Note

A ladder polysilane wrapped with amylose

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ABSTRACT

A mixture of tricyclic ladder polysilane **1** and amylose, upon pH adjustment of aqueous media from very basic to neutral, affords a supramolecular complex in which a preferential twisted (helical) conformation is induced on the ladder polysilane to display optical activity. Under the experimental conditions used, **1** assumes a left-handed twisted structure in the left-handed helical channel of amylose.

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1. Introduction

Ladder polysilanes constitute a family of polysilanes where two polysilane chains are connected by bridging Si–Si bonds [1]. The first ladder polysilane, decaisopropylbicyclo[2.2.0]hexasilane, was reported in 1987 [2]. Since then, one of us has extensively studied the structure, photophysical properties, and reactions of ladder polysilanes [3], inclusive of the theoretical aspects [4]. It is interesting to note that ladder polysilanes were considered as a stable building block of single-walled silicon nanotubes [5].

The most remarkable structural feature of *anti*-ladder polysilanes lies in their twisted structures, which appear as silicon double helices. For example, tricyclic ladder polysilane **1** (Fig. 1) assumes a twisted structure with dihedral angles between neighboring cyclotetrasilane rings of 111.4° and 112.8°, confirmed by X-ray crystallography [3]. The twisted structures of ladder polysilanes arise from the systematic folding of the cyclotetrasilane rings upward or downward along the diagonal, leading to left-hand or right-hand twisted (helical) structures. A mixture of right-handed (*P*) and left-handed (*M*) double helical molecules was usually found as racemates in the molecular packing of ladder polysilanes upon crystallization, but tricyclic ladder polysilane **1** gave a crystal of an enantiomerically pure conformer (*P* or *M*) by slow crystallization from a solution without stirring, as shown in Fig. 2 [3j]. This is quite interesting because it demonstrates chiral crystallization without any external chiral sources. Further, the crystal of enanti-

omerically pure **1** displayed a clear Cotton effect in the circular dichroism (CD) measurement. Thus, the left-handed **1** (*M*-**1**) showed a negative Cotton signal, while the right-handed **1** (*P*-**1**) showed a positive Cotton signal.

On the other hand, we have recently found the preferential induction of a helical conformation in the main chain of oligosilanes and oligothiophenes within the helical channels of amylose and schizophyllan, where the helical sense of the guest molecules is controlled by wrapping with the host polysaccharides of either the left- or the right-handed helical conformation [6]. Other groups also reported supramolecular complexes of conjugated polymers wrapped with polysaccharides [7]. The wrapping approach provides an alternative synthetic strategy for insulated molecular wires [8] and is a simple approach to the design of new chiral materials.
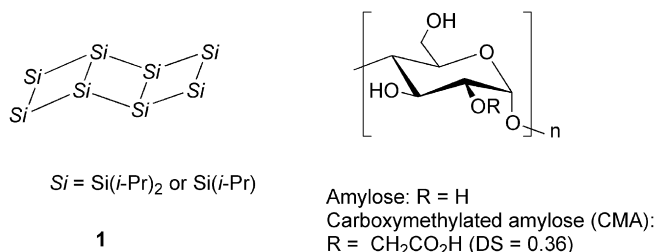
Here, we extend this wrapping approach to manipulation of ladder polysilane **1** used as a guest molecule. In solution, **1** is present in an equilibrium mixture of right-handed and left-handed double-twisted structures at room temperature, but when wrapped with amylose, it adopts a chiral conformation to display optical activity, as shown in Fig. 3. Further, the observed sign of the induced Cotton signal in the ladder polysilane is correlated to the direction of the twisted structure in the enantiomerically pure crystal.

2. Results and discussion

From 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,

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Si = Si(i-Pr)₂ or Si(i-Pr)

1

Amylose: R = H
Carboxymethylated amylose (CMA):
R = CH₂CO₂H (DS = 0.36)

Fig. 1. Chemical structures of tricyclic ladder polysilane **1** and carboxymethylated amylose (CMA).

1   Si = Si(i-Pr)₂ or Si(i-Pr)

chiral crystallization

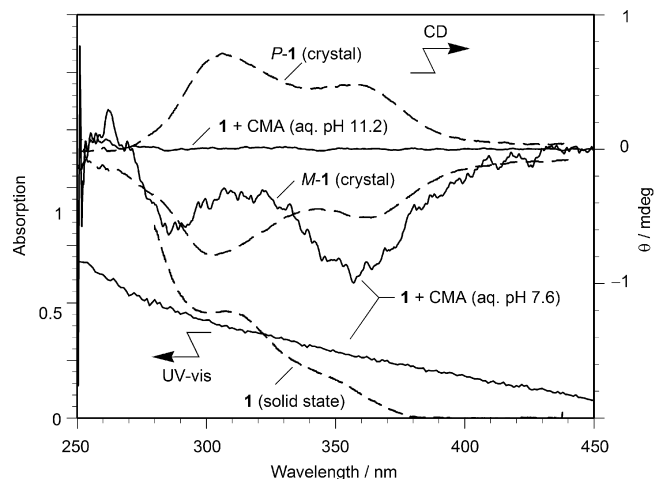*M*-**1** (left-handed)   *P*-**1** (right-handed)
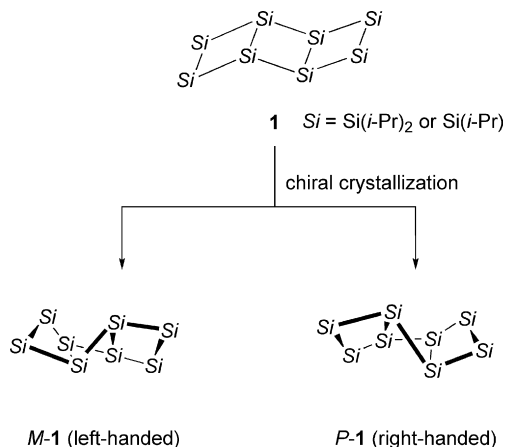
Fig. 2. Schematic representation of chiral crystallization of **1**.
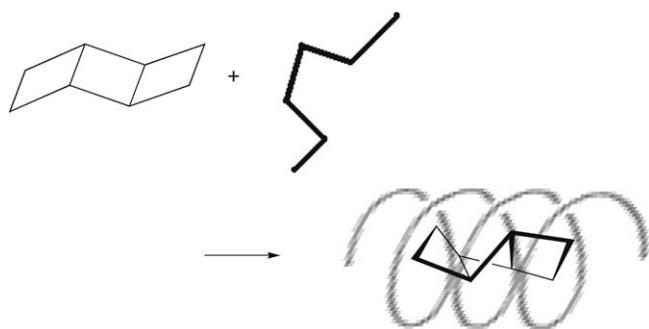
Fig. 3. Schematic illustration of supramolecular complexation between a ladder polysilane **1** and amylose.

Fig. 4. UV–Vis spectrum of **1** in the solid state (dashed line) and a mixture of **1** and CMA in an aqueous solution at pH 7.6 (solid line) and CD spectra of the enantiomeric crystals of pure *M*-**1** and *P*-**1** (dashed line) and a mixture of **1** and CMA in an aqueous solution at pH 11.2 and 7.6 (solid line).

as shown in Fig. 1. Amylose assumes a random-coil conformation in an acidic medium, but has a loose left-handed helical conformation in neutral or basic media. With an appropriate guest molecule, amylose can form an inclusion complex because of hydrophobic interactions with the guest molecule confined within the helical cavity [9]. The helical dimension of amylose can be adjusted to match the size of the guest. Amylose, however, serves as a polyelectrolyte above pH 11 and unfolds to a random-coil conformation, again leading to the loss of the inclusion ability [10]. In our experiments, we used partially carboxymethylated amylose (CMA) to increase the solubility of the resulting complex in water.

First, the complexation of amylose and ladder polysilane **1** was examined. In a typical experiment, to an aqueous NaOH solution of CMA was added a hexane solution of **1** and the mixture was dispersed ultrasonically and stirred. The resulting mixture was neu-

tralized and then subjected to spectroscopic measurements. As is discussed later, the change in pH of the medium, which causes a significant conformational change of amylose as the host polymer, was a prerequisite for the complexation with **1**.

Fig. 4 shows the UV–Vis and CD spectra of the resulting aqueous solution, together with the enantiomerically pure crystals of *M*-**1** and *P*-**1** obtained by spontaneous chiral separation upon crystallization. The parent ladder polysilane **1** shows an absorption at 345 nm resulting from σ-conjugation along the main chain. In the CD spectra, the enantiomerically pure crystals of *M*-**1** and *P*-**1** display negative and positive Cotton signals in the absorption region, respectively, although the racemic crystal of **1** and also **1** in hexane have no Cotton signal. On the other hand, a mixture of **1** and CMA in the aqueous solution at pH 11.2 does not show absorption and Cotton signal. However, the aqueous solution of **1** and CMA at pH 7.6 resulting from the foregoing process exhibits a broad UV absorption around 340 nm and a negative Cotton signal in the same wavelength range as the UV–Vis absorption, which is characteristic of the σ–σ* transition of the ladder polysilane chain. These observations indicate that a supramolecular complex between **1** and CMA is formed as a result of hydrophobic interactions since **1** alone is insoluble in aqueous solutions and CMA itself does not show any absorption in the wavelength region. The spectral features of the aqueous solution demonstrate that the ladder polysilane chain residing in the helical channel of CMA adopts a chiral conformation. Further, **1** in the left-handed helical channel of CMA assumes a left-handed twisted structure during the complexation under the experimental conditions used, because the observed sign and sharp of the Cotton effect are comparable to that of the enantiomerically pure crystal of *M*-**1**. Thus, the supramolecule is considered as a triple helix bundle.

From X-ray crystallography analysis, ladder polysilane **1** has a cross section diameter of ca. 10 Å, which is larger than that of conventional guest molecules (4.5–8.5 Å) [3]. Nevertheless, the ladder polysilane is accommodated into the helical channel of CMA. This is presumably associated with the diameter of the one-dimensional cavity of amylose being flexible [9]. Also, the renaturation of amylose, i.e., the conformational change from a random-coil to a helix upon the pH change, is envisioned to have been effectively accomplished during the complexation procedure executed. This rationalization in terms of renaturation is substantiated by a control experiment resulting in the lack of complexation upon plain mixing of the two partners in a neutral aqueous medium.

Recently, we have found chirality induction in α-sexithiophene, upon complexation with left-handed helical amylose, to produce optical activity, where the preferred screw sense induced in α-sexithiophene was dependent on the direction of pH change, either from acidic to neutral or from very basic to neutral [6d]. With this in mind, the chirality control upon pH change of the media was examined in the complexation of **1**, but no complexation occurred on the change from acidic to neutral. A further study of sample preparation is required to clarify the difference in the complexation behavior.

We also tested the complexation of **1** with another polysaccharide, schizophyllan (SPG) [11], but the addition of SPG did not result in a significant change, either in the UV–Vis absorption or in the CD spectra, suggestive of failure of complex formation between these partners.

3. Conclusions

We have demonstrated the supramolecular complexation of ladder polysilane **1** with amylose upon the pH adjustment from very basic to neutral of the medium and induction of the preferential twisted (helical) conformation on the ladder polysilane to display optical activity. Under the experimental conditions used, **1** assumes a left-handed twisted structure in the left-handed helical channel of amylose as compared with the CD spectra of the enantiomeric crystal of **1**. The present approach to induce chirality does not require introduction of e.g., chiral side chains into the ladder polysilane, thus providing an alternative strategy for chirality control in the design of new chiral materials.

4. Experimental

4.1. Instrumentation and materials

The UV–Vis spectra were recorded using an Agilent 8453 spectrometer. The CD spectra were obtained using a JASCO J-820 spectrometer using 10 cm quartz cells, with scanning conditions of: scan rate = 50 nm/min; bandwidth = 2.0 nm; response time = 1 s; and number of accumulations = 2.

All the solvents and reagents used were of reagent grade, purchased from commercial sources, and used without further purification unless otherwise noted below. Water used was purified using a Millipore Milli-Q system. Tricyclic ladder polysilane **1** [3b] and carboxymethylated amylose (CMA, $M_n = 5.8 \times 10^4$, $M_w/M_n = 1.7$, degree of substitution: 0.36) [12] were prepared according to the previously reported methods.

4.2. Complexation of **1** and CMA

To CMA (75 mg, 9.59×10^{-3} mmol) in 0.1 N NaOH aq. (2.0 mL) was added a hexane solution of **1** (1.22×10^{-2} M, 50 μL). The mixture was dispersed ultrasonically for 5 min. After addition of 0.1 M acetic acid/0.04 M sodium acetate (2.0 mL), the mixture was stirred for a period of one day. The mixture was then diluted with water and subjected to UV–Vis and CD measurements.

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