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ORIGINAL ARTICLE

Inclusion complexes between cyclic siloxanes and cyclodextrins: synthesis and characterization

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Abstract Molecular inclusion complexes between cyclodextrins and cyclic siloxanes were prepared and characterized via a combination of liquid and solid state NMR, FT-IR, TGA, powder X-ray diffraction, SEM–EDS and elemental analyses. The crystalline complexes adopted the channel-type conformation. Depending from the size of both the cyclic sugar cavity and the silicon guest, various yields (between 0 and 41%) and host–guest molar ratios (between 1:1 and 4:1) were obtained. α-cyclodextrin (α-CD) and β-cyclodextrin (β-CD) were observed to form crystalline inclusion complexes only with D_3 (cyclic dimethyltrisiloxane) due to steric effects, whereas the larger γ-cyclodextrin (γ-CD) formed inclusion complexes both with D_3, D_4 (cyclic dimethyltetrasiloxane) and D_5 (cyclic dimethylpentasiloxane). This study is believed to be the first step towards the selective removal of cyclic siloxanes impurities from commercial PDMS preparations.

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Introduction

Cyclodextrins (CDs) are a series of cyclic oligosaccharides composed of repeating units of glucose produced from the enzymatic conversion of starch. The three most frequently used CDs are composed of six, seven and eight sugar units and are named α-, β-, and γ-CD, respectively. CDs are known to form inclusion complexes with various low molecular weight compounds [1, 2]. Due to their hydrophilic outer layer and hydrophobic interior, CDs have been largely employed for the formation of supramolecular assembly between the cyclic sugars and hydrophobic guests, including steroids [3, 4], drugs such as β-blockers [5], furosemide [6], ketoprofen [7] and indomethacin [8], as well as other small molecules [9]. On the other hand, many reports have demonstrated the ability of CDs to form molecular inclusion complexes with organic polymers, including polyethylene glycol [10, 11], poly-(iminooligomethylene)s [12], polyacrylonitrile [13], poly(*N*-acetylethyleneimine) [14], poly(ε-lysine) [15] and polyisobutylene [16]. More recently, novel organic–inorganic hybrids have been reported where CDs formed inclusion complexes with inorganic polymers. In particular, the group of Harada has described the preparation and characterization of inclusion complexes of CDs with polydimethylsiloxanes (PDMS) [17, 18] and poly(dimethylsilane)s (PSI) [19, 20]. Consequently, it appears that organosilicon compounds are acceptable substrates for host–guest interactions with CDs.

In this work, we report the synthesis of inclusion complexes of CDs with cyclic dimethylsiloxanes (i.e. D_3–D_5). The obtained complexes were isolated and characterized

via a combination of analytical techniques including liquid and solid state NMR, FT-IR, TGA, powder X-ray diffraction, elemental and surface analysis. A successful complexation would be the first step towards the removal of cyclic siloxanes impurities from linear PDMS in commercial preparations, which is a specific challenge for today's silicone industry.

Experimental section

Materials

Solvents were from Fisher Scientific (Loughborough, UK). α-cyclodextrin, β-cyclodextrin and γ-cyclodextrin were purchased from Sigma-Aldrich (Poole, UK). Hexamethylcyclotrisiloxane (D_3), octamethylcyclotetrasiloxane (D_4) and decamethylcyclopentasiloxane (D_5) were supplied from Ohio Valley Specialty Chemical (Marietta, OH). Ultra high purity water (UHP) was obtained from a Milli-Q system at The Open University (Milton Keynes, UK).

Measurements

Scanning electron microscopy (SEM) images were acquired at Dow Corning Corporation (Midland, MI) on a JEOL JSM-6335 FESEM instrument. Images were acquired at various magnifications using 5 kV accelerating voltage. A Noran Vantage energy dispersive spectroscopy (EDS) system attached to a JOEL JSM-6100 SEM instrument was used to conduct the elemental analyses. EDS spectra were individually collected on various particles for 100 s with 15 kV accelerating voltage. Liquid state NMR spectra were obtained using a JEOL EX 400 NMR spectrometer fitted with multinuclear probes. All spectra were recorded at room temperature (20 °C) using deuterated solvents. The internal NMR reference compound was TMS, unless it interfered with the product peaks. Where this was the case, the residual solvent peak was used as the standard. Cross-polarization magic angle spinning spectra were run by the EPSRC solid-state NMR service at Durham University (UK). They were obtained using a Varian VNMRS spectrometer equipped with a 7.5 mm (rotor o.d.) probe and operating at 100.56 MHz for ^{13}C NMR and a Unity Inova spectrometer operating at 59.56 MHz for ^{29}Si. The external reference compound was TMS for ^{13}C and ^{29}Si NMR spectra. The Fourier transform infrared (FT-IR) analysis was conducted on a Perkin Elmer 1710 infrared Fourier transform spectrometer. Thermogravimetric analyses (TGA) were performed by heating approximately 25 mg of material in an alumina pan from room temperature to 400 °C at 10 °C/min under a N_2 atmosphere in a Rheometric Scientific Simultaneous Thermal Analyzer.

Synthesis of cyclodextrins-cyclic PDMS inclusion complexes

Preparation of α-cyclodextrin-D_3 inclusion complex

D_3 (0.111 g, 0.5 mmol) was put into a centrifuge tube. A saturated solution of α-cyclodextrin (0.486 g, 0.5 mmol) in UHP water (14.7 mL) was added at room temperature, and the mixture was sonicated in a sonic bath for 1 h and then allowed to stand overnight at room temperature. The mixture appeared clear as there was no complexation at all; however, after further sonication and centrifugation, a white solid precipitated. The solid collected by centrifugation was dried under vacuum at room temperature, then washed with THF (5 mL) to remove unreacted D_3, dried under vacuum, washed with water (10 mL) to remove uncomplexed cyclodextrin, and finally dried under vacuum for 24 h over silica gel.

The complex was observed to form more easily by mixing equimolar amounts of α-cyclodextrin and D_3 dissolved in water and hexane, respectively. The biphasic mixture was sonicated for half an hour, and the resultant solid was filtered and washed with copious amounts of THF and water, and finally dried for 24 h in vacuo over silica gel.

Yield 13%. ^1H NMR (pyridine-d_5, 300 MHz): δ 5.68 (*d*, 6H, *J* 3.3, C_1**H** of α-CD), 4.83 (*t*, 6H, *J* 9.3, C_3**H** of α-CD), 4.54 (*m*, 18H, C_5**H** and C_6**H** of α-CD), 4.30 (*t*, 6**H**, *J* 9.3, C_2**H** of α-CD), 4.15 (*m*, 6H, C_4**H** of α-CD), 0.24 (*s*, 18H, methyl **H** of D_3). CP MAS ^{13}C NMR (100.56 MHz): δ 104.7 (**C_1** of α-CD), 81.7 (**C_4** of α-CD), 74.0 (**C_2**, **C_3** and **C_5** of α-CD), 61.6 (**C_6** of α-CD) and 3.7 (**C**H_3 of D_3) ppm. ^{29}Si MAS (59 MHz): δ −8.9 ppm.

FT-IR (KBr disk): 3391 (ν_s, O–H), 2929 (ν_s, C–H), 1260 (ν_{as}, Si–C), 1157, 1080, 1029 (ν_s, C–O), 1029 (ν_s, Si–O) and 820 (ν_s, Si–C) cm^{-1}. Calculated for $(C_{36}H_{60}O_{30})_{2.0}(C_6H_{18}Si_3)_{1.0}(H_2O)_9$:C, 40.20; H, 6.75. Found: C, 40.09; H, 6.77%.

Preparation of β-cyclodextrin-D_3 inclusion complex

D_3 (0.159 g, 0.72 mmol) was put into a centrifuge tube. A saturated solution of β-cyclodextrin (0.816 g, 0.72 mmol) in UHP water (44.1 mL) was added at room temperature and the mixture was sonicated in a sonic bath for 1 h and then allowed to stand overnight at room temperature. The precipitated product was collected by centrifugation and dried under vacuum at room temperature, washed with THF (10 mL) to remove unreacted D_3 and dried under vacuum, washed with water (20 mL) to remove uncomplexed cyclodextrin, and finally dried under vacuum for 24 h over silica gel.

Yield 41%. ^1H NMR (pyridine-d_5, 300 MHz): δ 5.69 (*d*, 7H, *J* 3.3, C_1**H** of β-CD), 4.83 (*t*, 7H, *J* 9.3, C_3**H** of β-CD),

4.54 (*m*, 21H, $C_5\mathbf{H}$ and $C_6\mathbf{H}$ of β-CD), 4.30 (*t*, 7H, *J* 9.3, $C_2\mathbf{H}$ of β-CD), 4.15 (*m*, 7H, $C_4\mathbf{H}$ of β-CD), 0.24 (*s*, 18H, methyl **H** of D_3). CP MAS ^{13}C NMR (100.56 MHz): δ 103.9 ($\mathbf{C_1}$ of β-CD), 80.9 ($\mathbf{C_4}$ of β-CD), 73.4 ($\mathbf{C_2}$, $\mathbf{C_3}$ and $\mathbf{C_5}$ of β-CD), 61.1 ($\mathbf{C_6}$ of β-CD) and 3.0 ($\mathbf{C}H_3$ of D_3) ppm. ^{29}Si MAS (59 MHz): δ −8.9 ppm.

FT-IR (KBr disk): 3392 (ν_s, O–H), 2928 (ν_s, C–H), 1260 (ν_{as}, Si–C), 1158, 1080, 1029 (ν_s, C–O), 1029 (ν_s, Si–O) and 820 (ν_s, Si–C) cm^{-1}. Calculated for $(C_{42}H_{70}O_{35})_{2.0}(C_6H_{18}O_3Si_3)_{1.0}(H_2O)_7$:C, 41.28; H, 6.62. Found: C, 41.34; H, 6.62%.

Preparation of γ-cyclodextrin-D_3 inclusion complex

D_3 (0.054 g, 0.24 mmol) was put into a centrifuge tube. A saturated solution of γ-cyclodextrin (0.311 g, 0.24 mmol) in UHP water (1.34 mL) was added at room temperature, and the mixture sonicated in a sonic bath for half an hour and then allowed to stand overnight at room temperature. The precipitated product was collected by centrifugation, dried under vacuum at room temperature, and then washed with THF to remove unreacted D_3, dried under vacuum, washed with water in order to remove uncomplexed cyclodextrin, and finally dried under vacuum for 24 h over silica gel.

Yield 33%. ^{1}H NMR (pyridine-d_5, 300 MHz): δ 5.73 (*d*, 8H, *J* 3.6, $C_1\mathbf{H}$ of γ-CD), 4.64 (*t*, 8H, *J* 9.3, $C_3\mathbf{H}$ of γ-CD), 4.37 (*m*, 24H, $C_5\mathbf{H}$ and $C_6\mathbf{H}$ of γ-CD), 4.28 (*m*, 8H, $C_2\mathbf{H}$ of γ-CD), 4.09 (*m*, 8H, $C_4\mathbf{H}$ of γ-CD), 0.24 (*s*, 18H, methyl **H** of D_3). CP MAS ^{13}C NMR (100.56 MHz): δ 104.3 ($\mathbf{C_1}$ of γ-CD), 82.0 ($\mathbf{C_4}$ of γ-CD), 72.9 ($\mathbf{C_2}$, $\mathbf{C_3}$ and $\mathbf{C_5}$ of γ-CD), 61.1 ($\mathbf{C_6}$ of γ-CD) and 1.6 (CH_3 of D_3) ppm. ^{29}Si MAS (59 MHz): δ −9.1 ppm.

FT-IR (KBr disk): 3434 (ν_s, O–H), 2925 (ν_s, C–H), 1262 (ν_{as}, Si–C), 1159, 1081, 1027 (ν_s, C–O), 1027 (ν_s, Si–O), 810 (ν_s, Si–C) and 583 (ν_s, Si–O) cm^{-1}. Calculated for $(C_{48}H_{80}O_{40})_{1.0}(C_6H_{18}O_3Si_3)_{1.0}(H_2O)_4$:C, 40.75; H, 6.71. Found: C, 40.13; H, 6.51%.

Preparation of γ-cyclodextrin-D_4 inclusion complex

D_4 (0.07 g, 0.24 mmol) was put into a centrifuge tube. A saturated solution of γ-cyclodextrin (0.311 g, 0.24 mmol) in UHP water (1.34 mL) was added at room temperature, and the mixture sonicated in a sonic bath for approximately 20 min, then allowed to stand overnight at room temperature. The precipitated product was collected by centrifugation, dried under vacuum at room temperature, and then washed with THF to remove unreacted D_4, dried under vacuum, washed with water to remove uncomplexed cyclodextrin, and finally dried under vacuum for 24 h over silica gel.

Yield 38%. ^{1}H NMR (pyridine-d_5, 300 MHz): δ 5.74 (*d*, 8H, *J* 3.3, $C_1\mathbf{H}$ of γ-CD), 4.64 (*t*, 8H, *J* 9.6, $C_3\mathbf{H}$ of γ-CD), 4.38 (*m*, 24H, $C_5\mathbf{H}$ and $C_6\mathbf{H}$ of γ-CD), 4.28 (*m*, 8H, $\mathbf{C_2H}$ of γ-CD), 4.09 (*m*, 8H, $C_4\mathbf{H}$ of γ-CD), 0.22 (*s*, 24H, methyl **H** of D_4). CP MAS ^{13}C NMR (100.56 MHz): δ 104.2 ($\mathbf{C_1}$ of γ-CD), 82.1 ($\mathbf{C_4}$ of γ-CD), 73.2 ($\mathbf{C_2}$, $\mathbf{C_3}$ and $\mathbf{C_5}$ of γ-CD), 60.6 ($\mathbf{C_4}$ of γ-CD) and 1.8 ($\mathbf{C}H_3$ of D_4) ppm. ^{29}Si MAS (59 MHz): δ −20.1 ppm.

FT-IR (KBr disk): 3434 (ν_s, O–H), 2924 (ν_s, C–H), 1262 (ν_{as}, Si–C), 1160, 1081, 1026 (ν_s, C–O), 1026 (ν_s, Si–O), 815 (ν_s, Si–C) and 582 (ν_s, Si–O) cm^{-1}. Calculated for $(C_{48}H_{80}O_{40})_{3.0}(C_8H_{24}O_4Si_3)_{1.0}(H_2O)_{16}$:C, 41.04; H, 6.71. Found: C, 40.02; H, 6.68%.

Preparation of γ-cyclodextrin-D_5 inclusion complex

D_5 (0.266 g, 0.72 mmol) was put into a centrifuge tube. A saturated solution of γ-cyclodextrin (0.933 g, 0.72 mmol) in UHP water (4.02 mL) was added at room temperature, and the mixture sonicated for 20 min in a sonic bath, then allowed to stand overnight at room temperature. The resulting complex was isolated by centrifugation, dried under vacuum at room temperature, and then washed with THF to remove unreacted D_5, dried under vacuum, washed with water to remove uncomplexed cyclodextrin, and finally dried under vacuum for 24 h over silica gel.

Yield 11%. ^{1}H NMR (pyridine-d_5, 300 MHz): δ 5.74 (*d*, 8H, *J* 3.0, $C_1\mathbf{H}$ of γ-CD), 4.64 (*t*, 8H, *J* 8.7, $C_3\mathbf{H}$ of γ-CD), 4.38 (*m*, 24H, $C_5\mathbf{H}$ and $C_6\mathbf{H}$ of γ-CD), 4.29 (*m*, 8H, $C_2\mathbf{H}$ of γ-CD), 4.09 (*m*, 8H, $C_4\mathbf{H}$ of γ-CD), 0.22 (*s*, 24H, methyl **H** of D_4). CP MAS ^{13}C NMR (100.56 MHz): δ 104.2 ($\mathbf{C_1}$ of γ-CD), 82.5 ($\mathbf{C_4}$ of γ-CD), 73.2 ($\mathbf{C_2}$, $\mathbf{C_3}$ and $\mathbf{C_5}$ of γ-CD), 60.5 ($\mathbf{C_6}$ of γ-CD) and 2.3 ($\mathbf{C}H_3$ of D_5) ppm. ^{29}Si MAS (59 MHz): δ −20.5 ppm.

FT-IR (KBr disk): 3433 (ν_s, O–H), 2921 (ν_s, C–H), 1262 (ν_{as}, Si–C), 1159, 1081, 1026 (ν_s, C–O), 1026 (ν_s, Si–O), 811 (ν_s, Si–C) and 581 (ν_s, Si–O) cm^{-1}. Calculated for $(C_{48}H_{80}O_{40})_{4.0}(C_{10}H_{30}O_5Si_5)_{1.0}(H_2O)_{16}$:C, 41.49; H, 6.58. Found: C, 41.50; H, 6.68%.

Results and discussion

Figure 1 illustrates the structures of the three cyclosiloxanes employed in this study.

When cyclic PDMS compounds were added to aqueous solutions of CDs and the mixtures sonicated at room temperature for an appropriate amount of time, the heterogeneous solutions became turbid, and the complexes formed as crystalline precipitates (when complex formation was observed). CDs are normally water soluble, however, when a siloxane complex was formed, it precipitated out from the solution, confirming the formation of a new species, a supramolecular non-covalent assembly. Given the relatively low yield obtained for some of the formed inclusion complexes, it is reasonable to hypothesize

that soluble inclusion complexes may have formed, too. However, the potential formation of soluble macromolecular assemblies was not further investigated as it fell outside the scope of this study, namely the isolation of crystalline CD-cyclosiloxane inclusion compounds. The precipitated complexes were isolated by centrifugation and dried under vacuum. Thereafter, they were washed with THF to remove free (uncomplexed) silicon materials and dried under vacuum, and finally washed with water to remove free (uncomplexed) CDs and dried under vacuum.

Table 1 details some properties of the obtained complexes. Table 1 shows that α- and β-CDs only formed complexes with D_3, whereas no complex formation was observed with D_4 and D_5. Γ-CD was found to be able to complex all three cyclic compounds. It appears that the cavities of the two smaller CDs are only large enough to accommodate the cyclic trimer, whereas the cavity of γ-CD is large enough to host the cyclic tetramer and pentamer as well.

From the ^{1}H NMR and elemental analyses it was possible to estimate the stoichiometry of the complexes. Specifically, the yields were based on comparing the integrals of C1-H of the CDs and the methyl protons of the cyclic siloxanes. The molar ratio between CDs and guest units was calculated in a similar manner as was the determination of yield. As shown in Table 1, more than one CD unit was necessary to complex one molecule of cyclic siloxane, depending on the type of sugar and the cyclic oligomer used. The α-D_3 complex was obtained in a lower yield compared to the β-D_3 and γ-D_3 complexes. The smaller cavity diameter of the six-membered cyclic oligosaccharide may account for the poor yield, owing to the steric hindrance of the dimethyl groups of the siloxane molecule. The steric argument was also used to explain why there was no complex formation between the β-CD and D_4 and D_5. However, the β-CD did form a complex with D_3 with the highest yield observed in this study. β-CD is the most commonly used cyclic sugar within the class, for cost reasons and because it usually forms complexes with very high binding constants. In our study, it appears that β-CD-D_3 is the most stable complex formed, probably because it involves the optimum distances, and therefore interactions, between host and guest in the hybrid assembly. Finally, γ-CD showed complexation with all of the cyclics added, with yields and stoichiometries varying according to the cyclic siloxane used.

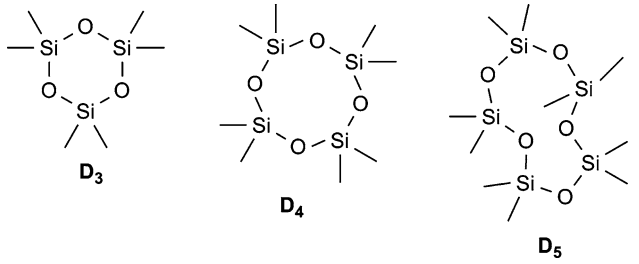

Fig. 1 Structures of the guest cyclic-siloxanes used in this study

Table 1 Complex formation between cyclic PDMS and CDs

Yield %				Molar ratio (CD to cyclic)		
Cyclic	α-CD	β-CD	γ-CD	α-CD	β-CD	γ-CD
D_3	13%	41%	33%	2:1	2:1	1:1
D_4	0	0	38%	/	/	3:1
D_5	0	0	11%	/	/	4:1

Estimated from ^{1}H NMR spectra

To fully characterize the complexes and to investigate the mode of complexation of the silicon compounds in the CDs, the inclusion complexes were analyzed using FT-IR, TGA, powder X-ray diffraction, solid-state NMR and SEM. FT-IR is a useful tool to confirm the presence of both guest and host components in the inclusion complex [21]. The FT-IR spectra of D_5, γ-CD and the crystalline inclusion complex between γ-CD and D_5 are presented in Fig. 2. A number of bands arising from the host and guest appeared to be affected by the formation of the inclusion complex, leading to changes of band position and relative intensities. For example, the band at 3,392 cm^{-1} due to the

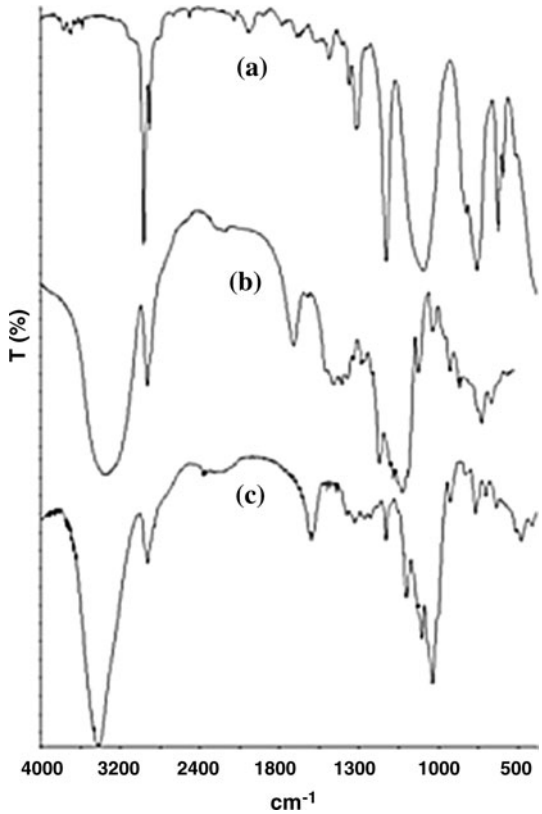

Fig. 2 FT-IR spectra of **a** D_5, **b** γ-CD and **c** γ-D_5 complex

symmetric and antisymmetric O–H stretching mode of the γ-CD is shifted to a higher frequency at 3,433 cm^{-1} in the inclusion complex. Moreover, the sharp and intense band at 1,261 cm^{-1} of the pure D_5, which is attributed to the symmetric C–H deformation of the methyl groups, can also be found in the crystalline inclusion complex, but it is absent in the pure cyclodextrin material. Other bands present in the cyclic siloxane, such as the peak at 805 cm^{-1}, are incorporated in the complex, suggesting that the silicon compound is included in the solid material.

The TGA thermograms for pure γ-CD and the inclusion complexes between D_4 and D_5 with γ-CD are shown in Fig. 3. Further TGA curves are also reported in the ESM.

The samples were subjected to thermal treatment at a heating rate of 10 °C/min between 25 and 400 °C. It can be seen that at around 100 °C there was a small loss of weight. This was attributed to the evaporation of the water that is always present in the cyclodextrins and in the hydrated complexes. However, pure cyclodextrin appeared to contain larger amount of water than the complexes. Although cyclodextrins and their complexes were dried in a vacuum oven in a similar manner, pure cyclodextrins seemed to contain more structural water than the host–guest hybrid complexes. We propose that, upon inclusion of the hydrophobic silicon compounds, the high enthalpy water molecules present in the host cavity are displaced, driving the formation of the complex. Furthermore, the complexes were thermally stable, and decomposed at around or above 300 °C, depending on the guest included. However, we did not observe any further loss of weight between 100 and 300 °C, which is the region in which the D_4 and D_5 boiling points fall (i.e. 175 and 209 °C, respectively). Therefore, it appears that the siloxane substrates are occluded and surrounded by cyclodextrin molecules, rather than the materials being simple physical mixtures of the hosts and guests.

The crystal structures of the CD-inclusion complexes can be of two types: channel and cage structures [1]. In the channel-type complexes CD molecules are stacked on top of each other like "coins in a roll", with the various CDs stabilized through hydrogen bonds in a head-to-head or head-to-tail fashion. This is the most typical conformation adopted by supramolecular assemblies when polymers are included in CD cavities. Pure CDs are normally arranged in the cage type, where each cavity is blocked off on both sides by adjacent CDs. Powder X-ray diffraction (PXRD) patterns were taken at room temperature using CuKα irradiation. The PXRD patterns of the pure cyclodextrins and some of the inclusion complexes are displayed in Fig. 4. The results confirm that the inclusion complexes formed are crystalline. Moreover, the appearance of a strong peak at 2-Θ 18 in the inclusion complexes and comparison of our data with some previously reported X-ray patterns [18, 20, 22, 23] suggest that the complexes adopt head-to-head channel-type structures. The reflection peaks of the CD-cyclic siloxane complexes are similar to the literature data for channel-type complexes, and differ

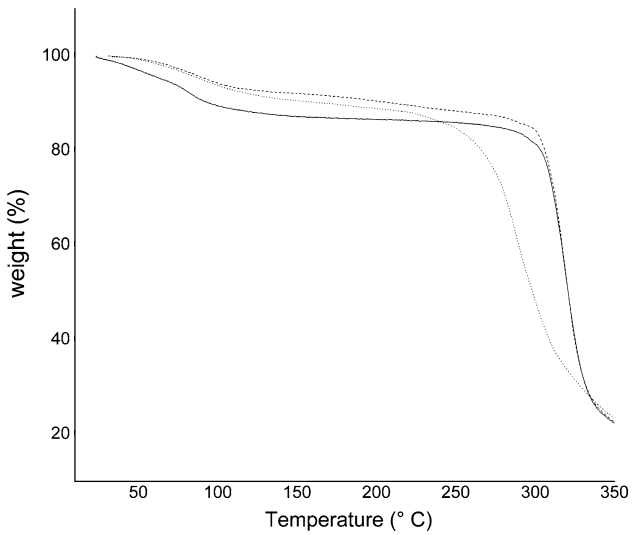

Fig. 3 TGA scans of γ-CD (*solid line*) and the inclusion complexes between D_4 (*dot line*) and D_5 (*dash line*) with γ-CD

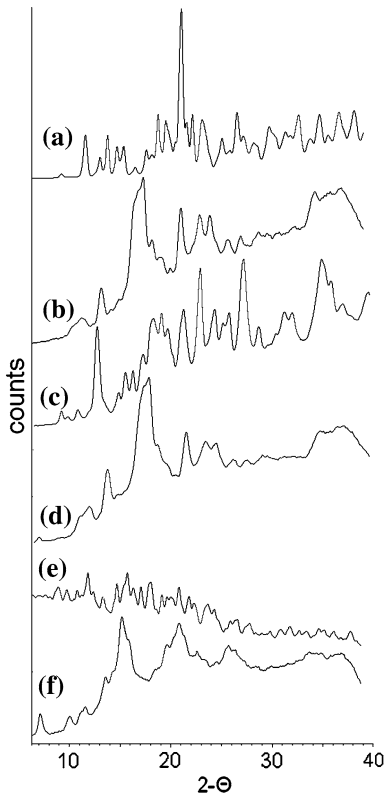

Fig. 4 Powder X-ray diffraction patterns for **a** α-CD, **b** α-D_3 complex, **c** β-CD, **d** β-D_3 complex, **e** γ-CD, **f** γ-D_5 complex

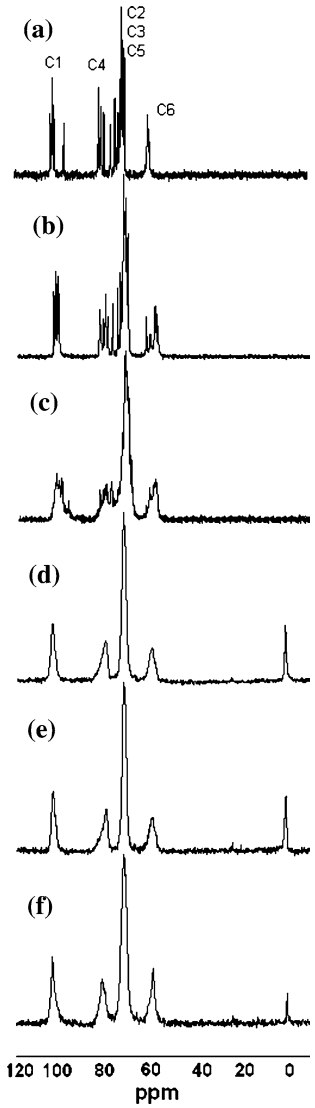

Fig. 5 ^{13}C CP MAS NMR of **a** α-CD, **b** β-CD, **c** γ-CD, **d** α-D_3 complex, **e** β-D_3 complex, **f** γ-D_5 complex

from the simple corresponding CDs, which are arranged in a cage-type packing.

Solid-state NMR was also used to study the inclusion modes of the complexes. Figure 5 shows the ^{13}C CP MAS NMR of the pure cyclodextrins and some of the inclusion complexes obtained when the cyclic PDMS were added to the aqueous CD solutions. Further NMR spectra are provided in the ESM.

The ^{13}C NMR resonances of the pure CDs gave multiplet lines because of the asymmetric glucopyranosyl conformations (cage-type arrangement). Conversely, the signals of the inclusion complexes appeared as broad but resolved singlets, suggesting that in this case the CDs are more ordered and symmetrically disposed when the host–guest complexes are formed. These results further supported the point that CDs formed channel-type complexes

Table 2 Chemical shift differences between isolated versus CD-included cyclics

Compound	^{13}C (ppm)	$\Delta^{13}C$ (ppm)	^{29}Si (ppm)	$\Delta^{29}Si$ (ppm)
D_3	1.63	/	−9.12	/
α-D_3	3.73	2.1	−8.95	−0.17
β-D_3	3.04	1.41	−8.95	−0.17
γ-D_3	1.99	0.36	−9.17	−0.05
D_4	0.65	/	−19.71	/
γ-D_4	1.38	0.73	−20.14	−0.43
D_5	0.77	/	−22.1	/
γ-D_5	2.36	1.59	−20.52	−1.58

The difference is calculated between the chemical shift of each cyclic in a complex and that of the corresponding neat cyclic

with cyclic siloxane molecules. Moreover, the data are in accordance with previous reports about the inclusion of linear PDMS [18, 23] and poly(dimethyl)silanes [20] (as well as many other channel-type complexes) in CD cavities.

It was also observed that the resonances of the cyclic siloxanes in the ^{13}C and ^{29}Si solid-state NMR spectra were shifted when compared to pure cyclic monomers, as detailed in Table 2. The observed shifts in the NMR resonances further supported the hypothesis that the silicon guests were included in the cavities of the cyclodextrins. In particular, the ^{13}C NMR resonances shifted downfield when the inclusion complexes were formed, whereas only slight upfield shifts were seen in the ^{29}Si resonances.

The downfield shifts in the cyclic PDMS carbons were attributed to the deshielding effect of the CD oxygens when the methyl groups of the cyclic siloxanes enter into the CD cavities. A similar explanation may be given for the observed changes in the ^{29}Si resonance. However, only small differences were seen in this case, as the silicon atoms would be further away from the CD oxygens. Furthermore, the downfield shifts of the D_3 complexes decreased from the six- to the eight-membered sugar rings. This can be attributed to the increasing distance between the methyl groups of the silicon guest and the oxygens of the internal torus of α-, β- and γ-CDs, respectively.

Finally, surface analysis was conducted to investigate the morphology of the formed inclusion complexes. Pure cyclodextrins have been reported to consist of highly irregular shaped particles [5–7]. As shown in Fig. 6, the cyclic siloxanes-CDs inclusion complexes appeared as tight agglomerates of mainly parallelepipedic-shape microparticles, suggesting the presence of a main single species (inclusion complex) in the crystalline materials. EDS spectra (ESM) revealed the presence of carbon, oxygen and silicon, as expected from the presence of both the organometallic and the organic phases.

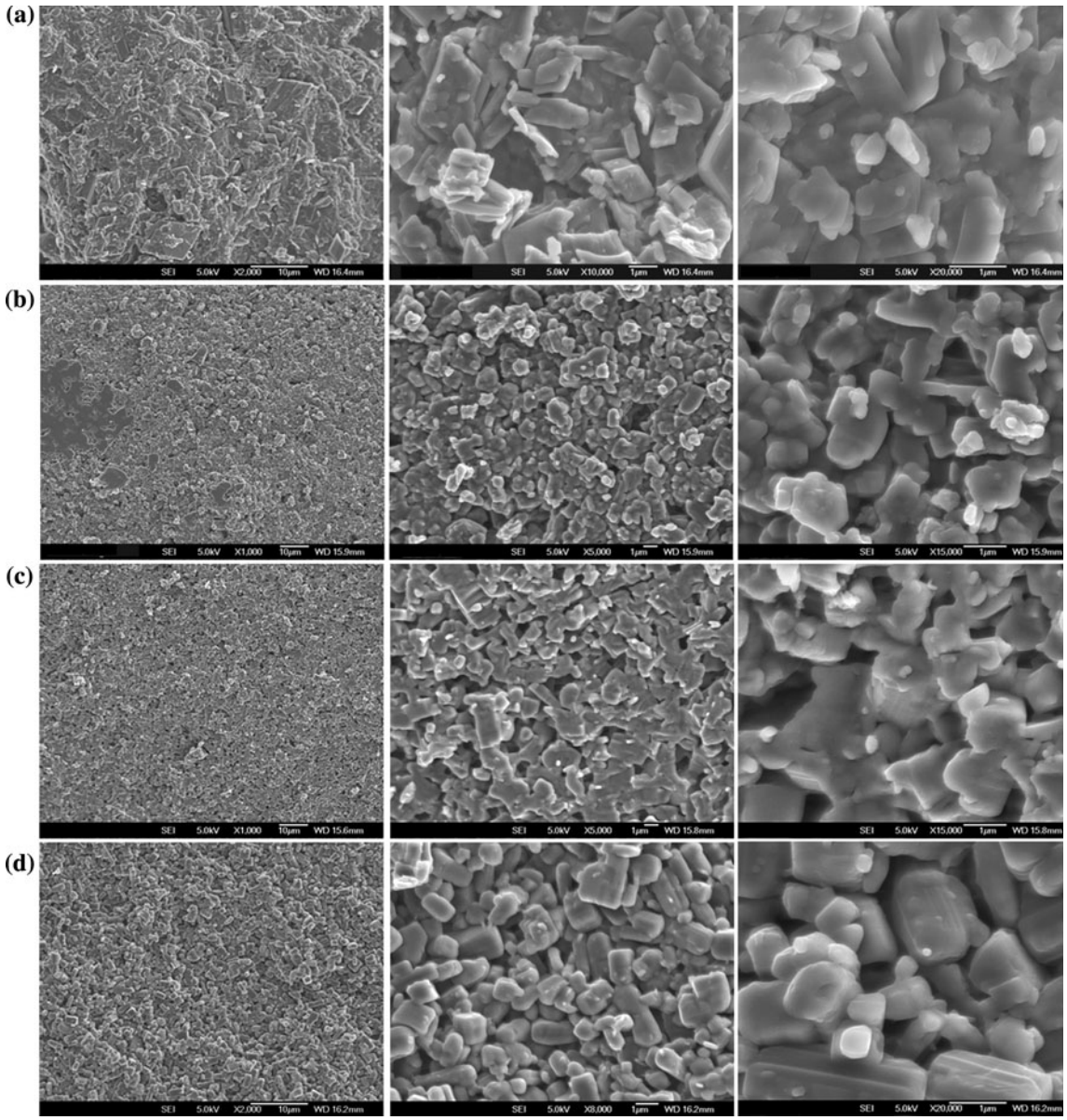

Fig. 6 SEM images of: β-D_3 complex (*row a*); γ-D_3 complex (*row b*); γ-D_4 complex; (*row c*). γ-D_5 complex (*row d*)

Conclusion

Cyclic dimethylsiloxanes formed molecular inclusion complexes with cyclodextrins. TGA, NMR and powder X-ray results suggested that the silicon guests are included in the CD cavities. The supramolecular assemblies arranged into head-to-head channel complexes. CDs were previously observed to form inclusion complexes with linear PDMS [18, 23], PSI [20], and many other organic and inorganic polymers. In order to selectively remove cyclic siloxanes impurities from commercial linear PDMS products, a further step was necessary in which a molecular imprinting approach was used to fabricate tailor-made organo silicon receptors; the study will be reported in a subsequent paper.

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