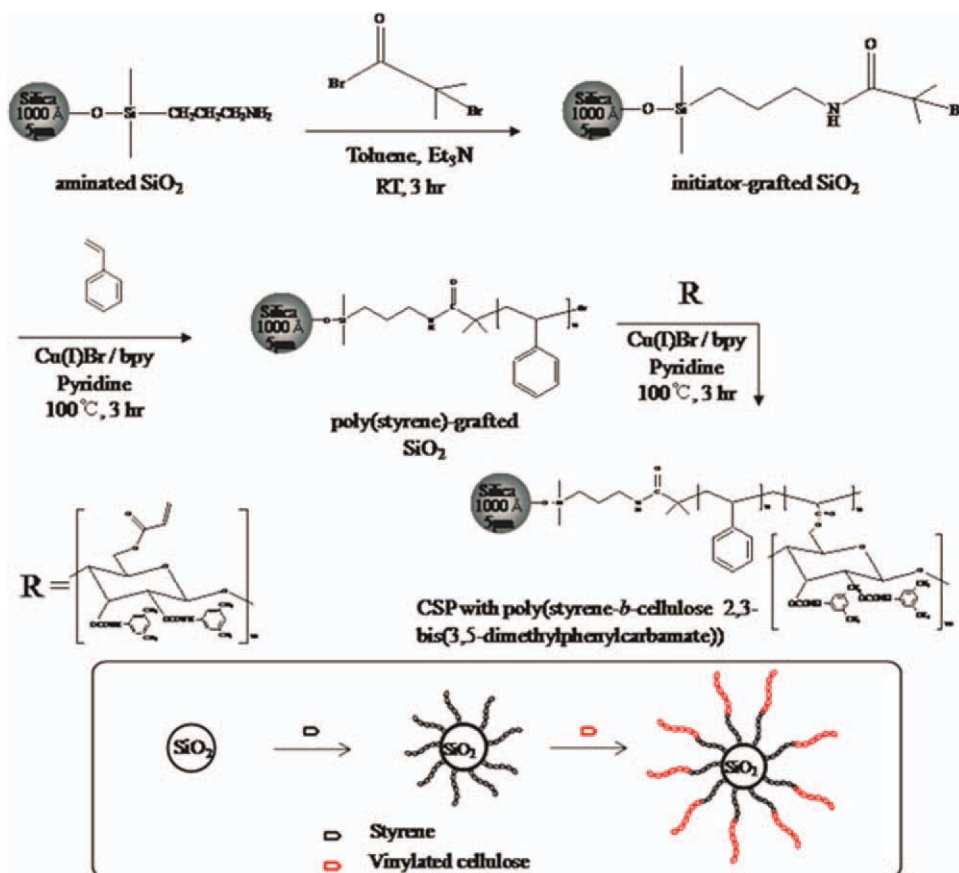
Atom transfer radical polymerization (ATRP) is a convenient and useful method for synthesizing polymers with well-controlled molecular weight and molecular weight distributions.<sup>1–4</sup> Not only linear homopolymers, but also many polymers with elaborate architectures, such as block copolymers,<sup>5,6</sup> graft copolymers,<sup>7–9</sup> branched polymers,<sup>10,11</sup> and brush polymers,<sup>12</sup> have been synthesized by ATRP. The ATRP process uses an alkyl halide as the initiator and metals in lower oxidation states with complexing ligands. The process involves the successive transfer of the halide from the dormant polymer chain to the liganded metal complex, thus establishing a dynamic equilibrium between active and dormant species.

The graft polymerization via ATRP is a highly useful method because various functional groups can be easily introduced onto solid substrates with rigid properties.<sup>13–16</sup> The rigidity of the solid substrates is a very important factor in regards to their use as column packing materials for high-performance liquid chromatography (HPLC), because soft packing material cannot be packed in an HPLC column. The synthesis of the packing materials for HPLC by ATRP on solid substrates such as SiO<sub>2</sub> spheres have been examined due to the rigid properties of SiO<sub>2</sub> spheres.

Covalent attachment of polymer chains to the solid substrate surface can be accomplished by either “grafting to” or “grafting from” techniques. “Grafting to” involves the bonding of a preformed end-functionalized polymer to reactive surface groups on the substrate. The “grafting from” technique involves the immobilization of initiators onto the substrate followed by *in situ* surface polymerization to generate the tethered polymer chains.<sup>17</sup>

In a previous study,<sup>18</sup> we prepared chiral stationary phase (CSP) by ATRP of cellulose 2,3-*bis*(3,5-dimethylphenylcarbamate) with a vinyl group at the sixth position on the glucose unit, which was anchored to the surface of the SiO<sub>2</sub> supports in pyridine. We also tested the chiral resolution by HPLC using 10 racemates with various mobile phases that consisted of hexane/2-propanol, hexane/THF, and hexane/chloroform. Based on these experiments, the CSP prepared by ATRP could be eluted using a THF and chloroform solution.

We also prepared the CSP with poly(styrene-*b*-cellulose 2,3-*bis*(3,5-dimethylphenylcarbamate)) by surface initiated-ATRP (SI-ATRP), “grafting from” method, on the surface of SiO<sub>2</sub> supports to obtain a hydrophobic CSP for chiral HPLC applications.<sup>19</sup> We tested the chiral resolution by HPLC using 10 racemates with various mobile phases that consisted of hexane/2-propanol, hexane/THF, and hexane/chloroform. In these



**Figure 1.** Synthesis procedure of a CSP with poly(styrene-*b*-cellulose 2,3-*bis*(3,5-dimethylphenylcarbamate)) prepared by “grafting from” method. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

experiments, the CSP prepared by SI-ATRP could be eluted using a THF and chloroform solution.

In this study, we prepared the CSP with poly(styrene-*b*-cellulose 2,3-*bis*(3,5-dimethylphenylcarbamate)) by ATRP via the “grafting to” method on the surface of SiO<sub>2</sub> supports. This prepared CSP was evaluated by FE-SEM, XPS, EA, and thermal analysis. The chiral resolution of the CSP prepared by the “grafting to” method was performed using 10 model racemates with various mobile phases. Furthermore, the chiral resolution of the commercial Chiracel OD and the CSP with poly(styrene-*b*-cellulose 2,3-*bis*(3,5-diphenylcarbamate)) prepared by the “grafting from” and “grafting to” method was examined for 10 model racemates.

## EXPERIMENTAL

### Chemicals

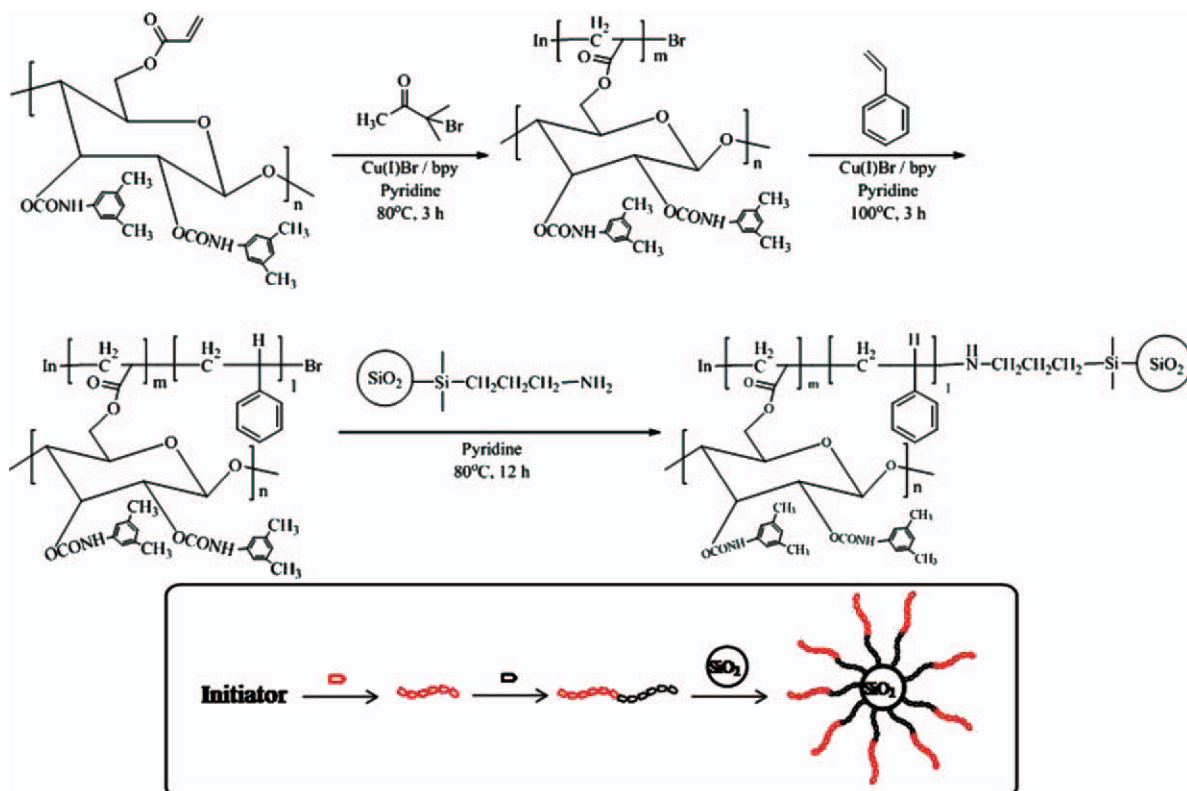
Cellulose (Avicel; degree of polymerization  $\sim 200$ ) was obtained from Merck (Korea). 2-Bromoisobutyryl bromide, triphenylmethyl chloride, 3,5-dimethylphenyl isocyanate, acryloyl chloride, copper(I) bromide (CuBr), styrene, and 2,2'-bipyridine (bpy, 99%) were purchased from Sigma-Aldrich (USA). 3-Bromo-3-methyl-2-butanone was purchased from TCI (Japan). The dehydrated solvents, such as pyridine and toluene, were also purchased from Sigma-Aldrich (USA). The macroporous silica gel (Daiso gel SP-100, with 100 nm pore size and 5 mm particle size) was pur-

chased from Daiso Chemical (Japan). The solvents used in the chromatographic experiments were HPLC-grade. The racemates were purchased from Sigma-Aldrich (USA) and TCI (Japan).

### Synthesis of a CSP Based on Cellulose Derivatives Via “Grafting from” and “Grafting to” Method

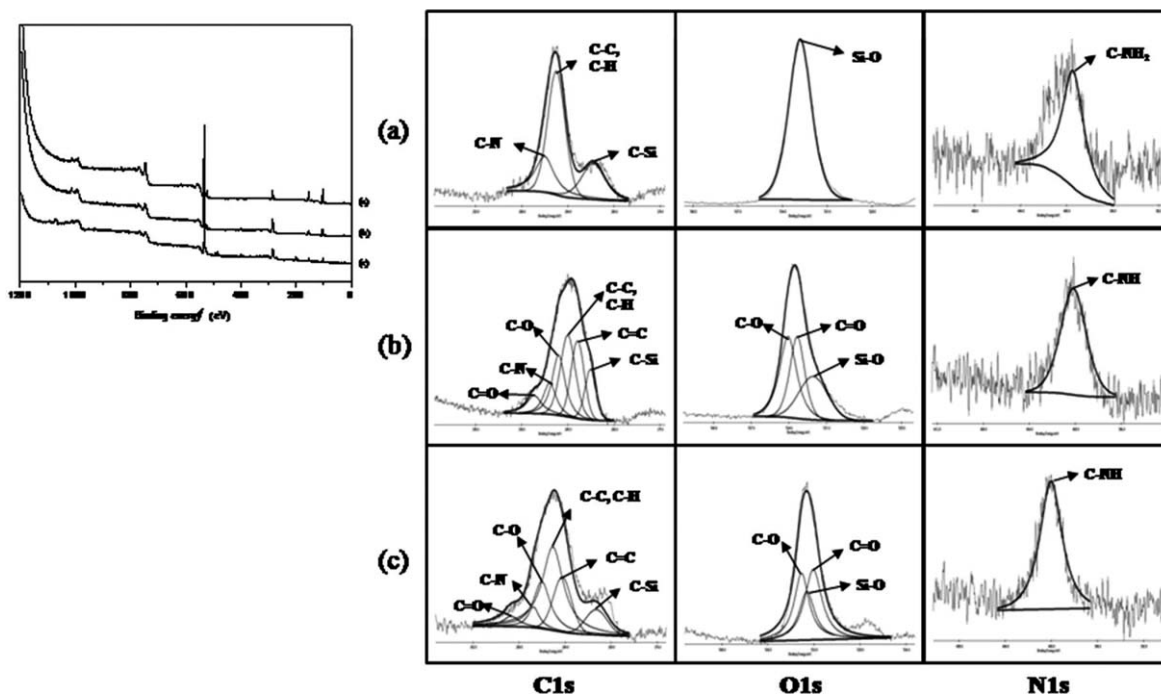
The cellulose 2,3-*bis*(3,5-dimethylphenylcarbamate)-6-acrylate, which contained a vinyl group at the sixth position, was synthesized using the same method described by Bae et al.<sup>18</sup> Figure 1 shows the procedure used to synthesize the CSP based on cellulose derivatives via the “grafting from” method.<sup>19</sup> Figure 2 shows the procedure used to synthesize the CSP based on cellulose derivatives via the “grafting to” method on the surface of the aminated SiO<sub>2</sub> supports.

The poly(cellulose 2,3-*bis*(3,5-dimethylphenylcarbamate)) was first synthesized by ATRP of cellulose 2,3-*bis*(3,5-dimethylphenylcarbamate)-6-acrylate (2.0 g) and 3-bromo-3-methyl-2-butanone (3.5 mmol) using bpy (4.0 mmol) and CuBr (2.0 mmol) in pyridine (60 mL) at 80 °C for 3 h under nitrogen. The reaction mixture was poured into a large excess of methanol for precipitation and centrifuged at 3000 rpm for 10 min, and then washed thoroughly with methanol and pyridine several times to remove unreacted cellulose derivatives and catalyst residue. Fourier transform infrared (FTIR) (KBr): 3407 (N-H); 1726 (C=O); 1060 (C-O); 1586, 1524 cm<sup>-1</sup> (phenyl).



**Figure 2.** Synthesis procedure of a CSP with poly(styrene-*b*-cellulose 2,3-*bis*(3,5-dimethylphenylcarbamate)) prepared by “grafting to” method. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

Poly(styrene-*b*-cellulose 2,3-*bis*(3,5-dimethylphenylcarbamate)) was then synthesized from poly(cellulose 2,3-*bis*(3,5-dimethylphenylcarbamate)) (1.5 g) and styrene (0.6 g, 5.8 mmol) using *bpy* (4.0 mmol) and CuBr (2.0 mmol) in pyridine (60 mL) at 100°C for 3 h under nitrogen. The reaction mixture was poured into a large excess of methanol for precipitation and centrifuged



**Figure 3.** XPS survey scan spectra of the aminated SiO<sub>2</sub> (a), CSP with poly(styrene-*b*-cellulose 2,3-*bis*(3,5-dimethylphenylcarbamate)) prepared by “grafting from” method (b) and “grafting to” method (c).

**Table I.** XPS Surface Compositions of the Aminated SiO<sub>2</sub>, CSP with Poly(styrene-*b*-cellulose 2,3-*bis*(3,5-dimethylphenylcarbamate)) Prepared by “Grafting from” and “Grafting to” Method

	Element surface compositions determined by XPS (wt %)			
	C 1s	O 1s	N 1s	Si 2p
Aminated SiO <sub>2</sub>	23.5	42.3	1.39	32.8
Grafting from method	46.5	35.1	2.05	16.3
Grafting to method	46.8	33.8	3.42	15.8

at 3000 rpm for 10 min, and then washed thoroughly with methanol and pyridine several times to remove unreacted cellulose derivatives and catalyst residue. FTIR (KBr): 3403 (N–H); 1721 (C=O); 1031 (C–O); 1591, 1529 cm<sup>-1</sup> (phenyl).

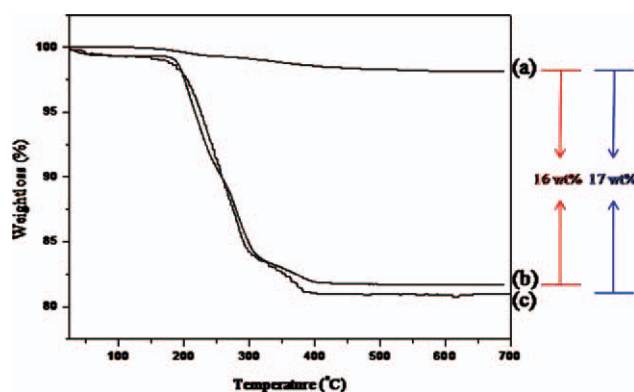
Finally, the CSP was obtained by reacting aminated SiO<sub>2</sub> and poly(styrene-*b*-cellulose 2,3-*bis*(3,5-dimethylphenylcarbamate)) as follows: aminated SiO<sub>2</sub> (4.0 g) was added to pyridine (30 mL) and then poly(styrene-*b*-cellulose 2,3-*bis*(3,5-dimethylphenylcarbamate)) (1.0 g), which was dissolved in a solution of pyridine, was added drop-by-drop into the solution containing aminated SiO<sub>2</sub> under nitrogen. The mixture was left at room temperature for 12 h. Afterward, the solution was filtered and the collected initiator-grafted SiO<sub>2</sub> was thoroughly washed with pyridine and methanol several times and then dried under vacuum overnight. FTIR (KBr): 3398 (N–H); 1730 (C=O); 1591, 1534 (phenyl); 1064 cm<sup>-1</sup> (SiO<sub>2</sub>).

#### 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 a density of 300–400 kg/cm<sup>2</sup> with hexane/2-propanol (90/10) using the slurry packing method for HPLC.

#### Instrumentation

The surface morphology of the samples was analyzed by field-emission scanning electron microscopy (FE-SEM, S-4800, Hitachi Science System, Japan). FTIR spectra were recorded in the range of 400–4000 cm<sup>-1</sup> with a 4 cm<sup>-1</sup> resolution from KBr pel-

**Figure 4.** TGA curves for the aminated SiO<sub>2</sub> (a), CSP with poly(styrene-*b*-cellulose 2,3-*bis*(3,5-dimethylphenylcarbamate)) prepared by “grafting from” method (b) and “grafting to” method (c). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]**Table II.** Elemental Analysis of Aminated SiO<sub>2</sub> and CSP with Poly(styrene-*b*-cellulose 2,3-*bis*(3,5-dimethylphenylcarbamate)) Prepared by “Grafting from” and “Grafting to” Method

	Nitrogen (%)	Carbon (%)	Hydrogen (%)
Aminated SiO <sub>2</sub>	0.54	0.38	0.12
Grafting from method	1.35	13.3	1.14
Grafting to method	1.97	14.4	1.85

lets on a Perkin-Elmer spectrum 1000 system (Perkin-Elmer Life and Analytical Sciences, USA). The X-ray photoelectron spectra of the samples were obtained using Thermo Fisher Scientific, MultiLab ESCA2000, USA. Thermal analysis of the samples was determined using a thermogravimetric analyzer (N-1000/1500, SCINCO, Korea). Elemental analysis of samples was determined with an automatic elemental analyzer (Thermo Fisher Scientific, Flash EA 1112 series, USA). In addition, the separation efficiency of the prepared column was determined by HPLC (Agilent, 1100 series, USA) using a UV detector. The following conditions were used during HPLC: column, 25 × 0.46 cm I.D.; mobile phase, hexane/2-propanol or THF or chloroform flow rate, 0.5 mL/min; room temperature; detector, UV 254 nm.

## RESULTS AND DISCUSSION

### Comparison of a CSP Based on Cellulose Derivatives Prepared by “Grafting from” and “Grafting to” Methods

As described above, the CSPs based on cellulose derivatives were prepared by the “grafting from” method and “grafting to” method as shown in Figures 1 and 2. To compare the CSP property, XPS analysis was performed on a CSP prepared by the “grafting from” method and “grafting to” method. Figure 3 shows the XPS scan spectra of the aminated SiO<sub>2</sub> (a), CSP based on cellulose derivatives prepared by the “grafting from” method (b) and “grafting to” method (c). The poly(styrene-*b*-cellulose 2,3-*bis*(3,5-dimethylphenylcarbamate)) was covalently immobilized onto aminated SiO<sub>2</sub> supports via XPS peak fitting for C, O, and N elements. In C1s peaks, which corresponds to the C–Si fitting peak of aminated SiO<sub>2</sub> [Figure 3(a)], was larger than that of the CSP based on cellulose derivatives prepared by both the “grafting from” method and “grafting to” method [Figure 3(b,c)]. This result indicated that the poly(styrene-*b*-cellulose 2,3-*bis*(3,5-dimethylphenylcarbamate)) was successfully grafted onto the SiO<sub>2</sub> support surface via the “grafting from” method and “grafting to” method.

Table I shows the XPS surface compositions of the aminated SiO<sub>2</sub>, CSP with poly(styrene-*b*-cellulose 2,3-*bis*(3,5-dimethylphenylcarbamate)) prepared by the “grafting from” and “grafting to” method. After the poly(styrene-*b*-cellulose 2,3-*bis*(3,5-dimethylphenylcarbamate)) was grafted, the C and N element composition ratios were increased when compared to that of the aminated SiO<sub>2</sub> supports, while the SiO<sub>2</sub> content was decreased. This results indicated that a CSP with poly(styrene-*b*-cellulose 2,3-*bis*(3,5-dimethylphenylcarbamate)) was successfully synthesized via the “grafting from” method and “grafting to” method, respectively. When the N element composition ratio was





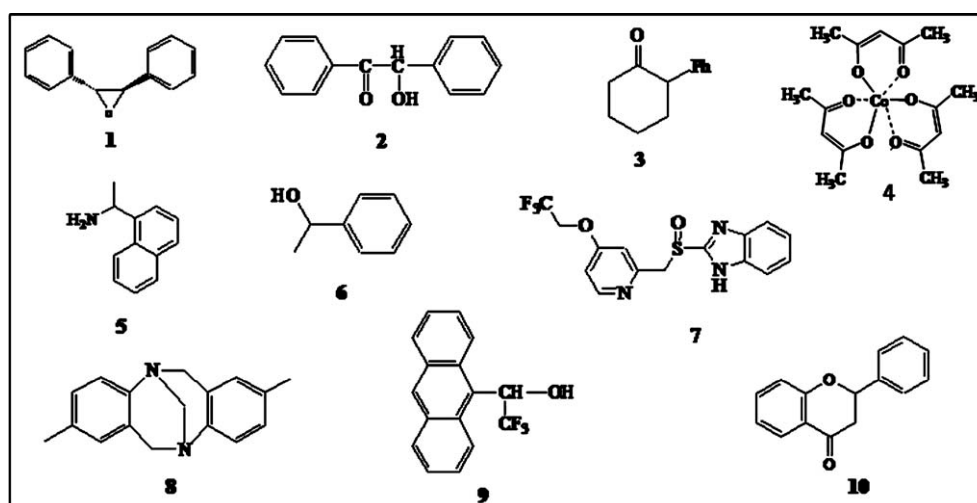
**Figure 5.** SEM images of the aminated SiO<sub>2</sub> (a), CSP with poly(styrene-*b*-cellulose 2,3-*bis*(3,5-dimethylphenylcarbamate)) prepared by “grafting from” method (b) and “grafting to” method (c).

compared, the CSP prepared by the “grafting to” method was found to be larger than that of the CSP prepared by the “grafting from” method. Thus, the “grafting to” method was more effective for the synthesis of CSP with poly(styrene-*b*-cellulose 2,3-*bis*(3,5-dimethylphenylcarbamate)) than the “grafting from” method.

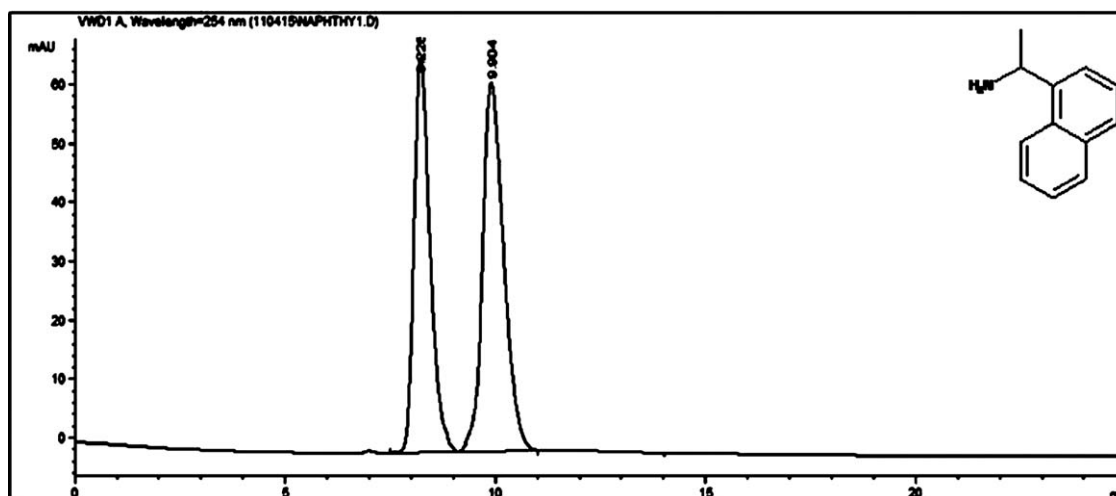
Figure 4 shows the TGA curves for the aminated SiO<sub>2</sub> (a), CSP with poly(styrene-*b*-cellulose 2,3-*bis*(3,5-dimethylphenylcarbamate)) prepared by the “grafting from” method (b) and “grafting to” method (c). Based on the TGA analysis, the grafting yield (average ± SD) of the CSP with poly(styrene-*b*-cellulose 2,3-*bis*(3,5-dimethylphenylcarbamate)) was 16 ± 0.28% and 17 ± 0.14% when prepared by the “grafting from” method and “grafting to” method, respectively. Slightly higher grafting yields were obtained using the “grafting to” method when compared to the “grafting from” method. However, the 1% difference in the weight loss is likely not significant to confirm that the grafting process is more or less efficient, without information concerning the structure of the grafted chains. In this study, the structure of the grafted chain could not be properly discussed due to the limitation of solubility. Since the cellulose derivative used contains acrylate groups on a chain, these groups readily crosslink by radical process to give an insoluble network material.

Table II shows the elemental analysis results of aminated SiO<sub>2</sub> and CSP with poly(styrene-*b*-cellulose 2,3-*bis*(3,5-dimethylphenylcarbamate)) prepared by the “grafting from” and “grafting to” method. The C and N element content (%) of CSP with poly(styrene-*b*-cellulose 2,3-*bis*(3,5-dimethylphenylcarbamate)) prepared by the “grafting to” method was larger than that of the CSP with poly(styrene-*b*-cellulose 2,3-*bis*(3,5-dimethylphenylcarbamate)) prepared by the “grafting from” method (Table II).

Figure 5 shows SEM images of the aminated SiO<sub>2</sub> (a), CSP with poly(styrene-*b*-cellulose 2,3-*bis*(3,5-dimethylphenylcarbamate)) prepared by the “grafting from” method (b) and “grafting to” method (c). The CSP with poly(styrene-*b*-cellulose 2,3-*bis*(3,5-dimethylphenylcarbamate)) prepared by the “grafting from” method and “grafting to” method contained an amorphous pattern as shown in Figure 5(b,c). We expected to observe a core shell structure for the CSP with a core-SiO<sub>2</sub> support and poly(styrene-*b*-cellulose 2,3-*bis*(3,5-dimethylphenylcarbamate)) shell. However, the poly(styrene-*b*-cellulose 2,3-*bis*(3,5-dimethylphenylcarbamate)) was partially grafted on the surface of the SiO<sub>2</sub> supports. This most likely occurred because the amine group of the aminated SiO<sub>2</sub> supports (calculated from XPS analysis, 5.5% N content) method could both be used to prepare CSP with cellulose derivative. Based on the FT-IR, XPS, TGA, TEM, and elemental analysis results, the



**Figure 6.** Racemic compounds for determination of chiral resolution: (1) stilbene oxide, (2) benzoin, (3) 2-phenylcyclohexanone, (4) cobalt(III) tris(acetylacetonate), (5) 1-(1-naphthyl)ethylamine, (6) phenethyl alcohol, (7) lansoprazol, (8) Tröger's base, (9) 2,2,2-trifluoro-1-(9-anthryl) ethanol, and (10) flavanone.



**Figure 7.** HPLC chromatograms of 1-(1-naphthyl)ethylamine (5) for chiral column (25 × 0.46 cm (id)). Flow rate: 0.5 mL/min, eluent: *n*-hexane/2-propanol (90/10), and UV-detector: 254 nm.

“grafting from” method and “grafting to” method could both be used to prepare CSP with cellulose derivatives.

#### Comparison of Chiral Resolution of the CSP Based on Cellulose Derivatives Prepared by “Grafting from” and “Grafting to” Methods

In order to use a chiral column to resolve racemates, the prepared CSP was packed in stainless steel columns and the resolution of 10 racemates (Figure 6) was evaluated by HPLC.

Figure 7 shows the chromatogram of 1-(1-naphthyl)ethylamine (5 in Figure 6) on CSP based on cellulose derivatives. The (–)-enantiomer was first eluted at retention time  $t_1$ , which was followed by the (+)-enantiomer eluted at retention time  $t_2$ . On the basis of the retention times of each enantiomer and

dead time, the capacity factors  $k_1'$  [ $(t_1 - t_0)/t_0$ ] and  $k_2'$  [ $(t_2 - t_0)/t_0$ ] were estimated to be 0.23 and 0.48, respectively. The separation factor,  $\alpha$ , ( $k_2'/k_1'$ ) and resolution factor,  $R_s$ , [ $2(t_2 - t_1)/(w_1 + w_2)$ ] were determined to be 2.09 and 1.52, respectively.

Table III summarizes the chiral resolution results for the 10 racemates with a mobile phase of hexane/2-propanol (90/10, v/v) using commercial Chiralcel OD, CSP based on cellulose derivatives prepared by the “grafting from” method and “grafting to” method. As shown in Table III, the separation factor ( $\alpha$ ) of the CSP prepared by the “grafting from” method and “grafting to” method was lower than that of the commercial Chiralcel OD. The chiral resolution number for the 10 racemates on chiral column (3) prepared by the “grafting to” method was remarkably lower

**Table III.** Chiral Resolution for 10 Racemates Using the Commercial Chiralcel OD (1), CSP Based on Cellulose Derivatives Prepared by “Grafting from” Method (2) and “Grafting to” Method (3)

Racemate	$t_1$			$t_2$			$\alpha$			$R_s$		
	1	2	3	1	2	3	1	2	3	1	2	3
<i>trans</i> -Stilbene oxide (1)	9.00	8.67	8.19	10.7	9.20	-	2.67	1.25	-	1.02	1.16	-
Benzoin (2)	16.6	18.7	13.8	18.8	19.8	25.1	1.28	1.09	2.60	0.75	0.70	1.42
2-Phenylcyclohexanone (3)	8.84	11.3	13.0	8.75	11.9	-	1.38	1.14	-	1.08	0.92	-
Cobalt(III) tris (acetylacetonate) (4)	8.84	10.7	17.4	8.81	11.7	19.9	1.22	1.26	1.23	1.58	1.18	1.26
1-(1-naphthyl)ethylamine (5)	ND	8.66	8.23	-	8.86	9.90	-	1.39	2.09	-	1.17	1.52
DL-sec-phenethyl alcohol (6)	9.58	9.49	9.46	13.8	-	10.8	4.40	-	1.51	1.03	-	1.47
Lansoprazol (7)	ND	11.1	12.3	-	12.4	-	-	1.30	-	-	1.31	-
Tröger's base (8)	8.08	10.2	13.5	18.9	11.0	-	5.68	1.24	-	1.07	1.19	-
2,2,2-Trifluoro-1-(9-anthryl) ethanol (9)	29.5	16.3	12.0	40.7	19.5	-	4.50	1.34	-	2.03	1.25	-
Flavanone (10)	11.9	13.0	13.9	13.3	-	-	2.00	-	-	0.75	-	-

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

**Table IV.** Effect of Eluents for Chiral Resolution Using the CSP with Poly(styrene-*b*-cellulose 2,3-*bis*(3,5-dimethylphenylcarbamate)) Prepared by “Grafting to” Method<sup>a</sup>

Racemates	$\alpha$ Values		
	A	B	C
Benzoin (2)	2.60	2.54	2.61
1-(1-Naphthyl)ethylamine (5)	2.09	2.01	1.98
D,L-sec-phenethyl alcohol (6)	1.51	1.49	1.53

<sup>a</sup> The eluent was (A) hexane/2-propanol(90/10), (B) hexane/CHCl<sub>3</sub> (95/5) and (C) hexane/tetrahydrofuran(95/5). Flow rate, 0.5 ml/min; detector, UV 254 nm.

than that of chiral column (2), as shown in Table III. This may be due to a change in the main chain structure of the cellulose derivatives poly(styrene-*b*-cellulose 2,3-*bis*(3,5-dimethylphenylcarbamate)) during atom transfer radical polymerization.

As mentioned earlier, traditionally coated CSPs have a limited use 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 including hexane/2-propanol, hexane/THF, and hexane/chloroform. Table IV shows the effect of eluents on chiral resolution using CSP with poly(styrene-*b*-cellulose 2,3-*bis*(3,5-dimethylphenylcarbamate)) prepared by the “grafting to” method. These results suggest that this CSP based on cellulose derivatives prepared by the “grafting to” method was very stable, even when THF and chloroform were used as the mobile phase.

## CONCLUSION

The covalent bonded-type of CSP based on cellulose derivatives can be successfully synthesized via the “grafting from” and “grafting to” methods. The grafting yield and chiral resolution of the “grafting to” method was slightly higher than the “grafting from” method. However, the chiral resolution of 10 racemates for the CSP prepared by the “grafting from” method was higher than that of the CSP prepared by the “grafting to” method. The CSP with cellulose derivatives prepared by the “grafting from” method and “grafting to” method were very stable in the presence of several solvents, such as THF and chloroform. Thus, this increased solubility in different solvents will

extend the range of potential applications of CSP in regards to the resolution of enantiomers.

## ACKNOWLEDGMENTS

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