Copolymeric Cyclodextrin Polysiloxane Stationary Phases Prepared from $6^A,6^C$- and $6^A,6^D$-Dialkenyl-substituted β-Cyclodextrin

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Dedicated to the memory of Professor Bryant E. Rossiter who passed away on February 5, 1995.

The syntheses of four new β-cyclodextrin-hexasiloxane copolymers from heptakis(2,3-di-*O*-methyl)-β-cyclodextrin (**2**) by multi-step processes are described. $6^A,6^C$-Di-*O*-[*p,p'*-methylenebis(benzenesulfonyl)]heptakis(2,3-di-*O*-methyl)-β-cyclodextrin (**3**), which was prepared by the reaction of **2** with *p,p'*-methylenebis(benzenesulfonyl chloride), is a key intermediate for the preparation of permethylated $6^A,6^C$-bisalkenyl-β-cyclodextrins **5**, **6**, and **9**. Permethylated $6^A,6^C$-bissulfonate ester **4**, which was obtained from **3** by a methylation reaction under mild conditions, was reacted with sodium allyloxide or sodium ω-undecenyloxide to produce permethylated $6^A,6^C$-bisallyl- (or bis-ω-undecenyl)-β-cyclodextrin **5** or **6** or was hydrolyzed with 2% sodium amalgam in methanol to yield diol **7**. Compound **7** was oxidized with periodinane, followed by Wittig's reaction with methyltriphenylphosphonium iodide to give permethylated $6^A,6^C$-dideoxy-$6^A,6^C$-dimethylene-β-cyclodextrin (**9**). Treatment of **2** with *p,p'*-methylenebis(benzenesulfonyl chloride) or *p,p'*-biphenyldisulfonyl chloride gave bissulfonate esters **10** or **11**, respectively. Both of them were treated with sodium *p*-allyloxyphenoxide in DMF, followed by methylation, to form permethylated $6^A,6^D$-di-*O*-(*p*-allyloxyphenyl)-β-cyclodextrin (**16**). Bisalkenes **5**, **6**, **9** and **16** were copolymerized with α,ω-dioctyldecamethylhexasiloxane by a hydrosilylation process to give the cyclodextrin-containing copolymers **17-20**.

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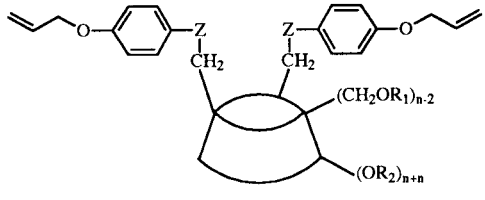
Introduction.

The analytical separation of enantiomers has become very important in light of interest in the resolution and enantiomeric purity of drugs [1]. The use of chiral stationary phases (CSPs) in chromatography is the most convenient and reliable method to determine enantiomeric compositions [2]. In recent years, *O*-derivatized cyclodextrins, when used as CSPs in capillary gas chromatography (gc) and supercritical fluid chromatography (sfc), have become powerful tools in modern enantiomer analysis [3]. The state of the art in this field has been reviewed by Schurig and Nowotny [3a]. Following the first strategy to make cyclodextrin phases by diluting the relevant cyclodextrin derivative with polysiloxane, permethylated alkenyl-substituted β-cyclodextrins have been chemically bonded to a polysiloxane backbone by a hydrosilylation reaction by Schurig and Fischer and their coworkers [4], and this process has been further developed by our group [5,6]. This type of CSP is an independent phase that has pendant groups with which the solute enantiomers interact. Another type of CSP, a cooperative phase, consists of a chiral sector and an achiral sector. This latter part helps by improving the dissolution of the solute enantiomers during the analysis process. We recently prepared several cooperative copolymeric phases composed of cyclodextrin and hexasiloxane copolymeric parts. These phases provided excellent resolution of a wide variety of chiral organic solutes in sfc [7-9].

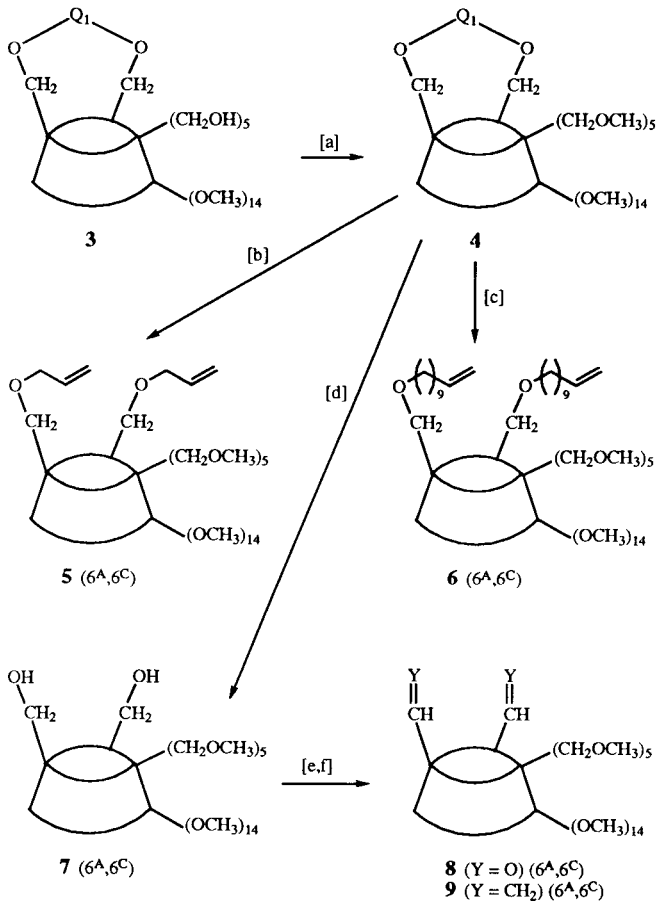
The previous cyclodextrin-containing cooperative copolymeric phases were prepared by the reaction of permethylated or partially methylated and partially pentylated $6^A,6^C$-di-*O*-(*p*-allyloxyphenyl)-β (α)-cyclodextrin, or permethylated $6^A,6^C$-di-(*p*-allyloxybenzamido)-β-cyclodextrin (see Figure 1) with dodecamethylhexasiloxane [7]. As a further improvement of these cyclodextrin-hexasiloxane copolymers, new permethylated $6^A,6^C$-bisalkenyl-β-cyclodextrins **5**, **6** and **9** containing aliphatic alkenyl groups rather than the *p*-allyloxyphenyl moiety (Scheme I) have been prepared. These alkenyl-substituted cyclodextrins allow the preparation of copolymers which contain only aliphatic carbon atoms in the polymer chain.



	n	Z	R_1	R_2
1a	7	O	CH_3	CH_3
1b	7	O	n-C_5H_{11}	CH_3
1c	7	O	CH_3	n-C_5H_{11}
1d	7	CONH	CH_3	CH_3
1e	6	O	CH_3	CH_3

Figure 1. Structure of peralkylated $6^A,6^C$-bisalkenyl-β-cyclodextrins [7].

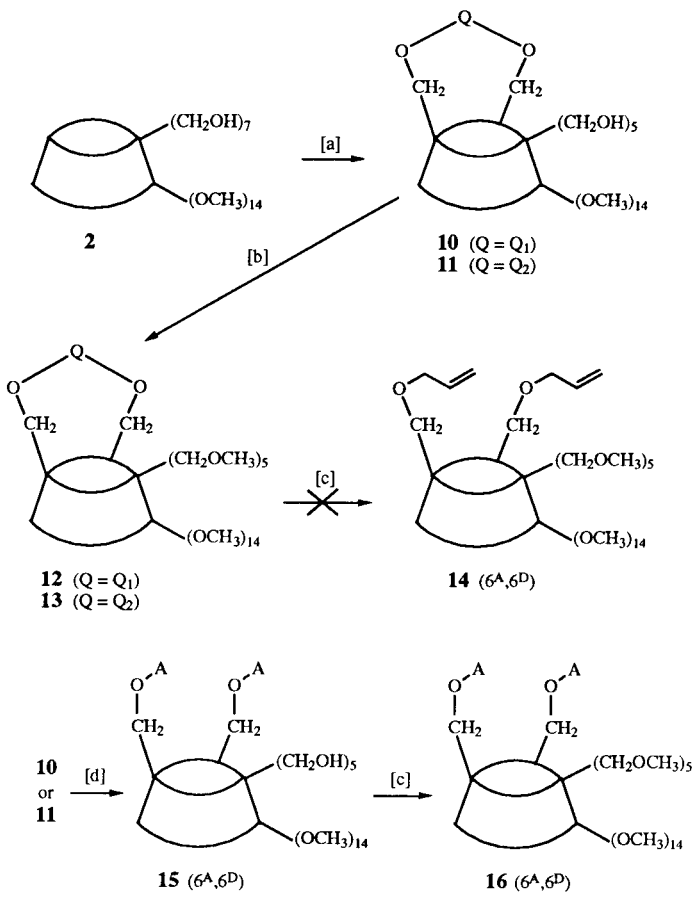
Scheme I. Preparation of Permethylated $6^A,6^C$-Bis-alkenyl-β-cyclodextrins



Q_1 = *p,p'*-Methylenebis(benzenesulfonyl)

[a] Methyl triflate, 2,6-di(*tert*-butyl)-4-methylpyridine, CH_2Cl_2. [b] Sodium allyloxide, DMF. [c] Sodium ω-undecylenoxide, DMF. [d] Na(Hg), CH_3OH. [e] Periodinane, CH_2Cl_2. [f] Ph_3PCH_3I, PhLi, THF.

Scheme II. Preparation of Permethylated $6^A,6^D$-Bis-alkenyl-β-cyclodextrins



A = *p*-allyloxyphenyl
Q_1 = *p,p'*-methylenebis(benzenesulfonyl)
Q_2 = 4,4'-biphenyldisulfonyl

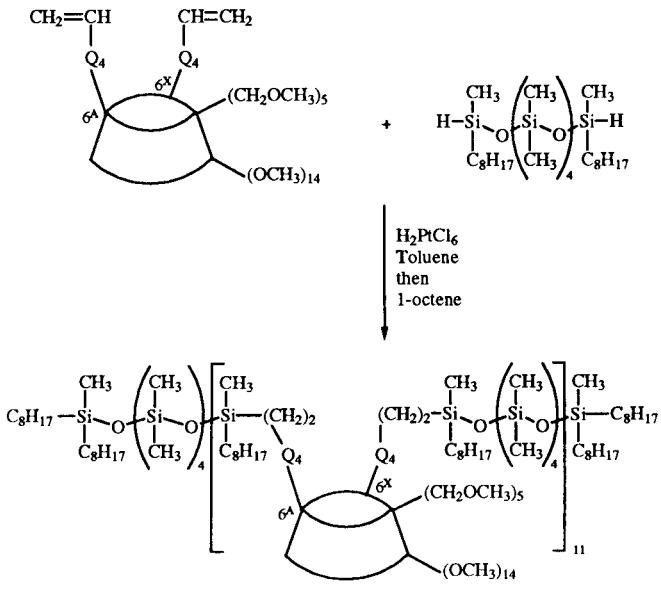
[a] For **10**: *p,p'*-methylenebis(benzenesulfonyl chloride), pyridine; for **11**: *p,p'*-biphenyldisulfonyl chloride, pyridine. [b] Methyl triflate, 2,6-di(*tert*-butyl)-4-methylpyridine, CH_2Cl_2. [c] Sodium allyloxide, DMF. [d] Sodium *p*-allyloxyphenoxide.

Permethylated $6^A,6^D$-di-*O*-(*p*-allyloxyphenyl)-β-cyclodextrin (**16**) was also prepared (Scheme II). These four dialkenes were copolymerized with a hexasiloxane to form copolymeric phases **17-20** (Scheme III). These new cyclodextrin-containing copolymeric phases provide enantiomeric resolution of a variety of chiral organic solutes in capillary sfc and gc [8 and 9]. This paper describes the syntheses of these CD-containing dialkenes and copolymeric phases.

Results and Discussion.

The key intermediate for the preparation of $6^A,6^C$-disubstituted cyclodextrins, $6^A,6^C$-di-*O*-[*p,p'*-methylenebis(benzenesulfonyl)]heptakis(2,3-di-*O*-methyl)-β-cyclodextrin (**3**) (Scheme I), was reported previously [7]. Methylation of **3** with methyl triflate in the presence of 2,6-di-*tert*-butyl-4-methylpyridine in dichloromethane gave permethylated $6^A,6^C$-bissulfonate ester **4** in a 60% yield. Ester **4** was treated with sodium allyloxide in DMF to yield permethylated $6^A,6^C$-di-*O*-allyl-β-cyclodextrin (**5**) in an 82% yield. A similar reaction with sodium ω-undecenoxide in DMF gave permethylated $6^A,6^C$-di-*O*-(ω-undecenyl)-β-cyclodextrin (**6**) in 20% yield. The crude product of the reaction of **4** with allyloxide exhibited only one spot on tlc analysis, while the crude product of the reaction of **4** with ω-undecenoxide exhibited three spots. In the latter case, the compound with the highest R_f value was **6**, the middle spot was permethylated 6-mono-*O*-ω-undecenyl-β-cyclodextrin with one 6-hydroxy group and the compound with the lowest R_f was compound **7** as determined by nmr spectroscopy.

Scheme III. Preparation of Cyclodextrin-Hexasiloxane Copolymers



Copolymer	$6^A,6^X$	Q_4
17	$6^A,6^C$	CH_2OCH_2
18	$6^A,6^C$	$CH_2O(CH_2)_9$
19	$6^A,6^C$	Nothing
20	$6^A,6^D$	CH_2O-C$_6$H$_4$-OCH_2

Permethylated bissulfonate ester **4** was also transformed into diol **7** in an 80% yield by reductive detosylation with 2% sodium amalgam/methanol. Oxidation of **7** with periodinane in methylene chloride gave dialdehydo-β-cyclodextrin derivative **8** in a good yield. $6^A,6^C$-Dimethylene-β-cyclodextrin derivative **9** was obtained by a Wittig reaction with Ph_3PCH_3I and C_6H_5Li in THF in a 45% yield. The above three permethylated $6^A,6^C$-bisalkenyl-substituted β-cyclodextrins have the alkene group located at different lengths from the cyclodextrin. These chiral dienes form copolymers with the hexasiloxane which will have varying aliphatic spacers between the hexasiloxane and the cyclodextrin parts.

The selective activation of the $6^A,6^D$-dihydroxy groups of β-cyclodextrin is a key step in the preparation of permethylated $6^A,6^D$-di-*O*-alkenyl-substituted β-cyclodextrin. Treatment of **2** with *p,p'*-methylenebis(benzenesulfonyl chloride) in pyridine not only gave $6^A,6^C$-bissulfonate ester **3** [7], but also the $6^A,6^D$-bissulfonate ester **10**. It was found that the total yield as well as the regioisomer distribution of **3** and **10** was related to the reaction temperature. The total yield of **3** plus **10** was 51% and the ratio of **3** to **10** was 71/29 at room temperature. At 60°, the total yield was 31% with a **3/10** ratio of 85/15. Tabushi and coworkers reported that *p,p'*-biphenyldisulfonyl dichloride selectively reacted with the $6^A,6^D$-dihydroxy groups of unsubstituted β-cyclodextrin [10]. We found that selective activation of the $6^A,6^D$-dihydroxy groups of **2** was also accomplished by treatment with *p,p'*-biphenyldisulfonyl dichloride in pyridine to yield **11** but in very low yields (4.9% and 3.4% at room temperature and 50°, respectively). Analysis (tlc) showed that the starting material had reacted and that the byproduct had a lower R_f value than **2**. This indicates that the main reaction was intermolecular condensation. Both **10** and **11** were methylated with methyl triflate in the presence of 2,6-di-*tert*-butyl-4-methylpyridine in methylene chloride to give permethylated $6^A,6^D$-bissulfonate esters **12** and **13**, respectively. Unfortunately, treatment **12** and **13** with sodium allyloxide in DMF did not form the expected permethylated $6^A,6^D$-di-*O*-allyl-β-cyclodextrin (**14**). Treatment of intermediates **10** and **11** with sodium *p*-allyloxyphenoxide gave $6^A,6^D$-di-*O*-(*p*-allyloxyphenyl)-β-cyclodextrin (**15**) in yields of 42% and 74%, respectively. Methylation of **15** with methyl triflate in the presence of 2,6-di-*tert*-butyl-4-methylpyridine in methylene chloride formed permethylated $6^A,6^D$-di-*O*-(*p*-allyloxyphenyl)-β-cyclodextrin (**16**) in a 91% yield.

Copolymers **17-20**, shown in Scheme III, were synthesized by a hydrosilylation reaction of **5**, **6**, **9** and **16** with α,ω-dioctyldecamethylhexasiloxane in a manner similar to that reported [7]. These copolymeric phases have been coated on capillary fused silica columns and tested as stationary phases in capillary sfc and gc. Although these phases provide excellent enantiomer separations, the phases containing cyclodextrin attached to a polysiloxane by a single arm are superior [8,9].

EXPERIMENTAL

Proton and carbon nmr spectra were recorded in deuteriochloroform on a Varian Gemni 200 MHz spectrometer. Analysis (tlc) was performed on aluminum-backed silica gel 60, 0.2 mm plates. Pyridine was purified by stirring over calcium hydride powder for 10 hours and then distilled. Heptakis(2,3-di-*O*-methyl)-β-cyclodextrin (**2**) [7], $6^A,6^C$-di-*O*-[*p,p'*-methylenebis-(benzenesulfonyl)]heptakis(2,3-di-*O*-methyl)-β-cyclodextrin (**3**) [7], and periodinane [11] were prepared as reported.

$6^A,6^C$-Di-*O*-[*p,p'*-methylenebis(benzenesulfonyl)]heptakis(2,3-di-*O*-methyl)-$6^B,6^D,6^E,6^F,6^G$-penta-*O*-methyl-β-cyclodextrin (**4**) (Scheme I).

A mixture of **3** (2.03 g, 1.25 mmoles), methyl triflate (0.89 ml, 7.50 mmoles) and 2,6-di-*tert*-butyl-4-methylpyridine (1.93 g, 9.38 mmoles) in 15 ml of methylene chloride was stirred in a sealed tube for 2.5 hours at 80°. Methanol (10 ml) was added after the mixture was cooled to room temperature, and stirring was continued for 30 minutes. The mixture was evaporated and the residue in chloroform was washed successively with water,

cold 3% hydrochloric acid, aqueous sodium bicarbonate, water, and dried and concentrated. The product was subjected to column chromatography on silica gel (chloroform:methanol/80:1) to give 1.26 g (60%) of solid **4**, mp 152-153°; $[\alpha]_D^{25}$ + 132.9° (c 1.30, chloroform); ^{1}H nmr: δ 7.78 (d, J = 8.83 Hz, 2 H), 7.80 (d, J = 8.83 Hz, 2 H), 7.45 (d, J = 8.83 Hz, 2 H), 7.40 (d, J = 8.83 Hz, 2 H), 5.18-4.96 (m, 7 H), 4.46-4.12 (m, 2 H), 4.09 (s, 2 H), 3.93-3.26 (m, 90 H), 3.26-3.02 (m, 7 H); ^{13}C nmr: δ 146.9, 146.7, 135.5, 134.7, 129.8, 129.6, 128.9, 99.6, 99.5, 99.4, 99.3, 82.8, 82.2, 82.1, 81.8, 81.7, 81.6, 81.5, 80.7, 80.2, 80.1, 71.9, 71.5, 71.4, 71.2, 69.6, 62.2, 62.0, 61.8, 61.6, 59.8, 59.6, 59.5, 59.0, 58.8, 58.7, 58.6, 42.9.

Anal. Calcd. for $C_{74}H_{116}O_{39}S_2$: C, 52.47; H, 6.90. Found: C, 52.29; H, 6.73.

$6^A,6^C$-Di-*O*-allylheptakis(2,3-di-*O*-methyl)-$6^B,6^D,6^E,6^F,6^G$-penta-*O*-methyl-β-cyclodextrin (**5**) (Scheme I).

A solution of allyl alcohol (0.42 g, 7.2 mmoles) in 20 ml of dry dimethylformamide was treated with 0.14 g (6.0 mmoles) of sodium hydride for 4 hours at room temperature. Permethylated bissulfonate ester **4** (0.54 g, 0.15 mmole) was added at 0° and the mixture was stirred for 24 hours at room temperature. Methyl iodide was added to decompose the excess allyloxide at 0° and the mixture was concentrated under reduced pressure. The residue was partitioned between chloroform and water. The organic layer was separated, and washed twice with water, then dried and concentrated. Column chromatography (chloroform:methanol/80:1) of the product gave **5** (0.18 g, 82%), mp 79-81°; $[\alpha]_D^{25}$ + 144.4° (c 0.77, chloroform); ^{1}H nmr: δ 5.89 (m, 2 H), 5.33-5.02 (m, 11 H), 4.03 (d, J = 5.19 Hz, 4 H), 3.94-3.30 (m, 92 H), 3.23-3.10 (m, 7 H); ^{13}C nmr: δ 135.4, 117.1, 99.4, 82.6, 82.3, 81.0, 80.8, 72.6, 71.9, 71.4, 69.6, 61.3, 59.4, 59.0, 58.9.

Anal. Calcd. for $C_{67}H_{116}O_{35}$: C, 54.31; H, 7.89. Found: C, 54.26; H, 8.12.

$6^A,6^C$-Di-*O*-ω-undecenylheptakis(2,3-di-*O*-methyl)-$6^B,6^D,6^E,6^F,6^G$-penta-*O*-methyl-β-cyclodextrin (**6**) (Scheme I).

Cyclodextrin derivative **6** was prepared as **5** above from 1.02 g (6.0 mmoles) of ω-undecenyl alcohol, 0.14 g (6.0 mmoles) of sodium hydride and 0.25 g (0.15 mmoles) of **4** to give 0.051 g (20%) of **6**, mp 55-57°; $[\alpha]_D^{25}$ + 106.3° (c 0.88, chloroform); ^{1}H nmr: δ 5.89 (m, 2 H), 5.19-5.05 (m, 7 H), 4.95 (m, 4 H), 3.95-3.30 (m, 96 H), 3.17 (dd, J_1 = 9.35 Hz, J_2 = 3.24 Hz, 7 H), 2.00 (m, 4 H), 1.59 (m, 4 H), 1.44-1.13 (m, 24 H); ^{13}C nmr: δ 139.5, 114.7, 99.5, 99.4, 99.3, 99.2, 82.7, 82.6, 82.5, 82.2, 81.0, 80.9, 80.8, 80.4, 72.0, 71.9, 71.7, 71.6, 71.4, 70.0, 61.9, 59.4, 59.0, 34.3, 30.0, 29.9, 29.8, 29.6, 29.4, 26.7.

Anal. Calcd. for $C_{83}H_{148}O_{35}$: C, 58.43; H, 8.74. Found: C, 58.60; H, 8.94.

Heptakis(2,3-di-*O*-methyl)-$6^B,6^D,6^E,6^F,6^G$-penta-*O*-methyl-β-cyclodextrin (**7**) (Scheme I).

To a stirred solution of permethylated bissulfonate ester **4** (0.44 g, 0.26 mmole) in 10 ml of methanol was added 2% sodium amalgam [7.18 g, 6.24 mg-atoms of Na] in 10 portions over 7 hours. Stirring was continued over night at room temperature. The solution was filtered through filter paper, and the solid was washed with methanol. The combined filtrate was concentrated to yield a white solid which was treated with hot acetone. The acetone solution was filtered to remove disodium *p,p'*-methylenebis(benzenesulfonate), and the acetone was evaporated. The crude product was purified by column chromatography (chloroform:methanol/40:1) to give 0.29 g (80%) of **7**; mp 104-106°; $[\alpha]_D^{25}$ + 127.1° (c 0.99, chloroform); ^{1}H nmr: δ 5.22-4.99 (m, 7 H), 4.07-3.31 (m, 92 H), 3.28-3.10 (m, 7 H), 2.80 (t, J = 6.23 Hz, OH, 1 H), 2.67 (t, J = 6.23 Hz, OH, 1 H); ^{13}C nmr: δ 99.6, 99.4, 99.3, 99.0, 82.6, 82.5, 82.3, 82.2, 82.1, 81.8, 81.5, 81.3, 81.0, 80.8, 80.7, 80.0, 79.6, 72.4, 72.2, 72.1, 71.8, 71.7, 71.5, 62.2, 62.0, 61.9, 61.7, 59.6, 59.4, 59.2, 59.0, 58.9, 58.8.

Anal. Calcd. for $C_{61}H_{108}O_{35}$: C, 52.28; H, 7.77. Found: C, 52.40; H, 7.90.

$6^A,6^C$-Dialdehydoheptakis(2,3-di-*O*-methyl)-$6^B,6^D,6^E,6^F,6^G$-penta-*O*-methyl-β-cyclodextrin (**8**) (Scheme I).

A solution of **7** (0.60 g, 0.43 mmole) in 5 ml of methylene chloride was stirred with periodinane (0.81 g, 1.91 mmoles) for 2 hours at 0° and then for 20 hours at room temperature. The mixture was diluted with 20 ml of ethyl ether, poured into ice-cold saturated sodium bicarbonate containing sodium sulfite (2.5 g, 10 mmoles) and shaken for 5 minutes. The organic phase was separated and washed with saturated sodium bicarbonate, water and brine, and then dried and concentrated. Column chromatography on silica gel (chloroform:methanol/80:1) of the residue gave **8** (0.37 g, 62%), mp 92-94°; $[\alpha]_D^{25}$ + 142.7° (c 0.33, chloroform); ^{1}H nmr: δ 9.72 (d, J = 2.1 Hz, 1 H), 9.70 (d, J = 2.1 Hz, 1 H), 5.25-5.05 (m, 7 H), 4.28 (m, 2 H), 3.95-3.10 (m, 93 H); ^{13}C nmr: δ 198.1, 99.4, 99.2, 82.5, 82.4, 82.3, 82.2, 82.1, 82.0, 81.2, 80.9, 80.6, 79.9, 75.3, 71.6, 71.4, 71.3, 71.2, 71.1, 62.0, 61.9, 59.5, 59.4, 59.2, 59.0, 58.9.

Anal. Calcd. for $C_{61}H_{104}O_{35}$: C, 52.43; H, 7.50. Found: C, 52.67; H, 7.73.

$6^A,6^C$-Dideoxy-$6^A,6^C$-dimethyleneheptakis(2,3-di-*O*-methyl)-$6^B,6^D,6^E,6^F,6^G$-penta-*O*-methyl-β-cyclodextrin (**9**) (Scheme I).

A 100-ml three-necked round-bottomed flask equipped with a pressure-equalizing dropping funnel, thermometer, magnetic stirring bar, and serum caps, was charged with 0.28 g (0.69 mmole) of methyltriphenylphosphonium iodide and 10 ml of THF, and then was flushed with argon. The flask was cooled in an ice-bath and the suspension was stirred under a positive pressure of argon. About 30 μl of 2 *M* phenyl lithium in 30:70 ether-cyclohexane was added dropwise until the suspension developed a permanent yellow color. Phenyl lithium (0.35 ml of 2 *M*) was added dropwise over 10 minutes. The ice-bath was removed and the orange suspension containing excess phosphonium salt was stirred at room temperature for 30 minutes. The reaction mixture was stirred and cooled to 0-5° and a solution of **8** (0.32 g, 0.23 mmole) in 10 ml of THF was added dropwise over 10 minutes. The dropping funnel was rinsed with a small amount of THF. The mixture was hydrolyzed by adding 2 ml of methanol and most of the solvent was removed under reduced pressure to give a slurry. The slurry was diluted with 50 ml of ethyl acetate and the suspension was filtered through 5 g of Celite and 5 g of Florisil. The Celite and Florisil were washed with 100 ml of ethyl acetate. Rotary evaporation of the filtrate gave 0.37 g of crude product, which was subjected to silica gel chromatography (chloroform:methanol/80:1) to give **9** (0.145 g, 45%), mp 44-45°; $[\alpha]_D^{25}$ + 139.7° (c 1.45, chloroform); ^{1}H nmr: δ 6.08 (m, 2 H), 5.48-4.95 (m, 11 H), 4.18 (t, J = 7.79 Hz, 2 H), 4.01-3.03 (m, 93 H); ^{13}C nmr: δ 136.8, 136.6, 118.6, 118.4, 99.4, 99.2, 99.1, 98.9, 98.6, 82.9, 82.8, 82.7, 82.3, 82.2, 81.9, 81.5, 81.3, 80.9, 80.3, 79.7, 72.0, 71.9, 71.6, 71.3, 71.1, 70.9, 62.2, 62.1, 62.0,

61.9, 61.8, 61.7, 59.4, 59.1, 59.0, 58.8, 58.7, 58.6.

Anal. Calcd. for $C_{63}H_{108}O_{33}$: C, 54.30; H, 7.81. Found: C, 54.40; H, 8.00.

$6^A,6^D$-Di-*O*-[*p,p'*-methylenebis(benzenesulfonyl)]heptakis(2,3-di-*O*-methyl)-β-cyclodextrin (**10**) (Scheme II).

A solution of **2** (5.99 g, 4.5 mmoles) in 500 ml of dry pyridine was heated under nitrogen and pyridine (*ca.* 40 ml) was distilled to remove traces of water. The solution was cooled to room temperature, and *p,p'*-methylenebis(benzenesulfonyl chloride) (2.0 g, 5.4 mmoles) was added slowly. The mixture was stirred at room temperature for 24 hours. Pyridine was removed by vacuum distillation (0.2 mm, T <40°). A solution of the residue in chloroform was washed with water, then dried and concentrated. The crude product was chromatographed on silica gel (chloroform:methanol/20:1) to give 1.10 g (15%) of **10**, mp 169-170°; $[\alpha]_D^{25}$ + 126.0° (c 1.72, chloroform); ^{1}H nmr: δ 7.82 (overlapping d, J = 8.8 Hz, 4 H), 7.44 (d, J = 8.8 Hz, 2 H), 7.39 (d, J = 8.8 Hz, 2 H), 5.41 (d, J = 3.2 Hz, 1 H), 5.15 (d, J = 3.2 Hz, 1 H), 5.13-5.03 (m, 3 H), 5.03-4.90 (m, 2 H), 4.59-2.92 (m, 86 H), 2.73 (broad s, OH, 5 H); ^{13}C nmr: δ 147.2, 146.8, 134.3, 134.2, 130.8, 130.2, 128.9, 128.4, 99.8, 98.6, 98.4, 82.9, 82.7, 82.4, 82.2, 81.8, 81.4, 81.2, 80.8, 79.8, 76.0, 73.4, 72.8, 72.7, 72.6, 62.1, 62.0, 61.8, 61.6, 61.5, 61.2, 61.1, 60.4, 59.6, 59.4, 59.2, 58.8, 58.5, 58.4, 42.1.

Anal. Calcd. for $C_{69}H_{106}O_{39}S_2$: C, 51.04; H, 6.58. Found: C, 50.78; H, 6.50.

$6^A,6^D$-Di-*O*-*p,p'*-biphenyldisulfonylheptakis(2,3-di-*O*-methyl)-β-cyclodextrin (**11**) (Scheme II).

A solution of **2** (6.75 g, 5.07 mmoles) in 300 ml of pyridine was stirred with *p,p'*-biphenyldisulfonyl chloride (1.78 g, 5.07 mmoles) at room temperature for 24 hours. Pyridine was removed by vacuum distillation (0.2 mm, room temperature). The residue was partitioned between chloroform and water, and the organic layer was separated, washed with water, and dried and concentrated. Column chromatography (chloroform:methanol/20:1) of the residue gave 0.40 g (4.9%) of **11**, mp 170-171° dec; $[\alpha]_D^{25}$ + 122.6° (c 1.80, chloroform); ^{1}H nmr: δ 8.23-7.99 (m, 8 H), 5.35-5.24 (m, 2 H), 5.20 (d, J = 3.2 Hz, 1 H), 4.95 (d, J = 3.2 Hz, 1 H), 4.91 (d, J = 3.2 Hz, 1 H), 4.84 (d, J = 3.2 Hz, 1 H), 4.71 (d, J = 3.2 Hz, 1 H), 4.57-3.00 (m, 84 H), 2.92 (broad s, OH, 5 H); ^{13}C nmr: δ 144.6, 143.9, 137.0, 135.3, 129.1, 129.0, 128.8, 99.1, 99.0, 98.8, 83.0, 82.9, 82.8, 82.7, 82.6, 82.4, 82.3, 81.9, 81.8, 81.7, 81.6, 81.3, 81.2, 81.1, 73.3, 70.7, 70.6, 69.6, 62.3, 62.1, 62.0, 61.8, 61.6, 61.0, 60.8, 60.3, 60.2, 59.0, 58.9, 58.7.

Anal. Calcd. for $C_{68}H_{104}O_{39}S_2$: C, 50.74; H, 6.51. Found: C, 50.49; H, 6.48.

$6^A,6^D$-Di-*O*-[*p,p'*-methylenebis(benzenesulfonyl)]heptakis(2,3-di-*O*-methyl)-$6^B,6^C,6^E,6^F,6^G$-penta-*O*-methyl-β-cyclodextrin (**12**) (Scheme II).

Permethylated bissulfonate ester **12** was prepared as **4** above from 0.45 g (0.28 mmole) of **10**, 0.32 ml (2.78 mmoles) of methyl triflate and 0.86 g (4.17 mmoles) of 2,6-di-*tert*-butyl-4-methylpyridine to give 0.24 g (51%) of **12**, mp 149-151°; $[\alpha]_D^{25}$ + 142.7° (c 1.14, chloroform); ^{1}H nmr: δ 7.89-7.74 (m, 4 H), 7.49-7.35 (m, 4 H), 5.32 (d, J = 3.2 Hz, 1 H), 5.23 (d, J = 3.2 Hz, 1 H), 5.17-4.97 (m, 5 H), 4.67-4.48 (m, 2 H), 4.25 (t, J = 10.4 Hz, 2 H), 4.09 (s, 2 H), 4.04-3.00 (m, 95 H); ^{13}C nmr: δ 147.0, 146.4, 135.8, 135.1, 130.0, 129.8, 129.1, 128.9, 99.8, 99.7, 99.6, 99.0, 98.5, 98.2, 82.7, 82.5, 82.4, 82.2, 81.9, 81.3, 81.2, 80.8, 80.7, 78.6, 76.6, 72.0, 71.7, 71.3, 71.0, 70.8, 70.6, 70.0, 69.9, 62.4, 62.3, 61.8, 61.4, 61.1, 60.4, 59.5, 59.4, 59.2, 58.8, 58.7, 58.4, 58.2, 42.6.

Anal. Calcd. for $C_{74}H_{116}O_{39}S_2$: C, 52.47; H, 6.90. Found: C, 52.29; H, 6.94.

$6^A,6^D$-Di-*O*-*p,p'*-biphenyldisulfonylheptakis(2,3-di-*O*-methyl)-$6^B,6^C,6^E,6^F,6^G$-penta-*O*-methyl-β-cyclodextrin (**13**) (Scheme II).

Permethylated bissulfonate ester **13** was prepared as **4** above from 0.32 g (0.20 mmole) of **11**, 0.33 ml (2.0 mmoles) of methyl triflate and 0.61 g (2.99 mmoles) of 2,6-di-*tert*-butyl-4-methylpyridine to give 0.17 g (51%) of **13**, mp 144-145°; $[\alpha]_D^{25}$ + 118.0° (c 0.91, chloroform); ^{1}H nmr: δ 8.15-7.89 (m, 8 H), 5.28 (d, J = 3.2 Hz, 1 H), 5.22 (d, J = 3.2 Hz, 1 H), 5.12 (d, J = 3.2 Hz, 1 H), 5.02 (d, J = 3.2 Hz, 1 H), 4.94 (d, J = 3.2 Hz, 2 H), 4.73 (d, J = 3.2 Hz, 1 H), 4.32-3.02 (m, 99 H); ^{13}C nmr: δ 144.3, 144.2, 136.9, 135.9, 129.0, 128.8, 128.6, 128.4, 100.2, 99.8, 99.7, 99.3, 99.2, 98.4, 83.1, 82.8, 82.3, 82.1, 81.8, 81.7, 81.4, 81.3, 81.0, 80.4, 78.8, 75.5, 72.9, 72.7, 72.0, 71.9, 71.8, 71.6, 71.3, 71.1, 70.7, 70.4, 69.6, 62.2, 62.0, 61.7, 61.3, 61.0, 60.5, 60.4, 60.0, 59.9, 59.8, 59.6, 59.4, 58.9, 58.8, 58.7, 58.5.

Anal. Calcd. for $C_{73}H_{114}O_{39}S_2$: C, 52.20; H, 6.84. Found: C, 51.98; H, 6.99.

$6^A,6^D$-Di-*O*-(*p*-allyloxyphenyl)heptakis(2,3-di-*O*-methyl)-β-cyclodextrin (**15**) (Scheme II).

A solution of **10** (0.24 g, 0.15 mmole) and 0.25 g (1.5 mmoles) of sodium *p*-allyloxyphenoxide (prepared from sodium hydride and *p*-allyloxyphenol) in 20 ml of DMF was stirred at room temperature for 24 hours and then concentrated under reduced pressure. The residue was partitioned between chloroform and water. The organic layer was separated, dried and concentrated to dryness. The crude product was subjected to column chromatography (chloroform:methanol/20:1) to yield 0.10 g (42%) of **15**, mp 210-212°; $[\alpha]_D^{25}$ + 136.1° (c 0.71, chloroform); ^{1}H nmr: δ 6.91-6.77 (m, 8 H), 6.03 (m, 2 H), 5.36 (m, 4 H), 5.25-4.98 (m, 7 H), 4.45 (d, J = 5.12 Hz, 4 H), 4.40-3.20 (m, 77 H), 3.31-3.05 (m, 7 H), 2.90 (broad s, OH, 5 H); ^{13}C nmr: δ 153.6, 153.3, 134.0, 118.0, 116.2, 116.0, 99.4, 99.1, 98.8, 98.6, 82.6, 82.4, 82.2, 82.0, 81.7, 81.5, 80.9, 80.6, 80.3, 79.2, 72.8, 72.7, 71.2, 69.9, 69.6, 68.4, 62.3, 62.0, 61.8, 61.5, 61.4, 59.5, 59.2, 59.1, 58.9, 58.8.

Anal. Calcd. for $C_{74}H_{114}O_{37}$: C, 55.70; H, 7.20. Found: C, 55.90; H, 6.95.

Compound **15** was also prepared in the same manner from 0.46 g (0.29 mmole) of **11** and 0.50 g (2.86 mmoles) of sodium *p*-allyloxyphenoxide in a 74% yield.

$6^A,6^D$-Di-*O*-(*p*-allyloxyphenyl)heptakis(2,3-di-*O*-methyl)-$6^B,6^C,6^E,6^F,6^G$-penta-*O*-methyl-β-cyclodextrin (**16**) (Scheme II).

A mixture of **15** (0.10 g, 0.063 mmole), methyl triflate (0.071 ml, 0.63 mmole) and 2,6-di-*tert*-butyl-4-methylpyridine (0.19 g, 0.94 mmole) in 5 ml of methylene chloride was stirred in a sealed tube for 2.5 hours at 80°. Methanol (5 ml) was added after the reaction mixture was cooled to room temperature, and stirring was continued for 30 minutes. Evaporation of the above mixture gave a solid which was dissolved in chloroform. The organic layer was washed successively with water, cold 3% hydrochloric acid, aqueous sodium bicarbonate, and water, and then dried and concentrated. Column chromatography of the

crude product gave 0.095 g (91%) of **16**, mp 100-102°; $[\alpha]_D^{25}$ + 127.4° (c 0.46, chloroform); ^{1}H nmr: δ 6.95-6.78 (m, 8 H), 6.03 (m, 2 H), 5.36 (m, 4 H), 5.25-5.00 (m, 7 H), 4.47 (d, J = 5.12 Hz, 4 H), 4.30-3.10 (m, 99 H); ^{13}C nmr: δ 153.6, 153.5, 134.0, 118.0, 116.0, 99.7, 99.6, 99.5, 82.7, 82.5, 82.3, 82.1, 82.0, 80.7, 71.8, 71.6, 71.5, 71.4, 69.9, 69.6, 62.0, 59.5, 59.4, 59.3, 59.1, 58.9.

Anal. Calcd. for $C_{79}H_{124}O_{37}$: C, 56.96; H, 7.50. Found: C, 57.12; H, 7.55.

General Procedure for Preparation of Cyclodextrin-Hexasiloxane Copolymers **17-20** (Scheme III).

The procedure to prepare **17** follows. Alkene **5** (0.14 g, 0.091 mmole) and 0.062 g (0.1 mmole of Si-H) of 1,11-dioctyl-1,3,3,5,5,7,7,9,9,11-decamethylhexasiloxane (redistilled, Silar Laboratories) was placed in 4 ml of toluene in a 50-ml Teflon centrifuge tube. Parafilm was placed around the cap to keep moisture out. The mixture was left in an oil bath for 1 hour at 85-90° and cooled to room temperature. Then 40 µl of 1% chloroplatinic acid (in THF-ethanol) and 2.50 µl (0.016 mmole) of 1-octene were added. The mixture was stirred at 85-90° for 72 hours. The solvent was evaporated under reduced pressure. The residue was dissolved in 10 ml of methylene chloride, followed by 10 ml of methanol and 10 ml of water. The mixture was centrifuged and the water-methanol layer was removed. This process was repeated three more times. The methylene chloride was evaporated and the residue was dried under vacuum for 10 hours at 60° to give 0.165 g (84%) of **17**. The proton nmr spectrum indicated the structure shown in the Scheme III. The other polymers were prepared in a like manner.

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