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Naproxen-derived segmented and sidechain-modified polysiloxanes as chiral stationary phases

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Abstract

The preparation of a series of polysiloxane-based chiral stationary phases (CSPs) derived from (*S*)-naproxen diallyl amide is described. Two types of chiral polysiloxanes have been synthesized. Segmented polymers were obtained by double hydrosilylation of the diallyl amide with difunctional oligomethylhydrosiloxanes. The latter are obtained by a linear homologation strategy, thus allowing systematic variation of the spacing of the chiral selectors along the polymer chain. This spacing clearly affects chromatographic behavior, for increased spacing decreases retention even when the total amount of chiral selector present is unaltered. Alternatively, chiral polysiloxanes were prepared by adding, through hydrosilylation, the diallyl amide as pendent sidechains to a polymethylhydrosiloxane. The resulting polymers were coated on silica gel, packed into HPLC columns and evaluated using normal and reversed-phase conditions. Comparison of the performance of both types of chiral polysiloxane-based CSPs shows them to afford less retention and comparable or higher enantioselectivity than does the corresponding brush-type CSP.

1. Introduction

Chiral biopolymers have found extensive usage as chiral stationary-phase (CSP) components. In many instances, how the biopolymer is deposited (or immobilized) greatly influences the performance of the CSP [1]. This behavior, also noted for some chiral synthetic polymers, occurs when the secondary and tertiary structure of the polymer is largely responsible for its ability to discriminate between the enantiomers of analytes. In contrast, the chiral selectors developed for brush-type CSPs largely function independently of their neighbors, a feature which greatly facilitates the understanding of their modes of action. Since the introduction of Chirasil-Val [2], it has been clear that polysiloxane-based CSPs have much to offer in terms of desirable chromatographic properties. Accordingly, the incorporation of effective "brush-type" chiral selectors into polysiloxane-based CSPs was deemed to be a fruitful field of study.

Initial studies in which brush-type chiral selectors of proven ability were incorporated into polysiloxane-based CSPs suggested that it is selector structure and not the secondary or tertiary structure of the polymer which is largely responsible for the enantiodiscrimination abilities of the CSP [3–5]. This is clearly an advantage in terms of understanding the details of the operative chiral recognition processes, something which augers well for the develop-

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ment of still better chiral selectors. Polysiloxane CSPs have several additional advantages. For example, the polymers may be prepared reproducibly on large scale, thus leading to greater batch-to-batch column uniformity [6–11]. As with brush-type CSPs, the structure of the chiral selectors is completely controllable. Additionally, while the mass transfer characteristics of polymeric CSPs often cause them to have lower chromatographic efficiencies than brush-type CSPs, this is not the case for the polysiloxane CSPs, presumably because of their nonpolar backbones. Finally, the thickness of the polymeric layer coated onto the support can be controlled. Residual silanol groups are detrimental to the performance of CSPs, hence the need to end-cap to lessen the effect of these groups. In the case of silica, the polysiloxanes appear to blanket residual silanol groups since end-capping produces little effect. In some circumstances, the spacing between strands of bonded phase influences the ability of brush-type CSPs to differentiate between enantiomers. These interstrand spacings are not yet controllable for brush-type CSPs. However, the spacings between selectors along a polymeric backbone are potentially controllable [8–11]. Hence, the effect of this variable in the primary structure of a polymeric CSP is one to be studied. The chiral polysiloxanes which might evolve from such studies are potentially useful as physically and chemically stable coatings for porous and nonporous supports which can be used as CSPs in GC, SFC, CE, and HPLC.

In this paper, we report the design, synthesis, and evaluation of CSPs based on segmented and sidechain-modified polysiloxanes. A series of ABAB-type copolymers of (*S*)-naproxen diallyl amide [12] and difunctional oligomethylhydrosiloxanes were prepared by hydrosilylation of the former by the latter using hexachloroplatinic acid as a catalyst. Sidechain-modified chiral polysiloxanes were obtained by similarly attaching the chiral selector to a polymethylhydrosiloxane containing 10 mol% Si–H groups. The resulting polymers were chemically bonded to silica gels of different pore size by thermal treatment. The chromatographic performance of these CSPs, studied by HPLC using normal-phase and reversed-phase conditions, is compared to that of the brush-type phase derived from the same chiral selector.

2. Experimental

Chromatography was carried out on a system consisting of an Alcott 760 HPLC pump equipped with a Rheodyne 7125 injector (20-μl sample loop) and a Milton Roy UV monitor D fixed-wavelength (254 nm) detector. Data was collected using a HP3394A recording integrator. The columns were immersed in a constant temperature bath. Tri-*tert.*-butylbenzene and sodium iodide were used as void volume markers. The analytes were available from prior studies [12,13].

China clay and hexachloroplatinic acid were purchased from Aldrich (Milwaukee, WI, USA). All other silicon reagents were obtained from Petrarch Systems (Bristol, MA, USA). Silica (Rexchrom 300 Å, 5 μm, and 100 Å, 5 μm) was provided by Regis Technologies (Morton Grove, IL, USA). LiChrospher Si 1000, 10 μm, and Si 4000, 10 μm, was from EM Science (Gibbstown, NJ, USA) as were the solvents used for HPLC analyses. (*S*)-Naproxen diallyl amide [12], the difunctional oligomethylhydrosiloxanes [14], and polymethylhydrosiloxane [5], were available from prior studies or were prepared using literature procedures.

2.1. Preparation of 1,1,3,3,5,5,7,7,9,9,11,11-dodecamethylhexasiloxane ($^{H}MD_4M^{H}$)

The described procedure is typical for the linear homologation of cyclosiloxanes. Following the reported procedure [14], 48.0 g (0.5 mol) of dimethylchlorosilane were added at room temperature to a slurry of 50.0 g (0.17 mol) octamethyltetrasiloxane, 30.4 g (0.169 mol) of water, and 5.0 g of silica gel over 2 h. After 4 h, the silica gel was removed by filtration and volatile byproducts were removed from the filtrate by rotary evaporation. The residue was diluted with 50 ml of benzene and, after separation of the

phases, the upper layer was washed sequentially with 50 ml of water, 50 ml of 1% sodium hydrogencarbonate solution (twice), and 50 ml of water (twice). The organic phase was dried over sodium sulfate and evaporated to afford a colorless liquid which was purified by vacuum distillation (bp 81°C, 0.1 torr) to give 10.9 g (29.2% based on consumed octamethyltetrasiloxane) of $^{H}MD_4M^{H}$.

2.2. Dimethyl-hydromethyl siloxane copolymer (10 mol% Si–H groups) [5]

To a slurry of 0.7 g of china clay in a mixture of 4.54 g (2.0 mmol, 68.0 mmol SiH) polymethylhydrosiloxane (PS 120) and 45.38 g (153 mmol) octamethylcyclotetrasiloxane was added 0.2 μl of 36 *M* sulfuric acid. The suspension was heated to 70°C under a nitrogen atmosphere for 24 h. The mixture was cooled and 150 ml of diethyl ether was added. The china clay was removed by suction filtration and the filtrate was washed with water until neutral. The ethereal solution was dried over, then decanted from, sodium sulfate and concentrated to leave a colorless viscous liquid which was vacuum distilled to remove residual octamethylcyclotetrasiloxane. The copolymer (33.75 g; 67.7%) remained as a highly viscous residue.

2.3. General procedure for the preparation of sidechain-modified polymethylsiloxanes

A typical synthetic method is given for a (*S*)-naproxen diallyl amide (2, see Fig. 1) modified polymer. (*S*)-Naproxen diallyl amide (2, 336 mg, 1.09 mmol), polymethylhydrosiloxane (1.0 g, 1.36 mmol SiH), and 100 ml of dry toluene were heated to 70°C under a nitrogen atmosphere. Then 50 μl of 1% hexachloroplatinic acid in tetrahydrofuran were added. After one hour, the temperature was lowered to 55°C and the mixture was stirred for 72 h. Evaporation of the solvent was followed by addition of 20 ml of dichloromethane, 20 ml of methanol, and 10 ml of water. The mixture was stirred thoroughly and the water–methanol layer was removed. This process was repeated three times. The remaining dichloromethane solution was concentrated and the residue was dried under vacuum at 50°C to give 1.30 g (97%) of the chiral polymer. The proton NMR spectrum is consistent with the anti-Markovnikov addition of the silane to the double bond.

2.4. General procedure for the preparation of diene–oligosiloxane copolymers

The same synthetic method as described for the preparation of sidechain-modified polymethylsiloxanes was used. A typical reaction is described for the copolymer of (*S*)-naproxen diallyl amide with 1,1,3,3,5,5,7,7,8,8,11,11-dodecamethylhexasiloxane. (*S*)-Naproxen diallyl amide (2, 309 mg, 1.0 mmol), 1,1,3,3,5,5,7,7,8,8,11,11-dodecamethylhexasiloxane (370 mg, 1.0 mmol), and 50 ml of toluene were treated with 50 μl of 1% hexachloroplatinic acid in tetrahydrofuran, as described above, to give 314.5 mg (85%) of the copolymer. The proton NMR of the copolymer does not show a resonance for Si–H protons.

2.5. Preparation of the CSPs

Brush-type phases (CSPs 7 and 8) were prepared as described in [12] by bonding of the organosilane to silica gel (CSP 7: 100 Å pore size, 5 μm diameter; CSP 8: 300 Å, 5 μm). Segmented and sidechain-modified polysiloxane

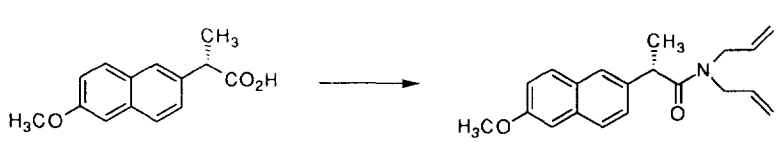

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Fig. 1. Preparation of (*S*)-naproxen diallyl amide 2.

derived CSPs were obtained using the same procedure, simply substituting the chiral polymer for the organosilane. The loadings of the stationary phases are summarized in Table 2. The CSPs were packed into stainless steel columns of 250 × 4.6 mm I.D. as methanol slurries. Residual silanol groups were end-capped by passing a solution of 2 ml of hexamethyldisilazane in 50 ml of dichloromethane through a dichloromethane equilibrated column at a flow-rate of 1.0 ml/min.

3. Results and discussion

3.1. Syntheses of the CSPs

It has previously been observed that the manner in which a chiral selector is immobilized sometimes exerts a secondary influence on the separation process [15,16]. Steric repulsion, attractive interactions with the underlying support, and simultaneous interaction of the analyte with more than one selector may result in nonreciprocal behavior [17,18]. Incorporation of the chiral selector into suitably designed polymers allows for a control of these effects. The approach chosen to control the mode of attachment and spacing between the chiral sites uses principles developed in polymer chemistry. Polymers of the ABAB-type (monomer A: selector, monomer B: spacer) allow for the precise control of spacing between the chiral selectors. Reaction of difunctional oligomethylhydrosiloxanes with dienes in the presence of hexachloroplatinic acid provides a versatile route to segmented polymers with variable spacer length. Sidechain-modified polymers can be generated by hydrosilylation of a polymethylhydrosiloxane with a chiral olefin. (*S*)-Naproxen diallyl amide (2) was used as a model compound for the preparation of different polymeric and brush-type CSPs. The chiral selector was prepared from commercially available

Table 1
(S)-Naproxen diallyl amide-derived CSPs

CSP	Polysiloxane[a]	Silica	Column length[c] (cm)
1	$^{H}MD_1M^{H}$	A	25
2	$^{H}MD_2M^{H}$	A	25
3	$^{H}MD_3M^{H}$	A	25
4	$^{H}MD_4M^{H}$	A	25
5	$^{H}MD_5M^{H}$	A	25
6	$MD^{H}_1D_{9.3}M$	A	25
7[d]	none, brush-type	B	25
8	none, brush-type	A	25
9	$MD^{H}_1D_{9.3}M$	C	15
10	$MD^{H}_1D_{9.3}M$	D	15

[a] $^{H}MD_nM^{H}$: $Me_2HSiO\text{-}(Me_2SiO)_nSiHMe_2$. Descriptors M and D are conventionally used in silicon chemistry to denote $Me_3Si\text{-O-}$ and $\text{-O-}SiMe_2\text{-O-}$. Superscripts on these descriptors denote a ligand or ligands substituting a Me or Me_2 ligands attached to silicon [14].
[b] Silica A: 300 Å, 5 μm; silica B: 100 Å, 5 μm; silica C: 1000 Å, 10 μm; silica D: 4000 Å, 10 μm.
[c] All columns: 4.6 mm I.D.
[d] This CSP was prepared by Patrick L. Spence of this group [12].

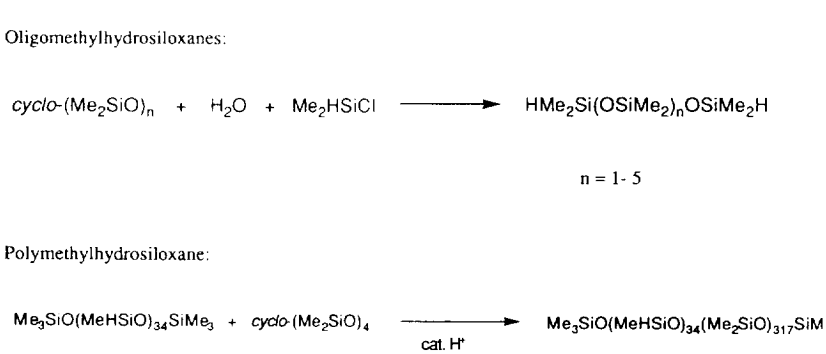
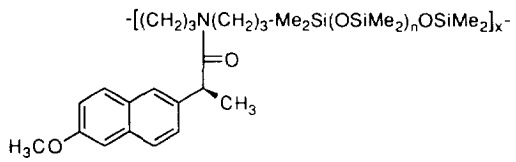
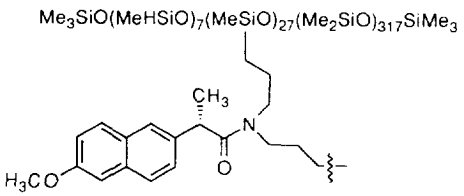


Fig. 2. Preparation of the polysiloxanes.



Segmented Polysiloxane (n = 1-5)



Sidechain Modified Polysiloxane

Fig. 3. Strucutral features of the segmented and sidechain-modified polysiloxanes.

(*S*)-naproxen (1) via the acid chloride by standard procedures (Fig. 2) [12]. A linear homologation strategy for the synthesis of oligosiloxanes developed by Uchida et al. [14] was used to prepare the difunctional oligosiloxanes $^{H}MD_nM^{H}$ ($n = 3$–5, see legend of Table 1 for use of the descriptors) [14]. The first two homologues ($n = 1$, 2) are commercially available products (Fig. 3).

In order to study the effect of the length of the dimethylsilyloxy spacer segments on chromatographic performance, the amounts of the various segmented polymers loaded onto the silica were adjusted so as to afford the same amount of selector in each column. The microanalytical data for each of these CSPs indicate a comparable selector content in each of the columns (Table 2).

The polymethylhydrosiloxane used for the preparation of a sidechain-modified polymeric phase was obtained by equilibrating an SiH-containing polysiloxane of suitable molecular weight with cyclooctamethyltetrasiloxane (Fig. 2) [3–5]. Hydrosilylation of this polymer with less than the stoichiometric amount of chiral olefin affords a sidechain-modified polysiloxane (Fig. 3).

Residual SiH groups were used for the chemical bonding to silica gel of 300, 1000, and 4000 Å pore size. (*S*)-Naproxen diallylamide (2) was transformed to the bis(dimethylethoxysilyl)-derivative and bonded to silica gel of 100 and 300 Å pore size to give the brush-type CSPs. All CSPs were slurry packed into 250 × 4.6 mm I.D. stainless steel columns as methanolic slurries and residual silanol groups were endcapped by pass-

Table 2
Microanalytical data of the CSPs

CSP	Found (%)			Loading calculated by %N (mmol selector/g silica)
	C	H	N	
1	7.64	1.26	0.25	0.18
2	6.84	1.15	0.23	0.16
3	7.76	1.50	0.20	0.14
4	6.47	0.92	0.30	0.21
5	10.86	2.16	0.30	0.21
6	10.04	2.07	0.25	0.18
7	6.32	0.95	0.30	0.21
8	6.46	0.97	0.35	0.28
9	13.22	2.59	0.35	0.28
10	13.04	2.48	0.33	0.24

ing a solution of hexamethyldisilazane through the packed columns [5].

3.2. Chromatographic properties of the CSPs

Racemic and partially resolved 3,5-dinitrobenzamides available from prior studies were used to evaluate the performance of the CSPs (Table 3). The results, using 20% 2-propanol in *n*-hexane as the mobile phase at a flow-rate of 2.0 ml/min, are summarized in Table 4.

For CSPs 1–5, prepared from segmented polysiloxanes, a decrease of retention is observed for a given analyte with an increase in the length of the oligosiloxane spacer. Since CSPs 1–5 were prepared from the same batch of silica, differences in the properties of the initial support cannot account for this observation. The microanalytical data obtained for these CSPs indicate that while there is some variation in the amount of chiral selector present in each of the columns containing CSPs 1–5 (Table 2), there is no correlation between these variations and retention. CSP 5 has the greatest nitrogen content but the lowest retention. Reduced retention with increasing spacer length might suggest (i) a more effective shielding of the support resulting in a suppression of superfluous interaction, (ii)

Table 3
Analytes used for the evaluation of the CSPs

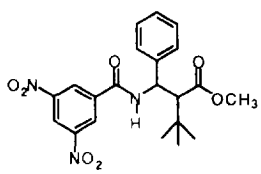
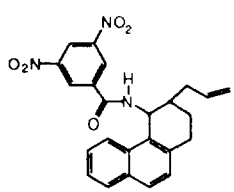
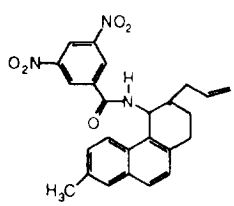
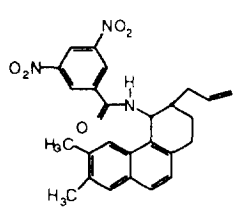
Analyte	
3	N-(3,5-Dinitrobenzoyl)alanine methyl ester
4	N-(3,5-Dinitrobenzoyl)phenylalanine methyl ester
5	N-(3,5-Dinitrobenzoyl)valine methyl ester
6	
7	
8	
9	

Table 4
Conditions: *n*-hexane–2-propanol (8:2), flow-rate: 2.0 ml/min

Analyte		CSP									
		1	2	3	4	5	6	7	8	9	10
3	k'_1	0.76	0.70	0.62	0.48	0.28	0.70	6.44	2.63	0.34	0.19
	k'_2	1.61	1.56	1.06	0.87	0.67	1.50	13.27	4.96	0.71	0.36
	α	2.12	2.22	1.7	1.81	2.39	2.14	2.06	1.88	2.04	1.92
4	k'_1	0.93	0.91	0.44	0.41	0.18	0.63	8.02	3.25	0.29	0.15
	k'_2	1.95	1.82	0.81	0.75	0.47	1.35	15.89	6.77	0.61	0.29
	α	2.10	1.99	1.84	1.79	2.61	2.12	1.98	2.08	2.09	2.00
5	k'_1	0.70	0.59	0.37	0.33	0.18	0.55	4.77	2.00	0.25	0.13
	k'_2	1.67	1.55	1.00	0.73	0.52	1.46	12.30	4.49	0.69	0.33
	α	2.38	2.63	2.70	2.20	2.88	2.62	2.58	2.25	2.73	2.50
6	k'_1	0.59	0.59	0.25	0.37	0.08	0.66	4.12	2.11	0.31	0.13
	k'_2	3.77	3.36	1.62	1.80	0.97	3.27	27.49	10.29	1.63	0.77
	α	6.39	5.69	6.50	4.86	12.12	4.91	6.67	4.88	5.30	5.80
7	k'_1	1.15	0.93	0.56	0.46	0.30	0.68	6.93	3.67	0.48	0.24
	k'_2	5.95	4.82	2.91	1.89	1.84	3.82	38.31	15.12	2.57	1.26
	α	5.19	5.16	5.19	4.12	6.14	5.56	5.53	4.12	5.36	5.27
8	k'_1	1.04	0.91	0.50	0.66	0.28	0.59	13.50	2.03	0.40	0.23
	k'_2	5.25	4.96	2.25	2.55	1.66	3.42	46.00	11.23	2.20	1.12
	α	5.05	5.45	4.50	3.83	5.93	5.80	3.41	4.27	5.50	4.91
9	k'_1	0.93	0.91	0.50	0.54	0.18	0.74	7.00	3.56	0.30	0.13
	k'_2	6.38	6.02	2.75	2.54	1.95	5.09	40.75	17.92	1.84	0.93
	α	6.87	6.61	5.50	4.71	10.83	6.87	5.82	5.03	6.41	6.87

more effective solvation of the chiral selectors owing to their greater spacing, (iii) a reduced extent of bridging of analytes between adjacent selectors owing to their greater spacing. However, reduction of retention does not reduce enantioselectivity nor should it necessarily do so. More effective masking of silanols can reduce retention while increasing enantioselectivity. Some separation factors are suspiciously large (e.g. Table 4: analytes 6, 9), presumably owing to elution of the least retained enantiomer so near the system void volume. The values are reported as determined but we hasten to point out that small errors in determining void volumes greatly affect separation factors when the retention of the least retained enantiomer is so slight. We also point out that injection of the sample in a solvent stronger than the mobile

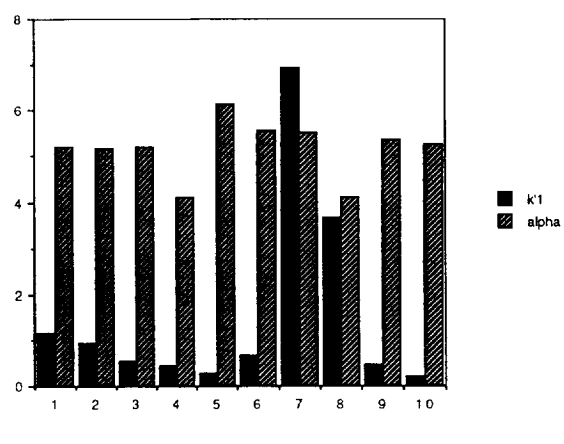


Fig. 4. Representation of the k'_1 and α values observed for analyte 7 on CSPs 1–10. Conditions: *n*-hexane–2-propanol (8:2) at a flow-rate of 2.0 ml/min.

phase can reduce the retention of an analyte, particularly when that retention is small to begin with. In the present case, enantioselectivity could be artificially increased.

Bonding of the chiral selector to a preformed polymethylhydrosiloxane affords CSP 6. The capacity and separation factors of the analytes on this phase are comparable to those on the lower homologues of the segmented polysiloxanes. To study the effect of varying the pore size of the underlying support, the sidechain-modified polymer was immobilized on Si 1000 (CSP 9) and Si 4000 (CSP 10). The chromatographic data show a clear reduction of retention with increasing pore size (Table 4: CSPs 6, 9, 10), doubtless because of the lesser surface area of the large pore silica. As a reference, two brush-type columns (CSPs 7 [12] and 8) were used. Increasing the pore size of the silica support from 100 Å (CSP 7) to 300 Å (CSP 8) decreases retention by a factor of 2–3 (Table 4). Comparison of brush-type CSP 8 with CSPs 1–5, prepared from segmented polysiloxanes, and CSP 6, prepared from a sidechain-modified polysiloxane, shows that resolutions of comparable or higher selectivity can be obtained on the polymeric CSPs in one third to one fifth the time using the same conditions. A graphic representation of these findings for analyte 7 is shown in Fig. 4.

The chromatographic data obtained on CSP 10 in the reversed-phase mode using the same set of analytes is shown in Table 5. Interestingly, the

Table 5
Chromatographic data obtained on CSP 10 at a flow-rate of 2.0 ml/min

Analyte		Solvent: × water/(100 − ×) methanol												
		10	20	30	40	50	60	70	80	90	95	97	98	99
3	k'_1	n.r.[a]	n.r.	0.04	0.21	0.56	2.21	6.56	15.14	31.25	51.10	61.93	65.34	66.69
	k'_2				0.38	1.04	3.85	11.13	25.19	49.89	77.77	93.56	98.46	99.68
	α	1.0	1.0	1.0	1.79	1.84	1.74	1.69	1.66	1.59	1.52	1.51	1.49	1.51
4	k'_1	n.r.	n.r.	n.r.	0.04	0.05	0.14	0.74	1.31	1.68	2.55	2.96	3.00	3.19
	k'_2						0.29	1.64	3.18	3.30	3.48	4.01	4.10	4.31
	α	1.0	1.0	1.0	1.0	1.0	2.07	2.22	2.43	1.96	1.36	1.35	1.37	1.34
5	k'_1	n.r.	0.03	0.04	0.1	0.16	0.68	1.73	3.26	6.13	9.36	11.01	11.43	11.67
	k'_2					0.45	1.70	3.41	6.15	10.98	16.02	18.44	19.20	19.61
	α	1.0	1.0	1.0	1.0	2.80	2.50	1.97	1.88	1.79	1.71	1.67	1.68	1.68
6	k'_1	n.r.	0.01	0.13	0.50	1.48	4.66	24.78	n.d.[b]	n.d.	n.d.	n.d.	n.d.	n.d.
	k'_2		0.19	0.45	1.71	5.22	17.38	85.91						
	α	1.0	15.8	3.55	3.38	3.52	3.72	3.47						
7	k'_1	0.08	0.59	1.78	6.77	28.35	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	k'_2	0.43	2.61	8.28	31.88	141.75								
	α	5.40	4.42	4.65	4.71	5.00								
8	k'_1	0.13	0.83	2.65	10.0	53.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	k'_2	0.55	3.49	11.72	43.67	n.d.								
	α	4.11	4.18	4.42	4.36	n.d.								
9	k'_1	0.05	0.27	1.89	10.14	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	k'_2	0.92	1.58	9.97	n.d.									
	α	10.08	5.81	5.27	n.d.									

[a] n.r.: not retained.
[b] n.d.: not determined, no peak detected after 2.5 h.

composition of the mobile phase can be altered over a wide range without a significant alteration of enantioselectivity. As expected, decreasing the concentration of the organic component in the mobile phase results in increased retention of the analytes. This feature is valuable as it allows one to adjust the mobile-phase composition for better separation of multicomponent mixtures without adversely affecting the separation of the enantiomers of interest. These columns have been used with a variety of mobile phases (hexane, 2-propanol, methanol, ethanol, acetonitrile, water, tetrahydrofuran, ethyl acetate, dichloromethane, buffers) for over a year with no adverse effects. Some of these columns have been used at temperatures exceeding 100°C with no lasting effect. Since these polysiloxanes are anchored to silica, one might suppose that the usual admonitions about pH extremes should be heeded but we have not yet sought the tolerable limits of these CSPs.

4. Conclusions

In summary, ten (*S*)-naproxen-derived CSPs were utilized to study the properties of brush-type and polymeric coatings of a chromatographic support. Reduction of retention times without significant loss of enantioselectivity was observed upon increasing the pore size of the silica gel used to prepare the CSPs. Synthesis of a series of difunctional oligosiloxanes provided starting materials for the preparation of copolymers with variable spacer length. CSPs based on these segmented polysiloxanes show strongly reduced retention times and enantioselectivities comparable or higher than those obtained on the corresponding brush-type CSPs. Immobilization of a sidechain-modified polysiloxane affords CSPs capable of rapid resolutions of enantiomers. It has been shown that the incorporation of a chiral selector into polysiloxanes affords CSPs of high enantioselectivity in combination with short analysis time under either normal- or reversed-phase conditions.

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