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Correlation between conformational feature in solution and chiral
separation ability of linear and nonlinear amylose
tris(alkylcarbamate)s

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ABSTRACT

Five immobilized-type chiral columns were prepared from linear, cyclic, and hyperbranched amylose tris(*n*-octadecylcarbamate) (ATODC) and amylose tris(*n*-butylcarbamate) (ATBC). A small amount of the linker site, 3-(triethoxysilyl)propylcarbamate, significantly reduced the chain dimensions of ATBC for which high chain stiffness is attained by intramolecular hydrogen bonding between butylcarbamate groups located on the neighboring glycosidic residue. This phenomenon was not found for ATODC, which is mainly stiffened by bulky side groups. While both columns have appreciable chiral recognition ability, number of separated racemates decreased with decreasing side group bulkiness. The bulkiness of the side groups thus plays a definite role in the chiral separation ability. Furthermore, chain linearity on the silica surface is an important factor for the chiral separation because no substantial chiral separation was found for the chiral columns consisting of cyclic ATODC and cyclic ATBC. The chiral column made of hyperbranched ATODC has an intermediate chiral separation ability between linear and cyclic ATODC, supporting this suggestion.

Key Words: Chiral HPLC, chiral stationary phase, amylose derivatives, ring polymer, hyperbranched polymer, immobilization

1. Introduction

Polysaccharide phenylcarbamate derivatives are widely used for chiral selectors of chiral stationary phases (CSPs) [1-6]. High-performance liquid chromatography (HPLC) with chiral columns made of the CSPs are utilized both for the analysis to determine the enantiomer excess as well as purification of chiral reagents and drugs. It is thus of interest to investigate the mechanism of chiral separation.

Polymer-based chiral selectors for HPLC often have rigid helical main chains. The high chain rigidity of helical polymers in solution can be related to the performance of CSPs [7]. High-performance CSPs were developed for amylose phenylcarbamate derivatives including amylose tris(3,5-dimethylphenylcarbamate) (ADMPC) [7-11], which has rigid helical main chain even in solution [12]. Although the high chain stiffness of amylose phenylcarbamate was found several decades ago [13-16], we recently found that amylose alkylcarbamates [16-18] have high chain stiffness in organic solvents. Three examples are shown in Fig. 1. All the three polymers have high chain stiffness in the indicated solvent while the origin of the chain stiffness depends on the side groups. Amylose tris(*n*-butylcarbamate) (ATBC) has high chain stiffness for which Kuhn segment length L_K is 75 nm in tetrahydrofuran (THF) [17]. Notably, L_K is the chain stiffness parameter and twice the persistence length. This value is much higher than $L_K = 16$ nm for cellulose tris(3,5-dimethylphenylcarbamate) [19, 20], a commercially available chiral selector [1-3]. The chain stiffness of ATBC is mainly retained by the intramolecular hydrogen bonds between NH and C=O groups on the neighboring glucose unit [17, 21] (Type-A). On the other hand, similar high chain stiffness ($L_K = 73$ nm) was found for ADMPC in 4-methyl-2-pentanone (MIBK) [12]. The chain stiffness of ADMPC significantly depends on the molecular size of ketone and ester solvents. Namely, the chain stiffness significantly increased with increasing the molar volume of the solvents [12]. This is likely because hydrogen bonding solvent molecules hinder the internal rotation of the amylosic

main chain (Type-B). Amylose tris(*n*-octadecylcarbamate) (ATODC) has a conformational feature intermediate between ATBC and ADMPC [18].

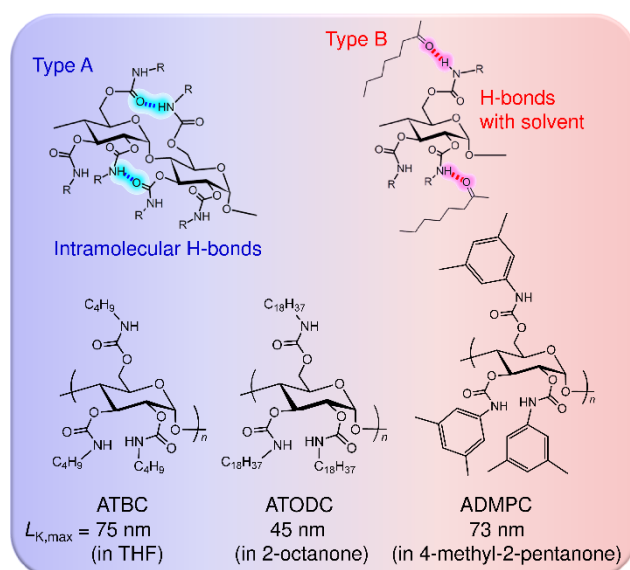


Fig. 1. Relationship between the bulkiness of side groups and origin of the chain stiffness for amylose carbamates. Type A, intramolecular hydrogen bonds and type B, intermolecular hydrogen bond with solvent molecules play an important role for the high chain stiffness. $L_{K,max}$ denotes the highest Kuhn segment length in the investigated solvents.

A few reports were found on the chiral separation ability of amylose alkylcarbamates. ATBC can be used as a CSP for gas chromatography [22] and amylose tris(cyclohexylcarbamate) has high performance as CSP [23, 24]. High solubility of amylose alkylcarbamates in common organic solvents, however, makes it difficult to use them as CSPs. In our preliminary study, we recognized that amylose alkylcarbamates are slightly soluble in typical eluents including hexane and propan-2-ol (iPrOH). We thus prepared immobilized type CSP (Fig. 2) for ATBC and ATODC to avoid elution of polysaccharide derivatives during chiral HPLC measurement. The chiral separation behavior was examined for 14 racemates.

Dimensional properties of ATODC and ATBC with immobilizing site were also investigated to compare the dimensional properties with or without the immobilizing site.

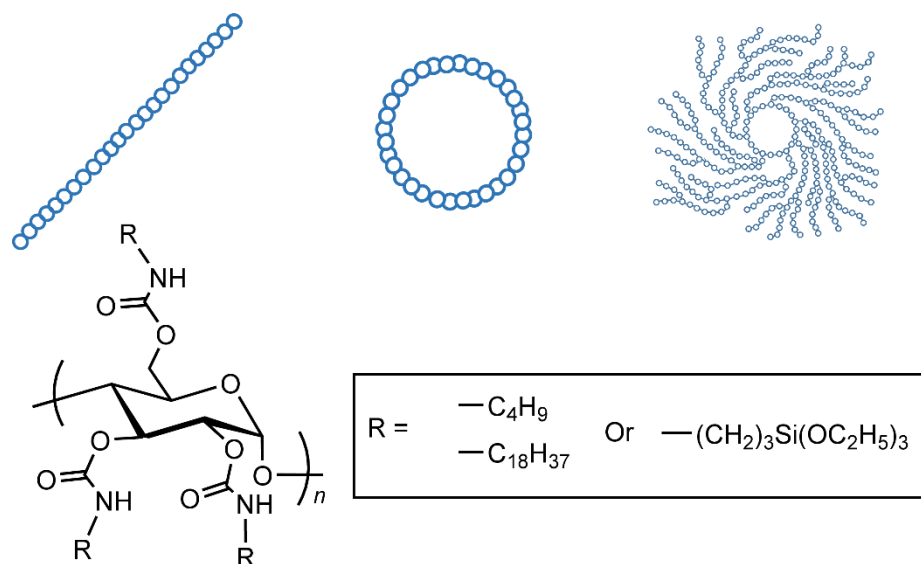


Fig. 2. Chain architecture and chemical structures of the chiral selectors investigated.

Recently, we also found that the chain architecture, namely, cyclic and branched structures, appreciably influences the chiral separation ability of ADMPC [25-27]. To verify the generality of the phenomena, CSPs consisting of cyclic ATBC (cATBC), cyclic ATODC (cATODC), and hyperbranched ATODC (HTODC) were also prepared to compare the performance of the CSPs with the linear analogues.

2. Experimental section

2.1. Chemical reagents

A linear amylose (ESA) sample was prepared with the previously reported method [28]. Cyclic amylose (cESA) samples were synthesized enzymatically from ESA [29]. A highly

branched cyclic dextrin (HBCD) sample was purchased from Fujifilm-Wako (Osaka, Japan). Lithium chloride (Fujifilm), *N,N*-dimethylacetamide (dehydrated grade, Fujifilm), pyridine (Fujifilm), calcium hydride (Nacalai Tesque, Kyoto, Japan), octadecyl isocyanate (Fujifilm), butyl isocyanate (Fujifilm), 3-(triethoxysilyl)propyl isocyanate (TCI chemical, Tokyo, Japan), toluene (Fujifilm), and ethanol (Fujifilm) were used to synthesize polysaccharide carbamate derivatives. A wide-pore silica gel (Daiso gel SP-1000-7, Osaka Soda, Osaka, Japan) with a mean particle diameter of 7 μm and a mean pore size of 100 nm and *i*PrOH (Fujifilm) were chosen to prepare chiral columns. Chloroform-*d* containing 0.05 vol% TMS (Fujifilm) was used as the solvent for ^1H -NMR measurement. Tetrahydrofuran (THF, Fujifilm) and *t*-butyl methyl ether (MTBE, Fujifilm) were used as solvents for small-angle X-ray scattering (SAXS) measurement. The chiral columns were tested with the following racemates **1.** benzoin (Fujifilm), **2.** 1,1'-bi-2-naphthol (TCI), **3.** anisoin (TCI), **4.** 6,6'-dibromo-1,1'-bi-2-naphthol (TCI), **5.** 2,2,2-trifluoro-1-(9-anthryl)ethanol (Fujifilm), **6.** α -benzoin oxime (Alfa Aesar), **7.** trans-stilbene oxide (Sigma-Aldrich), **8.** Tröger's base (Fujifilm), **9.** 4-methylbenzhydrol (TCI), **10.** flavanone (TCI), **11.** 1-(2-Naphthyl)ethanol (TCI), **12.** tropic acid (Combi-Blocks), **13.** 2-(4-chlorophenyl)-3-methylbutyric acid (Combi-Blocks), **14.** 3-hydroxy-3-phenylpropionic acid (TCI). Mixed eluent consisting of hexane (Fujifilm) and *i*PrOH was used with calibration reagents of benzene (Fujifilm) and 1,3,5-tri-*tert*-butylbenzene (TCI).

2.2. Polysaccharide carbamate samples

Carbamate derivatives of ESA, cESA, and HBCD with 3-(triethoxysilyl)propylcarbamate linkers were prepared in the manner reported previously [25, 30]. A typical procedure is as follows. An ESA sample ($M_w = 50 \text{ kg mol}^{-1}$, 1.68 g, 0.103 mmol of the repeat unit) and lithium chloride (3.11 g) were dried in a vacuum at 110 $^{\circ}\text{C}$ for 24 h. *N,N*-Dimethylacetamide (40 mL) was added to them and stirred at 110 $^{\circ}\text{C}$ under Ar

atmosphere to dissolve both lithium chloride and ESA. Pyridine (100 mL) and octadecyl isocyanate (8.4 mL, 24 mmol) were added to the reaction mixture at 50 °C. It was stirred at 105 °C for 6 h. After 3-(triethoxysilyl)propyl isocyanate (0.56 mL, 3.0 mmol) was added, the mixture was further stirred at 105 °C for 24 h. To diminish residual hydroxyl groups on the glucose ring, we further added octadecyl isocyanate (8.4 mL, 24 mmol) to the resulting solution and stirred at 80 °C for 6 h. The mixture was poured into an excess amount of ethanol at room temperature. The precipitate was dried in a vacuum. The crude product was redissolved in THF and poured in ethanol again. The precipitate was centrifuged to obtain the purified sample. Water was used instead of ethanol for butylcarbamate derivatives because of the high solubility in ethanol. A linear amylose octadecylcarbamate (**ATODCi180k**), a linear amylose butylcarbamate (**ATBCi170k**), a cyclic amylose octadecylcarbamate (**cATODCi120k**), a cyclic amylose butylcarbamate (**cATBCi170k**), and a HBCD octadecylcarbamate (**HTODCi1500k**) with the linker group were used for the following column preparation. The chemical structure of each sample was confirmed by ¹H-NMR (Fig. S1 in the Supporting Information) in CDCl₃ at 25 °C. The small peak **a** assigned to the methyl proton of the 3-(triethoxysilyl)propylcarbamate group represents at most 5% of all the carbamate groups. The ultimate analysis was examined for all samples. Results are summarized in Table S1. The weight ratio of nitrogen to carbon was close to full substitution.

2.3. Small-angle X-ray scattering (SAXS) measurement

SAXS measurements for **ATODCi180k**, **cATODCi120k**, **ATBCi170k**, and **cATBCi170k** were made at the BL40B2 beamline in SPring-8. THF was used as solvent for all samples. MTBE was used for **ATODCi180k** and **cATODCi120k**. A quartz capillary with the diameter of 2.0 mm ϕ was adhered in a thin aluminum block. The same capillary cell was

used for solution, solvent, and reference solution, that is, previously studied **ATODC102K** [18] and **ATBC53K** [17] with known molar masses in the corresponding solvent. Four solutions with different polymer mass concentrations c between 2 and 20 mg mL⁻¹ were measured to extrapolate the scattering data to $c = 0$. The wavelength λ_0 and the sample-to-detector distance were 0.10 nm and 4.2 m, respectively. A Dectris PILATUS3 2M detector was used to determine the scattering intensity as a function of the magnitude q of the scattering vector with a SAngler circular averaging software [31]. Silver behenate was used to calibrate the detector. The excess scattering intensity $\Delta I(q)$ was evaluated by the numerical difference of the scattering intensities between the solution and the solvent. Notably, each scattered intensity was calibrated by the intensity of the direct beam detected at the lower end of the solution cell to compensate for both the intensity fluctuation of the incident light and the transparency of the solution. The ratio of the absolute scattering intensity R_q to the X-ray optical constant K was calculated from $\Delta I(q)$ with the aid of the scattering intensity from the reference samples (**ATODC102K** [18] and **ATBC53K** [17]). It is noted that weight-average molar mass M_w can be estimated from R_q/Kc at $q = 0$ and $c = 0$.

2.4. Preparation of chiral columns

Five ATAC-based CSPs were prepared from **ATODCi180k**, **cATODCi120k**, **ATBCi170k**, **cATBCi170k**, and **HDOCDi1500k** with the following procedure in the manner reported previously [25, 30]. A sample, **ATODCi180K** (0.375 g), was dissolved in THF (4.22 mL) and filtered to remove a small amount of insoluble part. The solution was added to the silica gel (2.8 g) drop by drop. THF was evaporated in a vacuum at room temperature after every 0.5 mL of the solution was added. The silica gel was further dried in a vacuum for 3 days. During this process, polysaccharide chain can keep the rigid helical structure because the chain stiffness of ATODC and ATBC chains are quite high in THF [17, 18]. The resulting

product (0.9956 g) was dispersed with the mixture of ethanol (9.2 mL) and water (2.3 mL). After adding 0.15 mL of chlorotrimethylsilane, the mixture was kept under reflux condition at 110 °C for 10 min to crosslink the polymer chains. Interpolymer crosslinking may not significantly affect the helical structure of polysaccharide derivatives due to the flexible nature of the crosslinking dipropyldisiloxane chain. The obtained CSP was washed with an excess amount of acetone, THF, and acetone to remove impurities including free polymer molecules.

Thermogravimetric analyses were made for all the CSPs prepared. The obtained weight fraction w_{PS} of the polysaccharide derivative is summarized in Table S1. These values correspond that almost polysaccharide ($100 \pm 20 \%$) was immobilized on the silica surface.

Each stationary phase was packed in a stainless-steel column (ChemcoPlus, Osaka, Japan) with 2.1 mm of the inner diameter and 250 mm of the length by using a slurry method. A typical procedure is as follows. A CSP (0.8940 g) made of **ATODCi170k** was added to iPrOH and sonicated. The obtained suspension was filtered through a stainless-steel mesh (270 mesh) and incubated at room temperature for 1 h to precipitate the CSP. The precipitant was dispersed in iPrOH (30 mL) and filled into the column with a specially designed column packer pressured with a DP-8020 HPLC pump (Tosoh, Tokyo, Japan). The flow rate was set to be 1.3 mL min⁻¹ to achieve the back pressure of 30 – 40 MPa for about 4 h.

2.4. Chiral HPLC of the columns

The chiral separation performance of the five columns was tested with the above-mentioned 14 racemates. Each column was installed in an HPLC system equipped with a Chromaster 5160 pump (Hitachi, Tokyo, Japan), a Rheodyne 7125 injector with a 20 μ L sample loop, an online UV absorption detector (UV-8001, Tosoh) with a wavelength $\lambda_0 = 254$ nm in a vacuum, and an SF-3120 fraction collector (Advantec, Tokyo, Japan). The mobile phase and

flow rate were chosen to be hexane/iPrOH (9/1) and 0.1 mL min⁻¹, respectively. The plate number N and the dead volume V_0 of the column were estimated from the peak shape of benzene (Fujifilm) and 1,3,5-tri-tert-butylbenzene (TCI), respectively. The obtained N values for **ATODCi180k**, **cATODCi120k**, **ATBCi170k**, **cATBCi170k**, and **HDOCDi1500k** columns were 240, 680, 634, 734, and 514, respectively. When we obtained two peaks in the chromatogram, circular dichroism (CD) measurements were made on a J-720WO CD spectrometer (Jasco, Tokyo, Japan) to characterize each fraction (Fig. S2). One of the fractions having negative CD signal at the highest λ_0 was designated to be (-) and the other was (+); note that the sign of the CD signal at the highest λ_0 was not recognizable for some racemates. Retention volumes were determined as peak top positions for each chromatogram to estimate capacity factors k_1 and k_2 with $k_1 < k_2$, where k_1 and k_2 are defined with peak retention volumes V_1 and V_2 as

$$k_1 = \frac{V_1 - V_0}{V_0}, \quad k_2 = \frac{V_2 - V_0}{V_0} \quad (1)$$

3. Results and discussion

3.1. Molar mass and chain dimensions of linear and cyclic amylose derivatives with linker groups

The weight-average molar mass M_w and radius of gyration R_g were determined from the square root Zimm plot (Berry plot, Fig. S3) and Guinier plot (Fig. S4) for linear and cyclic amylose derivative samples, respectively. The obtained M_w values for **ATODCi180k** and **cATODCi120k** in the two solvents were consistent within $\pm 4\%$ and $\pm 12\%$, respectively. The resulting average M_w values for **ATODCi180k**, **cATODCi120k**, **ATBCi170k** and **cATBCi170k** are 182, 120, 165, and 167 kg mol⁻¹, respectively. Considering that the degree

of polymerization evaluated for the linear samples is the same or slightly lower than that for the ESA sample, essentially no crosslinking reactions occurred during the purification process. In the absence of SAXS data for **HTODCi1500k**, it was estimated to be 1520 kg mol^{-1} from the weight-average degree of polymerization $N_w = 1400$ of the recently reported 3,5-dimethylphenylcarbamate derivative of HBCD [26].

In Fig. 3, the evaluated R_g values are plotted against M_w/M_0 with M_0 being the average monomeric molar mass assuming that the linker group content of the current samples (red circles) was 5%. Previous data without linker groups [17, 18, 32] are shown as triangles. It should be noted that the difference in M_0 between with and without linker groups is smaller than the radius of the circles. The R_g values for linear and cyclic ATBCi samples are appreciably smaller than those for the corresponding ATBC without the linker groups whereas previously investigated linear and cyclic ADMPCs with linker groups have substantially the same R_g as the corresponding ADMPC without linkers [25]. As mentioned above, the high chain stiffness of ATBC in THF is mainly attained by the intramolecular hydrogen bond. Therefore, the local helical structure stabilized by the hydrogen bond can be perturbed by the 3-(triethoxysilyl)propylcarbamate groups. On the other hand, the R_g data for ATODC with linker groups in the two solvents are only slightly smaller than those without linker groups. This is an intermediate behavior between ATBC and ADMPC. The reduction in chain stiffness by the linker group becomes more significant in the order $\text{ATBC} > \text{ATODC} > \text{ADMPC}$. This order shows that the high chain stiffness retained by the bulky side groups is hard to perturb by the linker groups.

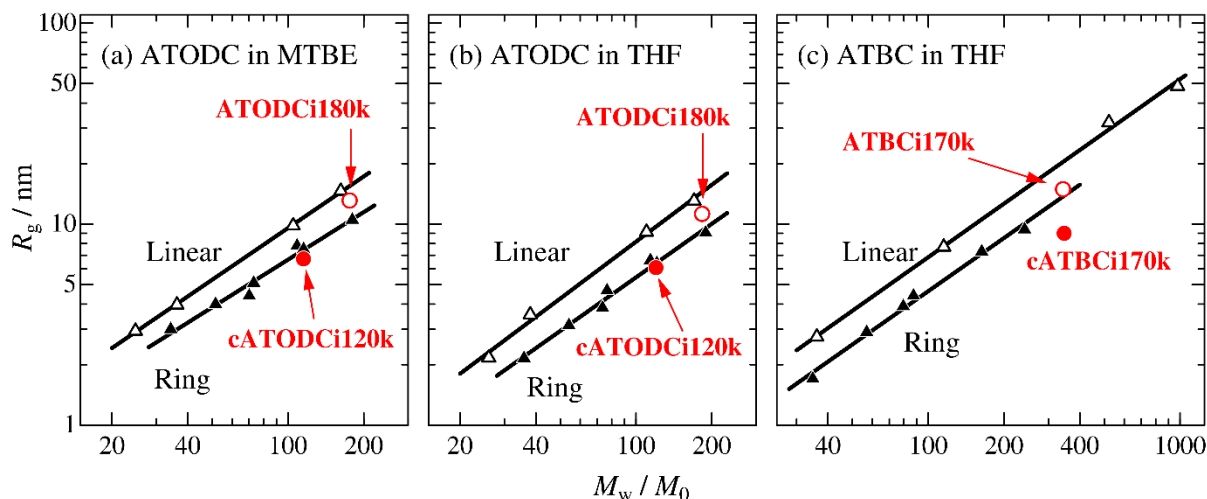


Fig. 3. Double logarithmic plots for the investigated chiral selectors (circles) along with those for the literature values for ATODC and cATODC [18], ATBC [17], and cATBC [32] (triangles). Unfilled and filled symbols indicate linear and cyclic (ring) samples, respectively. (a) ATODC in MTBE, (b) ATODC in THF, and (c) ATBC in THF.

3.2. Chiral separation behavior

Typical chromatograms are shown in Fig. 4 for a racemate, **2**, 6,6'-dibromo-1,1'-bi-2-naphthol. It can be recognized that the chiral separation was attained for the three columns made of **ATODCi180k**, **ATBCi170k**, and **HTODCi1500k** while no separation was found for the **cATBCi170k** column. The results for the linear chain columns are shown in Fig. 5, in which the 14 racemates are categorized by the separation behavior. Whole results are listed in Table 1.

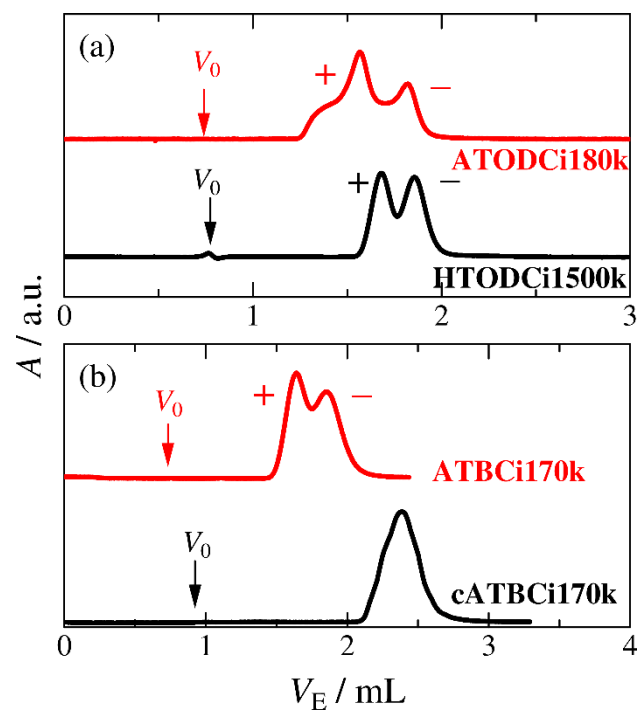
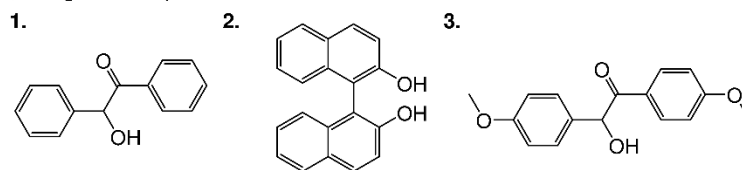
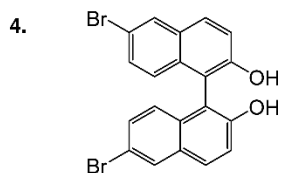


Fig. 4. Chromatograms of a racemate (**2.** 1,1'-bi-2-naphthol) for indicated CSPs using hexane/iPrOH (9/1) as the eluent. Arrows indicate the dead volume (V_0) of the column.

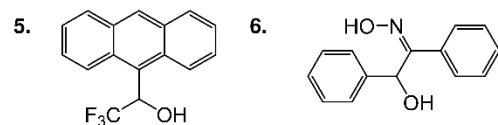
(a) Separated by the ATODC, ATBC, and ADMPC columns



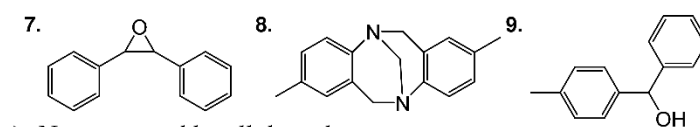
(b) Separated only by the ATODC columns



(c) Separated by the ATODC (not HTODC) and ADMPC columns



(d) Separated only by the ADMPC column



(e) Not separated by all the columns

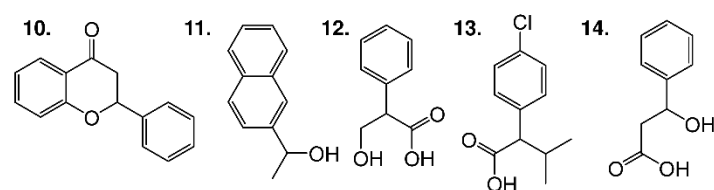


Fig. 5. Chemical structures of racemates investigated.

Table 1. Geometric-average capacity factor $\bar{k}$ and separation factor α for the racemates (**1-14**) separated the CSPs with hexane/iPrOH (9/1) as the eluent

	ATODCi180k		cATODCi120k		HTODCi1500k		ATBCi170k		cATBCi170k	
race mate	$\bar{k}$	α	$\bar{k}$	α	$\bar{k}$	α	$\bar{k}$	α	$\bar{k}$	α
1.	0.66	1.22(+)	0.31	1	0.47	1.16(+)	0.8	1.19(+)	0.72	1
2.	1.46	1.29(+)	0.73	1	1.42	1.20(+)	1.42	1.21(+)	1.67	1
3.	1.23	1.23(+)	0.75	1	0.99	1.18(+)	1.80	1.16(+)	0.44	1
4.	2.61	1.29(+)	1.28	1	2.97	1.32(+)	2.08	1	2.55	1
5.	0.91	1.17(−)	0.30	1	0.52	1	0.79	1	0.74	1
6.	1.35	1.13	1.00	1	1.38	1	1.76	1	2.49	1
7.	0.18	1	0.06	1	0.13	1	0.17	1	0.12	1
8.	0.39	1	0.24	1	0.34	1	0.33	1	0.30	1
9.	0.35	1	0.18	1	0.27	1	0.45	1	0.37	1
10.	0.32	1	0.15	1	0.92	1	0.33	1	0.28	1
11.	0.41	1	0.25	1	0.34	1	0.45	1	0.45	1
12.	N.E.	1	1.00	1	0.03	1	1.49	1	N.E.	1
13.	0.22	1	0.09	1	0.55	1	0.26	1	0.26	1
14.	1.05	1	0.72	1	0.61	1	1.42	1	1.75	1

(+)(−) firstly eluted enantiomer. N.E. not eluted.

Let us compare the chiral separation behavior of the columns made of linear amylose derivatives. While the previously reported ADMPC columns have appreciable resolution for the 8 racemates in categories a, c, and d, three racemates in category a were separated by the **ATBCi170k** column. The **ATODCi180k** column separated 6 racemates in categories a, b, and c. This clearly indicates that the currently investigated linear ATBC and ATODC columns have quite high chiral separation ability while the applicable racemates reduce in the order ADMPC ~ ATODC > ATBC. The order is similar to that of the origin of the chain stiffness in Fig. 1. Consequently, the high chiral separation ability is related to the origin of the chain stiffness in solution. Namely, the rigid helical structure stabilized by the bulky side groups can be a key factor for the chiral recognition ability of amylose derivatives.

To compare the chiral separation behavior for linear and nonlinear amylose derivatives, the separation factor α defined as k_2/k_1 and the geometric average $\bar{k}$ of the capacity factor [$\equiv \sqrt{k_1 k_2}$] are plotted in Fig. 6. The latter parameter $\bar{k}$ is related to the mean of molar Gibbs energies ΔG_1 and ΔG_2 of the adsorption of the two enantiomers as

$$\ln \bar{k} = \frac{\ln k_1 + \ln k_2}{2} = -\frac{1}{RT} \left(\frac{\Delta G_1 + \Delta G_2}{2} \right) + \ln \phi \quad (2)$$

with ϕ being the volume ratio of stationary to mobile phases in the column. The $\bar{k}$ values for most of the racemates except for **12** are substantially close to each other, suggesting that the average adsorption energy is not significantly influenced by the chain architecture. On the contrary, while the **HDODCi1500k** column can separate fewer racemates than that for **ATODCi180k**, those for ring amylose samples, **cATODCi180k** and **cATBCi170k** cannot resolve all the racemates investigated in spite of the similar or higher plate numbers. Namely, the chiral separation ability is in the order linear > branched > ring. Taking into consideration that the hyperbranched polymers may have a straight conformation at least at the chain ends, whole cyclic chains and the bending part of branched chains have a lower chiral recognition ability than the corresponding linear chain. In other words, even for the CSPs consisting of linear amylose derivatives, the straight chain conformation on the silica surface may play an important role in their performance of the chiral separation.

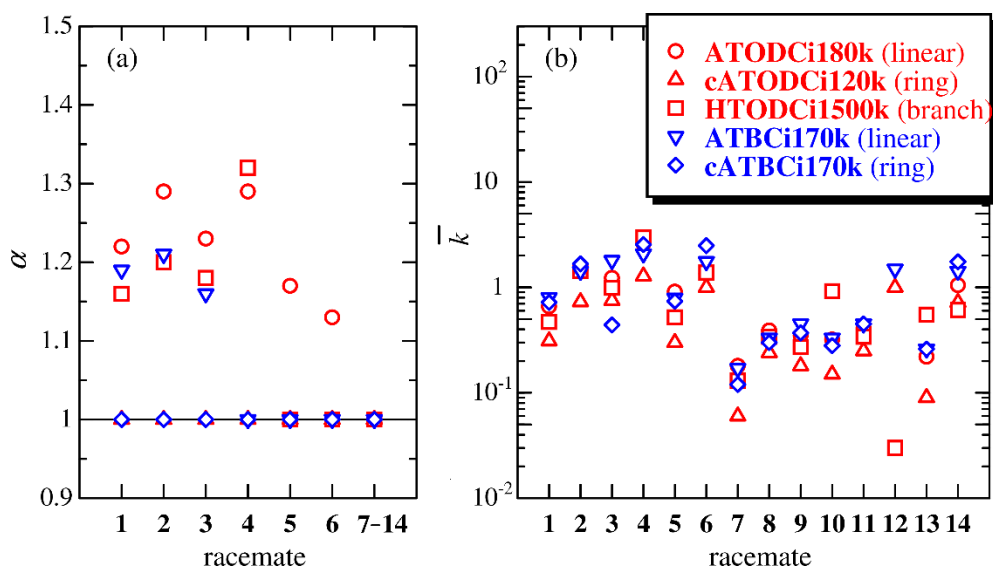


Fig. 6. Separation factor α and geometric average of the capacity factor $\bar{k}$ for the indicated CSPs with hexane/iPrOH (9/1) as the eluent.

4. Conclusion

Immobilized-type chiral stationary phases consisting of linear amylose alkylcarbamate derivatives have chiral separation ability for which alkyl side chain lengths were 18 (ATODC) and 4 (ATBC). The linker group, that is, 3-(triethoxysilyl)propylcarbamate, significantly perturbed the rigid helical structure of ATBC whereas it is less significant for ATODC as in the case of amylose tris(3,5-dimethylcarbamate) (ADMPC) [25]. The rigid helical structure stabilized by the bulky side groups is affected by the linker groups. The performance of the chiral columns made of the amylose alkylcarbamates was not as high as that of the previously investigated ADMPC column and became less significant with shortening the side alkyl chain length, indicating that the side chain bulkiness may be a key factor to separate racemates. Consequently, the high chain stiffness induced by the bulky side groups (Type B chain stiffness in Fig. 1) can be related to the chiral recognition ability. The chiral separation ability of nonlinear ATBC and ATODC is appreciably worse than that of the linear chain, especially for

ring polymers. This suggests that chain linearity on the silica surface is mandatory at least for the chiral separation ability of amylose alkylcarbamates.

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Appendix A. Supplementary data

¹H NMR spectra and ultimate analysis results for amylose derivative samples, CD spectra of each fraction of the separated racemates, the Berry and Guinier plots for the samples from SAXS measurements.

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Correlation between conformational feature in solution and chiral separation ability of linear and nonlinear amylose tris(alkylcarbamate)s

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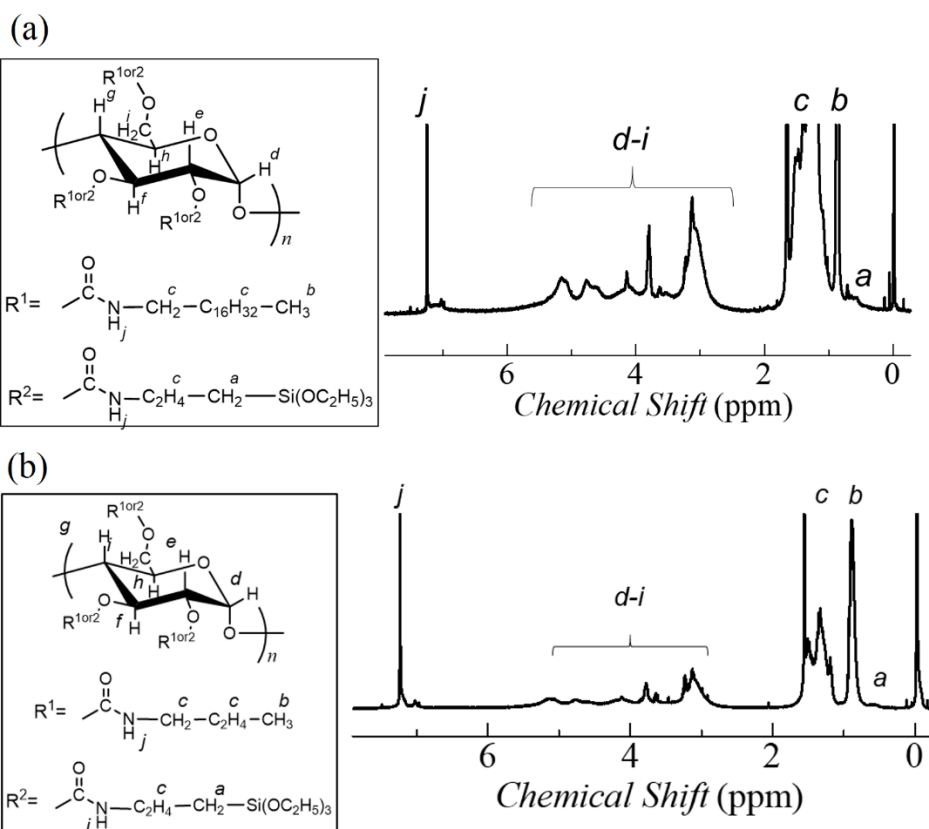


Fig. S1. ¹H NMR spectra for (a) ATODCi180k and (b) ATBCi170k in CDCl₃ at 25 °C.

Table S1

Weight fraction of elements, weight ratio $w(\text{N}) / w(\text{C})$, immobilization efficiency f_i , and weight fraction of polysaccharide derivative w_{PS} in CSP.

Sample	Weight fraction				w_{PS}	$f_i(\%)$
	H (%)	C (%)	N (%)	$w(\text{N}) / w(\text{C})$		
ATODCi180k	11.54	70.58	4.16	0.059	0.133	100
cATODCi120k	11.07	69.24	3.99	0.058	0.112	92.1
HTODCi1500k	11.60	71.60	4.29	0.060	0.129	81.7
Theoretical value for $DS_{\text{R1}} = 3$ and $DS_{\text{R2}} = 0$	11.63	72.16	4.01	0.056		
Theoretical value for $DS_{\text{R1}} = 2.7$ and $DS_{\text{R2}} = 0.3$	11.33	70.03	4.06	0.058		

Sample	Weight fraction				w_{PS}	$f_i(\%)$
	H (%)	C (%)	N (%)	$w(\text{N}) / w(\text{C})$		
ATBCi170k	7.43	49.00	8.38	0.171	0.165	89.0
cATBCi170k	7.21	47.39	7.66	0.162	0.159	120
Theoretical value for $DS_{\text{R1}} = 3$ and $DS_{\text{R2}} = 0$	8.12	54.89	9.15	0.167		
Theoretical value for $DS_{\text{R1}} = 2.7$ and $DS_{\text{R2}} = 0.3$	8.12	53.62	8.34	0.156		

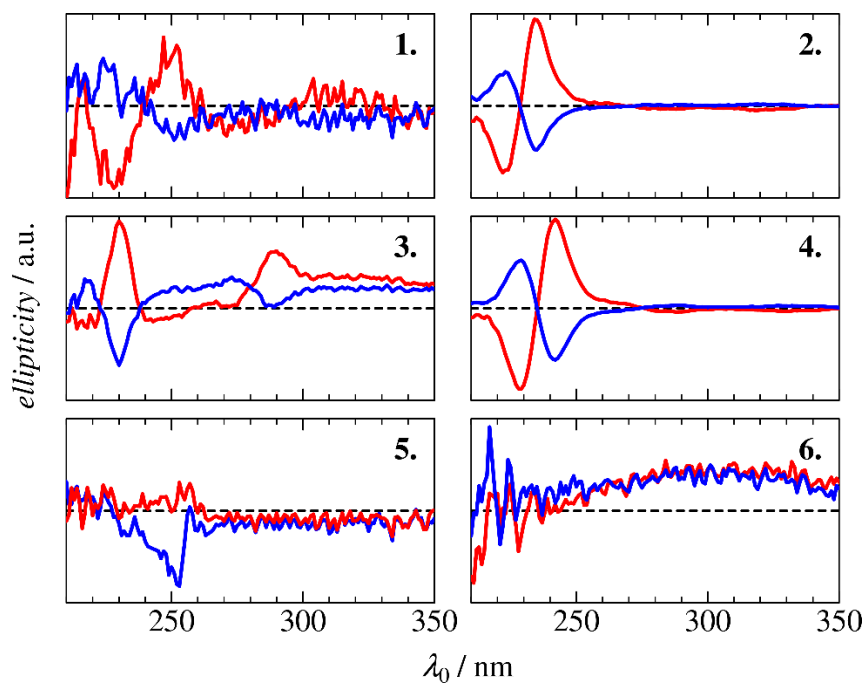


Fig. S2. CD spectra for the enantiomers separated from indicated racemates (1-6). Red and green curves indicate spectra for E- and E+, respectively, except for 6.

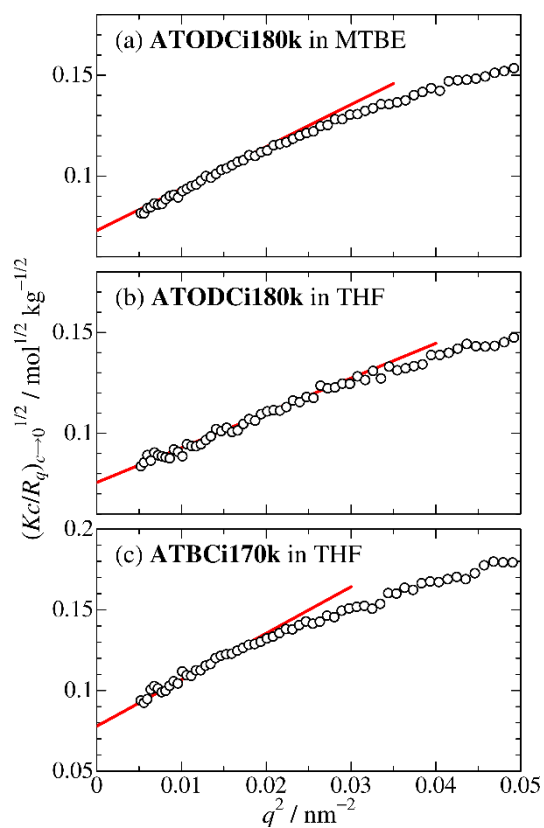


Fig. S3. Berry plots for indicated linear polymer sample – solvent systems at 25 °C. Red lines, initial slope to determine the weight average molar mass M_w and the radius of gyration R_g .

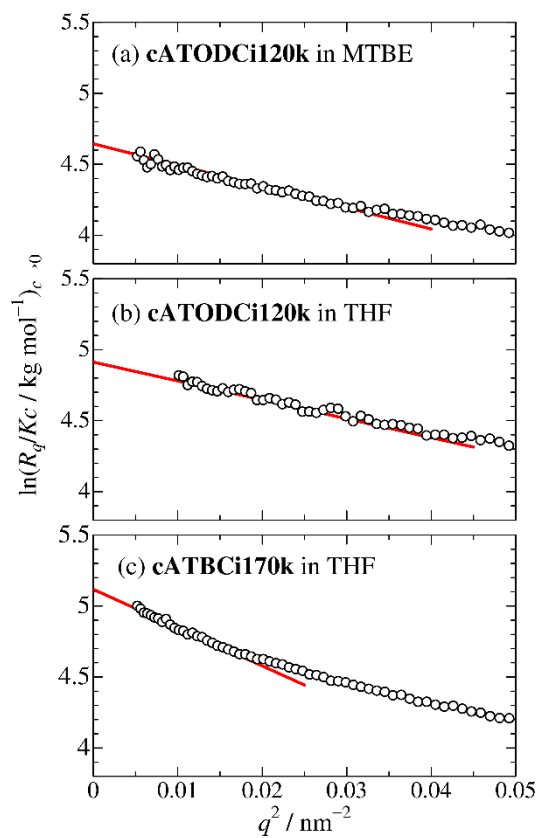


Fig. S4. Guinier plots for indicated ring polymer sample – solvent systems at 25 °C. Red lines, initial slope to determine the weight average molar mass M_w and the radius of gyration R_g .