Switching of Optical Activity in Oligosilane through pH-Responsive Chiral Wrapping with Amylose

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ABSTRACT: The chiral supramolecular complexation between amylose and oligosilane can be reversibly controlled by changing the pH, leading to a switching of the optical activity. Further, the induction of optical activity in oligosilane, synchronized with the supramolecular complexation, is reversible, as shown by data from pH cycling experiments.

Introduction

Control of the chirality of molecules is an important topic in chemistry. Chirality is observed at different hierarchical levels: from molecular to macromolecular and supramolecular systems. In recent years, research into the design and synthesis of optically active macro- and supramolecules has advanced and has promoted great interest in their relationship with biological phenomena and in their potential application in materials science, including as chiral selectors for separation, as catalysts, as adsorbents, and, especially, as chiroptical materials.[1] For example, in chiral supramolecular systems, besides the presence of chiral molecules, achiral molecules can also contribute to the supramolecular chirality through diastereoselective supramolecular interactions with the chiral molecules. These arise due to the induction of a helical conformation of preferred chirality as a result of the interaction.[2] In designing new functional materials, the control of chirality in response to an external stimulus, such as temperature, pH, and solvent, is particularly interesting.[3,4] Such systems would mimic biological phenomena and provide chiroptical materials for switching and memory devices.[5] In this work, we discuss a unique system exhibiting a pH-responsive switching of optical activity. This is based on the molecular communication through a supramolecular complexation between a helical polymer and a guest molecule, as illustrated in Figure 1. A change in pH of the medium causes a significant conformational change of the host polymer, which, depending on the pH value, results in either a supramolecular complexation with the guest molecules to induce optical activity or decomplexation leading to the loss of optical activity.

Experimental Section

Measurements. ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded using a Bruker DPX 300 FT-NMR spectrometer at 300, 75.4, and 59.6 MHz, respectively. The ^{1}H and ^{13}C chemical shifts were referenced to solvent residues (^{1}H, $\delta = 7.24$ ppm and ^{13}C, $\delta = 77.0$ ppm for $CDCl_3$). The ^{29}Si chemical shift was referenced to an external Me_4Si (0 ppm) reference. Gas−liquid chromatography data were recorded using a Shimadzu GC-8A chromatograph. Cross-polarization magic angle spinning (CP-MAS) ^{13}C and ^{29}Si NMR spectra were measured at 67 and 53.5 MHz, respectively, using a JEOL Excalibur 270 spectrometer. Gel permeation chromatography was performed using a Shimadzu LC 10 HPLC equipped with PL-gel mixed-C columns calibrated using a polystyrene standard with a DMAc/5% LiCl solution as the eluent. X-ray diffraction patterns were recorded using a Rigaku RAXIS-IIc X-ray diffractometer. UV spectra were recorded using an HP Agilent 8453 spectrometer. CD spectra were obtained using a JASCO J-820 spectrometer using 1 cm quartz cells, with the following scanning conditions: scan rate = 50 nm/min; bandwidth = 2.0 nm; response time = 1 s; and number of accumulations = 2.

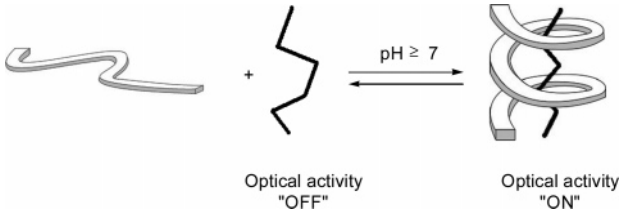

Figure 1. Schematic illustration of pH-dependent diastereoselective supramolecular complexation with a helical polymer.

Materials. All the solvents and reagents used were of reagent grade, purchased from commercial sources, and used without further purification unless otherwise noted below. The amylose used was obtained from Aldrich Chemicals. The number-average molecular weight (M_n) and the polydispersity index (M_w/M_n) of the amylose were $M_n = 5.8 \times 10^4$ and 1.7, respectively. The permethylhexasilane (PMHS) used was prepared according to a previously reported procedure.[6] The water used was purified using a Millipore Milli-Q system.

Molecular Modeling. Monte Carlo searches for minimum-energy conformations were performed using the HyperChem 7.5[7] and the AMBER force field software modeling packages.[8]

Carboxymethylation of Amylose.[9] Amylose (2.0 g) was dissolved in degassed 2 N NaOH (40 mL) solution. A solution (60 mL) of NaOH (38.0 g) was then added to form a 10 N solution. Subsequently, chloroacetic acid (0.94 g, 9.89 mmol) was added, and the mixture stirred for 18 h to form a white precipitate. After neutralization with HCl and filtration, the filtrate was dialyzed against water for 6 days. Then, the solution was concentrated and freeze-dried to give partially carboxymethylated amylose (CMA) as a white powder (1.52 g, 76%). The degree of substitution (DS) was found to be DS = 0.36 based on data obtained on titration of a solution of the sample in 0.01 M NaOH(aq) with a standard solution of 0.01 M HCl(aq).

Inclusion Complex with CMA and PMHS. A typical example of complex formation is as follows (pH = 8.3). A mixture of carboxymethylated amylose (CMA, 1.46 mg, 8.0×10^{-3} mmol glucose unit) in aqueous NaOH solution (1.0×10^{-4} M, 5 mL) was dispersed ultrasonically for 3 min and then stirred for 1 h.

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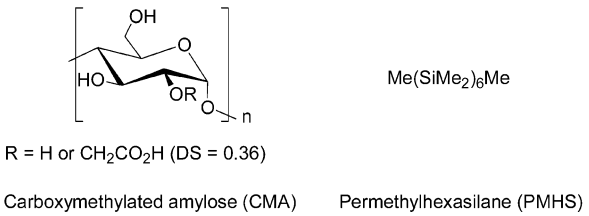

Figure 2. Chemical structures of the host (carboxymethylated amylose, CMA) and guest (permethylhexasilane, PMHS) molecules.

PMHS (0.19 mg, 5.0×10^{-4} mmol) was then added to the aqueous solution. The mixture was dispersed ultrasonically for 5 min and then stirred at room temperature for 2 h. After the addition of hexane (3 mL) to extract the noncomplexed oligosilane remaining in the reaction mixture, the aqueous layer and the hexane layer were subjected to spectroscopic measurements. The percentage of noncomplexed PMHS extracted from the aqueous layer to the hexane layer was calculated from the absorbance data based on the molar absorptivity of PMHS in hexane. The pH of the aqueous layer was monitored using a pH meter.

To isolate the complex, an aqueous NaOH solution (1.0×10^{-4} N) of CMA (154 mg, 0.844 mmol) and PMHS (21 mg, 0.055 mmol) was dispersed ultrasonically for 5 min, and then the mixture was stirred at room temperature for 7 days. The white precipitate product was collected by centrifugation, washed with water, and then washed with THF. The residue was dried under vacuum to give the complex as white powder (94 mg, 54%).

pH Cycling Experiments. A stock solution of CMA (7.31 mg, 4.0×10^{-2} mmol glucose unit) and PMHS (0.95 mg, 2.5×10^{-3} mmol) in aqueous HCl solution (5.0×10^{-4} M, 5.0 mL) was prepared following the procedure described above. A 1 mL aliquot of the stock solution was diluted to 5 mL with water. The mixture was allowed to stand overnight and was then subjected to spectroscopic measurements (cycle 1). A 3 mL aliquot of the stock solution was added to aqueous NaOH solution (1.0×10^{-3} M, 3.0 mL), and the mixture was stirred at room temperature for 2 h. A 2 mL aliquot of the mixture was then diluted to 5 mL with water. The mixture was allowed to stand overnight and was subjected to spectroscopic measurements (cycle 2). In a further pH cycle experiment, the aqueous solution was adjusted to be either acidic (pH $\approx$ 5.5) or basic (pH $\approx$ 8.0) using aqueous HCl solution (1.0×10^{-3}, 5.0 mL) or aqueous NaOH solution (1.0×10^{-3} M). The mixtures were then diluted to 5 mL with water and allowed to stand overnight, and they were then subjected to spectroscopic measurements. The pH of the aqueous layer was monitored using a pH meter. The pH of the solution was changed in the range pH = 4−9 because the oligosilane can cleave under strongly acidic or basic conditions outside this pH region.

Job Plots and Estimation of the Association Constants. Aqueous solutions of CMA and PMHS were mixed to prepare samples with various mole fractions of CMA (pH = 7.0). After the addition of hexane to extract any noncomplexed PMHS remaining in the mixture, the aqueous layer and the hexane layer were subjected to spectroscopic measurements at 25 °C to obtain Job plots of the complex. The association constant was estimated by fitting the observed data to the changes in absorption spectra on titrating the PMHS solution with CMA using a theoretical model assuming the formation of a 1:1 complex, where the molar concentration was based on 16 α-1,4-D-glucopyranose repeating units.[10]

Results and Discussion

Among a number of polymers that can adopt ordered helical conformations, we chose amylose as the host polymer. Amylose is composed of α-1,4-linkages between D-glucopyranose residues,[11] as shown in Figure 2. Amylose exists either as a random coil or as an interrupted loose left-handed helix in an aqueous solution, where the predominant conformation is sensitive to the pH and the solvent composition.[12] With an appropriate guest molecule, amylose can form inclusion complexes as a result of hydrophobic interactions with the guest molecule confined within the helical cavities.[13] In our experiments, we used

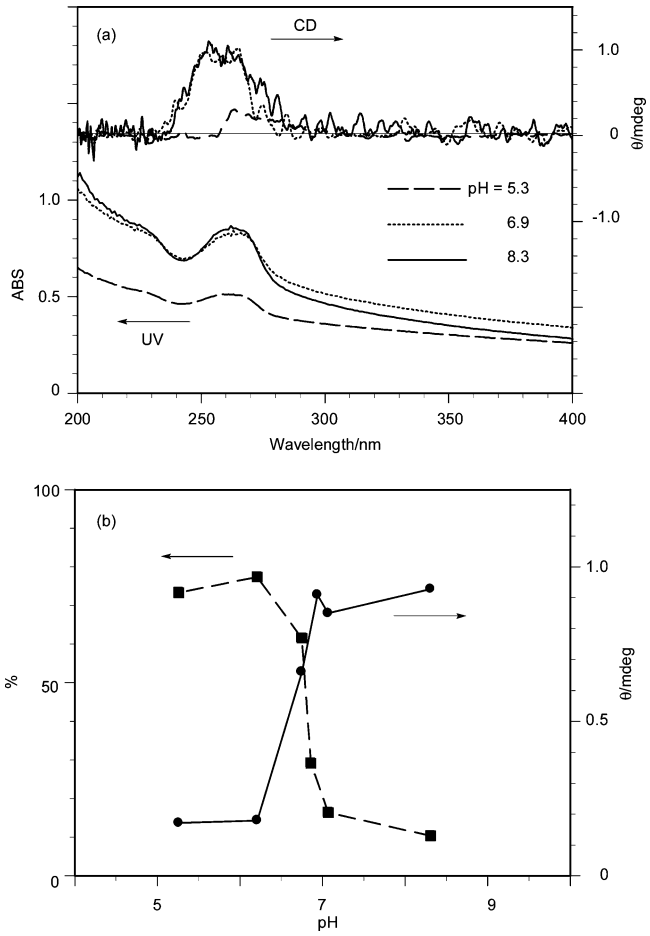

Figure 3. (a) pH-dependent UV and circular dichroism (CD) spectra of a mixture of CMA and permethylhexasilane in aqueous solution. [CMA] = 1.6×10^{-3} M, [PMHS] = 1.0×10^{-4} M. (b) Plots of the ICD intensity at 265 nm and percentage recovery of noncomplexed PMHS extracted from the aqueous layer into hexane as a function of pH.

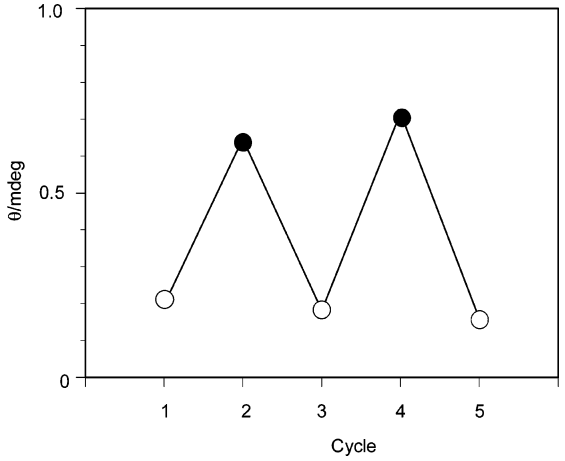

Figure 4. Change in the CD intensity at 265 nm of a mixture of CMA and PMHS in an aqueous solution upon pH changes between acidic (pH $\approx$ 5.5, ○) and basic (pH $\approx$ 8.0, ●) conditions. [CMA] = 1.6×10^{-3} M, [PMHS] = 1.0×10^{-4} M.

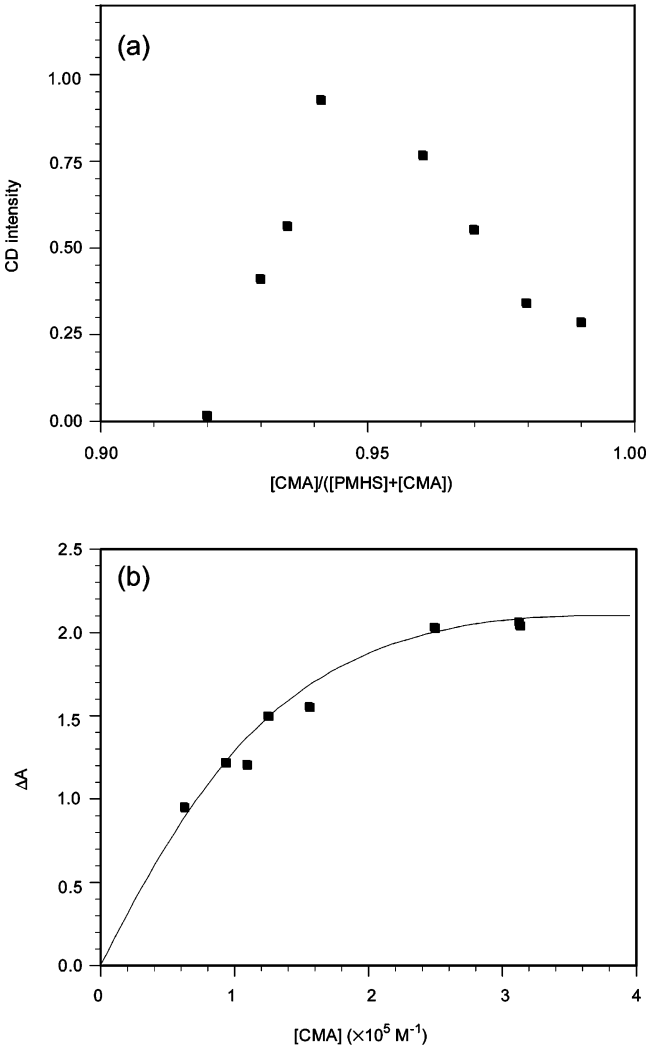

Figure 5. (a) Job plot of the change of the CD spectrum showing the stoichiometry of the complexation of CMA and PHMS under neutral conditions in H_2O. The CD intensity at 265 nm for the plot. [CMA] + [PMHS] = 1.7 mM. (b) UV titration data in H_2O at 25 °C (pH 7.0), monitored at 265 nm. $\Delta A = A_0 - A_{hex}$, where A_0 is the absorbance of total amount of PMHS used for the titration experiment and A_{hex} is the absorption of the noncomplexed PMHS in the hexane layer.

partially carboxymethylated amylose (CMA) to increase the solubility of the resulting inclusion complex in water. On the other hand, permethylhexasilane (PMHS) was chosen as the guest molecule because oligosilanes show absorption in the UV region due to the σ-bond conjugation along the main chain, which is extremely sensitive to the conformation.[14,15] Recently, we have observed the induction of a preferential helical conformation of the main chain of oligosilanes within the helical channel of a polysaccharide, where the helical sense of the guest molecule was controlled by its wrapping in either the left- or the right-handed helical sense conformation of the host polymer.[16,17] Shinkai and co-workers have also reported on supramolecular chiral complexes between polysaccharides and water-soluble polythiophene.[18]

pH-Dependent Complexation of Amylose and Oligosilane. The pH-dependent complexation of amylose and oligosilane was examined. In a typical experiment, a mixture of CMA and PMHS in an aqueous medium adjusted to an appropriate pH value was dispersed ultrasonically and then stirred at room temperature. After the addition of hexane to extract any noncomplexed oligosilane remaining in the reaction mixture, the aqueous layer and the hexane layer were subjected to spectroscopic measurements.

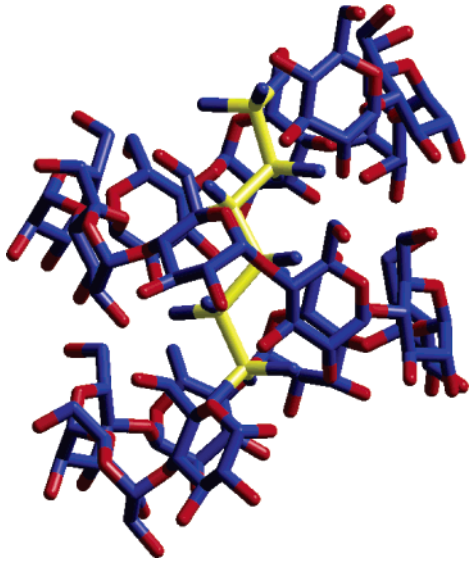

Figure 6. Energy-minimized model based on the AMBER force field for an inclusion complex of PMHS with an amylose fragment containing 16 repeating α-1,4-D-glucopyranose residues. The carbon, oxygen, and silicon atoms are shown in blue, red, and yellow, respectively. The hydrogen atoms have been omitted for clarity.

Figure 3 shows the UV and circular dichroism (CD) spectra of the resulting aqueous solutions at different pH values and plots of the induced circular dichroism (ICD) intensity at 265 nm and the percentage of noncomplexed PMHS extracted from the reaction mixture into hexane as a function of pH. At low pH, the UV absorption and Cotton signal of the aqueous solution were very weak, but the hexane layer showed an absorption band occurring at 260 nm, indicating that most of the oligosilane charged with CMA remained in the noncomplexed state in the acidic aqueous medium and was extracted to the hexane layer. However, at neutral and alkaline pH values up to pH = 9, the aqueous solution exhibited a broad UV absorption around 260 nm and a positive Cotton signal in the same wavelength range as the UV absorption, which is characteristic of the $\sigma-\sigma^*$ transition of the oligosilane main chain. PMHS is insoluble in aqueous solutions, and PMHS itself does not show any CD signal. Accordingly, these spectral characteristics of the aqueous layer demonstrate that a supramolecular complex had formed and that a preferential helical conformation had been induced on the oligosilane chain residing in the helical channel of the CMA as a result of complexation with the chiral helical host under the experimental conditions used. Thus, the abrupt change in optical activity of the oligosilane at a critical pH value is associated with supramolecular complexation with the CMA, whose conformation is pH-dependent.

The dissymmetry ratio of the complex, g_{abs} ($= \Delta\epsilon/\epsilon$),[19] which is usually used to characterize helical structures, such as right- and left-handed helix populations, was weak: $g_{abs} = 1.5 \times 10^{-5}$.

pH Cycling Experiments. Interestingly, the induction of optical activity in oligosilane synchronized with the supramolecular complexation was reversible, as shown by data from pH cycling experiments (Figure 4). When the pH of the aqueous solution was adjusted to pH = 8, the ICD signal appeared at 265 nm, but the signal faded on acidification to pH = 5.5. This CD spectral change on changing the pH could be repeated without observing any significant change in the intensity of the CD signal. The pH-dependent optical activity stems from the

reversible conformational change of the CMA host. Such a pH swing cycle is envisioned to be repeatable for even more times in the pH range where both the CMA and the oligosilane are stable and do not lose any structural integrity.

Identification of the Amylose−Oligosilane Complex. To confirm the structure of the amylose−oligosilane complex, the complex was isolated and characterized. A variety of spectroscopic techniques were examined; however, it was not possible to carry out NMR measurements in solution because of the complex's solubility in H_2O (up to concentrations of ca. 10^{-4} M). For example, a powder X-ray diffraction study demonstrated that an intense reflection pattern was observed at $2\theta = 16°$, which was similar to that reported for a complex of γ-cyclodextrin,[20] a macrocyclic molecule consisting of eight α-1,4-glucopyranose units, exhibiting a channel-type structure. These data suggest that the amylose is probably in the 8_1-helical structure (eight α-D-glucopyranose resides per turn), with a cross section diameter of 8.5−9 Å, necessary for fitting into the sequential size of the dimethylsilylene units of PMHS (ca. 6 Å). Indeed, mixing PMHS and γ-cyclodextrin affords a pseudorotaxane-type complex, in which a PMHS molecule forms a thread between two γ-cyclodextrin molecules, and the spectral features, as well as UV and CD spectra, are almost the same as those observed for the amylose complex above.[21]

Spectroscopic titration and Job plots of the solutions at pH = 7 suggest that PMHS forms a stable 1:1 inclusion complex with 16 amylose repeating units with an association constant, K_{assoc}, of $K_{assoc} = 1.9 \times 10^3\ M^{-1}$ (Figure 5).

According to molecular mechanics of our simple model for PMHS and an amylose fragment containing 16 repeating α-1,4-D-glucopyranose units, the amylose fragment adopts an 8_1 left-handed helical conformation by wrapping around the PMHS acting as an axle (Figure 6). In the helical cavity created by the amylose wrapping, the PMHS main chain assumes a twisted conformation with a Si−Si torsion angle of about 165°.

Conclusions

We have demonstrated the reversible supramolecular complexation between amylose and oligosilane displaying a pH-dependent switching of the optical activity. Further, the induction of optical activity in oligosilane synchronized with the supramolecular complexation was reversible, as shown by data from pH cycling experiments. The present system provides a new and simple approach to the design of new chiral materials and provides a good illustration of chirality control with molecular communication.

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Supporting Information Available: Data of the PMHS/γ-cyclodextrin complex. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) In a previous study, decasilane with a 2-naphthyl group at the terminal position was employed as the guest molecule for amylose. In this case, the overlapping of $\pi-\pi^*$ band of the naphthyl group with the $\sigma-\sigma^*$ band of the decasilane main chain causes difficulties. Further, the oligosilane may be unsuitable to observe the effect of pH on supramolecular complexation because the oligosilane containing an ester linkage can cleave. Therefore, the use of PMHS for the guest molecule is advantageous.

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